Separation of Bitumen from Brines Using Synthetic Membranes

By

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Statement of Contribution of Collaborators

I am the sole author of all the sections of this thesis. Dr. André Tremblay of the Department of Chemical and Biological Engineering, University of Ottawa, supervised my work throughout the MASc program, provided editorial corrections and revised most of my thesis. Dr. Saviz Mortazavi of Natural Resources Canada's Mining and Mineral Sciences Laboratories provided financial support and guidance throughout my work.

Abstract

The extraction of petroleum from oil sands by SAGD (Steam Assisted Gravity Drainage) method involves the underground injection of steam to extract the oil. Steam loses its latent heat to petroleum deposits, and condensed process waters along with liquefied oil are collected and piped out of the well. After the oil-water separation, process water saturated with bitumen is to be separated and recycled back into the extraction process.

As the steam boilers require high-purity feed water, it is proposed that synthetic membranes be used in the water-recycling scheme. Although membranes provide a high-quality filtrate, the accumulation of contaminants on the membrane surface, known as fouling, hinders the filtration process and eventually compromises water quality.

The objective of this project is to test the performance of synthetic membranes in this application, and perform physical and chemical modifications to the membrane and to the processed water to reduce the amount of foulants accumulating on the membrane surface. A total of 28 membranes are tested at two temperatures levels (45°C and 80°C). The pore size, the solution pH, the membrane type, the modification agents and the temperature are under investigation to determine the optimal conditions for fouling mitigation.

It is concluded that high pH levels increase the permeation rate by reducing fouling. This is the result of hydroxyl groups sorbing water molecules into the membrane pores. Such chemical activity reduces foulant attraction to the membrane surface. As for pore size, large pore membranes show less fouling than small pore membranes at low temperature. The reverse trend is observed at higher temperature.

Sommaire

L'extraction du pétrole des sables bitumineux à l'aide *du SAGD (Steam Assisted Gravity Drainage)* consiste en l'injection de vapeur sous - sol pour en extraire du pétrole. La vapeur perd son énergie de vaporisation à l’huile, et les eaux condensées avec le pétrole liquide sont recueillies et canalisées hors du puits. Après la séparation eau-huile, les eaux saturées de bitume doivent être filtrées et recyclées pour être réutilisé dans le procédé.

Étant donné que les évaporateurs ont besoin d'eau d'alimentation de haute pureté, il est proposé que les membranes synthétiques soient utilisées dans le système de recyclage d’eau. Bien que les membranes fournissent un filtrat de haute qualité, le colmatage des contaminants sur la membrane, appelé encrassement, entrave le processus de filtration.
L'objectif de ce projet est d’examiner la performance des membranes synthétiques dans cette application, et effectuer des modifications physiques et chimiques sur la membrane et sur l'eau traitée afin de pouvoir réduire le taux de colmatage sur la membrane. Un total de 28 membranes est testé à deux températures (45 ° C et 80 ° C). La grandeur des pores, le pH, le type de la membrane, l’agent de modification et la température sont mis à l’épreuve pour déterminer les conditions optimales pour l'atténuation d'encrassement.

En conclusion, les niveaux de pH élevés augmentent le taux de perméation. Ceci est le résultat des groupes hydroxyle qui ont l’habilité d’attirer les molécules d'eau à travers les pores de la membrane. Les membranes à grandes pores ont démontré moins d'encrassement que celles à petite pores, à basse température. La tendance inverse est observée à haute température.

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Nomenclature List

α = Pore constriction efficiency (combined model)

α_{block} = Pore blockage efficiency

α_{cake}= Specific cake resistance (m/kg)

α_{pore} = Pore constriction efficiency

A = Active area of the membrane (m^2)

C_b = Contaminant bulk concentration (kg/m^3)

d' = Active filtration area diameter (m)

f' = Fractional amount of total particles that contributes to deposit growth

J_o = Permeate flux through the clean, unfouled membrane ($L/m^2.h$)

J = Permeate flux ($L/m^2.h$)

k = Conductivity constant (m/kg)

K_{cake} = Constant in cake filtration model (h^{-1})

K_{clock} = Constant in complete blocking model (h^{-1})

$K_{constriction}$ = Constant in pore constriction model (h^{-1})

K_{inter} = Constant in intermediate blocking model (h^{-1})

K_1, K_2 and K_3 = Constants in the combined model (h^{-1})

n = Model dependent coefficient

ΔP = Transmembrane pressure (Pa)

ρ = Density (kg/L)

r_p = Particle diameter (m)

R = Resistance to filtration (m^{-1})

$R^{'}$ = Specific particle layer resistance (m/kg)

R_c = Resistance of the membrane cake (m^{-1})

R_f = Resistance of fouled membrane (m^{-1})

$R_{m,}$ = Resistance of unfouled membrane (m^{-1})

R_{p0} = Resistance of a single aggregate (m^{-1})

R_p = Resistance of the particle cake (m^{-1})

σ_{inter} = Blocked area per unit filtrate volume (m^2/m^3)

t = Filtration time (h)

μ = Solution viscosity (kg/s.m)

Acronym List

BTEX = (benzene, toluene, ethylbenzene and xylene)

CSP = Ceramic Supported Polymer

CSS = Cyclic Steam Stimulation

CVD = Chemical Vapor Deposition

DOC = Dissolved Organic Carbon

kDa = kilodaltons

lmh = $\frac{L}{m^2h} = \frac{Litre}{meter^2 x\ hour}$

MSTFA= *N*-Methyl-*N*-trimethylsilyltrifluoroacetamide

MWCO = Molecular Weight Cut Off

PAN= Polyacrylonitrile

PES = Polysulfone

PSV = Primary Separation Vessel

RMSE = Root Mean Square Error

SAGD = Steam Assisted Gravity Drainage

TOC = Total Organic Carbon

VAPEX = Vapor Extraction Process

PVP = Poly-vinylpyrrolidone

1. Introduction

1.1. General introduction

The rise in worldwide energy demand spurs the exploitation of versatile energy sources. This growth in energy consumption drives oil producers to boost petroleum deposits extraction as fossil fuels are the primary source for both industrial and domestic energy production activities. In addition to the traditional liquid form, fossil fuels deposits take a solid state form known as unconventional deposits or *oil sands*. The latter are petroleum droplets bonded to sand particles, forming heavy hydrocarbon chains, known as *bitumen*.

The extraction routes to access the bitumen are key in determining the feasibility of its exploitation. Extraction techniques have evolved and are currently under investigation to reduce the operational costs and improve the recovery rates of petroleum deposits.
Extraction techniques are divided into two categories: *Open-Pit* and *In-Situ*.
Open-pit consists of physically transporting the bitumen deposits for processing to separate oil and sand particles; *in-situ* entails the on-site removal of oil from the deposits.

Steam Assisted Gravity Drainage (SAGD) is an *in-situ* extraction method used to separate oil droplets from sand particles through phase change. It consists of injecting steam through a pipeline in the oil sands deposit area to reduce the viscosity of bitumen. As steam loses its latent heat, it transfers its energy to the bitumen deposit, condense, and flow along with liquefied bitumen to a lower well, to then be pumped to the surface. As SAGD requires a significant volume of steam to be injected (0.6 barrel of stream for every bitumen barrel produced (IHS CERA Inc., 2011)), and as the practice of SAGD process is expected to grow, the water demand for oil extraction is projected to rise.

The environmental impact of the SAGD oil extraction process emerges from the strong dependence on surface rivers as the sole source of boiler feed water for steam generation and from the disposal of contaminated condensate after the oil and water separation.

Recycling the steam condensate or processed water, after separating it from the bitumen and prior to rerouting it to a steam generation facility, is the only path to lower the environmental impact of oil extraction. The challenge for any processed water recycling route is the ability to regenerate water that meets the requirements for re-usage.

The level of water purity that allows the rerouting of the water back into the SAGD is dictated by the steam boiler specifications. The latter define the maximum contaminants concentration to avoid scale formation inside the boiler (specifications in appendix “A”).

Ultrafiltration membrane systems are a promising element that ensures a high quality of filtrate to feed the steam boilers. Acting as a barrier, the selectivity of the membrane divides the contaminated stream into a water-rich phase known as permeate (or filtrate) and a retentate, containing contaminant particles larger than the membrane pore size.

The primary obstacle for the membrane filtration processes is the accumulation of non-diffusive particles on the feed side, known as fouling. This build-up on the membrane surface impedes flux permeation and compromises permeate quality.

Given the harsh conditions of the SAGD extraction environment, synthetic membranes fabricated from ceramic materials are strong candidates for water filtration and are under investigation due to their strong stability at high temperatures over a wide range of pH.

1.2. <u>Thesis objectives</u>

The scope of this research is to study and enhance the performance of synthetic membranes for SAGD process water ultrafiltration. The performance is evaluated based on membrane fouling reduction, reflected in the ability to maintain a permeation flux.

At first, the pore size of the ultrafiltration membranes is examined to determine the optimal size for maximum filtration efficiency and permeation flux.
On the other hand, chemical modification agents are applied to the membrane to modify its properties and enhance permeability. The modification agents' role is to maximize the flux of permeates by reducing the adherence of foulant particles to the membrane surface. Polymeric membranes are also tested to better understand their behaviour and to be used as a comparison reference for ceramic membranes.

The physical conditions of the feed solution, more specifically the pH and temperature, are altered and put into test in the experiments to study their effect on fouling mitigation.

The last parameter to be studied is the effect of washing and the efficacy of regeneration techniques on membrane performance. The efficiency of backflushing, the latter being defined as the use of a fraction of the permeate in an opposite direction to the flow inside the filtration membrane for washing, is also under investigation in this study.

Mathematical modelling is employed to evaluate the performance of the tested membranes using liquid phase hydrodynamic based models. The flux permeation and the type of fouling occurring on the membrane are studied in parallel to determine the optimum conditions to improve ultrafiltration membrane performance.

2. Background

2.1. Oil sands

Worldwide, petroleum is the most exploited substance in energy generation practices. The first step of its production is the extraction of crude oil from the ground. The difficulty associated with its recovery is related to the type of deposit in which the petroleum is found. Oil is most often available in liquid deposits; however, oil deposits are also found under an unconventional quasi-solid form, known as oil sands or bitumen.

Oil sands or bituminous sands are deposits of petroleum particles adhered to loose soil particles along with other minerals and clays (Clark, 1945). The mixture is significantly dense and has an extremely high viscosity. The mixture is referred to as crude bitumen to differentiate it from conventional hydrocarbons extracted from conventional oil wells.

The deposits result from a biological phenomenon; plants absorb solar energy, water and carbon dioxide and then convert them into oxygen and carbohydrates such as cellulose.

Over millions of years, and under the influence of heat and pressure, carbohydrates are converted into a thick substance rich in hydrocarbon chains, known as fossil fuels. Petroleum deposits bonding to soil particles take a solid form (Alberta energy, 2013).

In Canada, the province of Alberta has the largest oil sands reserves in the country. These are repartitioned in three regions: Athabasca, Peace River and Cold Lake with a total area of 141000 km^2 and 2.56 trillion barrels of oil deposits (Strausz, 2010).

Oil sands in Canada consist of 3-5 % water content, 10 - 18 % bitumen and the rest are organics, minerals, clays and inorganic matter bonded to the surface sand particles.

Bitumen is composed of a high-density substance known as asphaltene as well as resins and saturates. The specific gravity of the mixture in Canada ranges from 0.977 to 1.016.

Physically, the presence of a layer of water between bitumen and other constituents make the oil sands processing more economically sustainable, due to the ability of water to weaken bonds between sand particles and oil droplets. However, the extremely high viscosity of the blend poses an important challenge for the extraction of its oil content and dictates the addition of diluents to the extracted bitumen for pipeline transportation. Due to the limited existence of refineries that can employ diluted bitumen as feedstock, bitumen is upgraded by physico-chemical transformations to synthetic crude oil prior to sending it through pipelines to classical upgrading facilities (Engelhardt, 2005).

The exploitation of oil sands has gained exceptional importance in the energy industry. Much attention has been placed on optimizing extraction methodologies in order to maximize the efficiency and the viability of unconventional deposits' exploitation.

2.2. <u>Extraction techniques</u>

Oil sands extraction methods are divided into two categories: surface mining and in-situ. The extraction technique utilized varies depending on bitumen's characteristics that can change from one region to another. The feasibility of the extraction method is determined by the topography and morphology of the bitumen deposits areas (Engelhardt, 2005). In Canada, the overburden, this is the layer of soil that covers the substance of interest, increases moving west. This geography makes surface mining more common in eastern Alberta (Athabasca) and in-situ techniques prevalent in the western part of the province.

2.2.1. Open-pit mining

Surface mining or open-pit mining, is a method of extraction that consists of removing the clay and sand layer "overburden", covering the oil deposits. Initially, the layer of water, known as water laden is removed from the top of the overburden prior to dislodging the latter to reach the buried oil sands sitting on a layer of limestone (Meyer, 2003). Afterwards, the oil sands deposits are removed and sent to a separation facility. Originally, the equipment used in the process consisted of bucket wheels, draglines and conveyers for oil sands transportation. The topography of the mine site led to the replacement of early conveyer belts and large moving equipment with shovel trucks and power shovels, considered more flexible and less susceptible to weather changes.

After removal, oil sands deposits undergo crushing, and are fed to a cyclofeeder where hot water is added to the bitumen to form a slurry mixture. The solution is then pumped to an extraction plant. A partial separation of bitumen and sand particles occurs in the pipelines. This reduces the energy usage at the extraction plant (Alberta Energy, 2013). Inside the extraction plant, steam at 85^{o} C and caustic soda are added to the mixture to separate sand particles from the organic phase. This is followed by the removal of large contaminants using screen vibration, and then the mixture is sent to the Primary Separation Vessel (PSV). A bitumen rich froth is formed at the surface of the water and sand particles settle at the bottom of the separation vessel. The froth is skimmed off and further processed to remove water traces from it via flotation. Subsequently, naphtha is added as a diluent prior to sending the mixture to a centrifuge unit where the separation is completed. Oil is then sent to an upgrading facility and water is routed to a tailing pond.

The downfall of the open mining method is that the yield of the process is low in a way that two tonnes of oil sands are to be processed to produce one barrel of oil. Moreover, this method can only reach shallow deposits: for instance, in Canada, only 20% of the bitumen can be extracted by surface mining due to the depth of the oil sands deposits.

2.2.2. In-Situ techniques

Steam Assisted Gravity Drainage

The extraction and transportation of large quantities of bitumen deposits depict a significant difficulty at the scientific and economic level.

In 1969, Dr. Roger Butler, a Canadian engineer working for Imperial Oil conceived the idea of extracting bitumen without the need to transport the sands bonded to oil particles to the extraction plant, eliminating the need of a sand-oil separation facility.

The method of Steam Assisted Gravity Drainage (SAGD) was first implemented in Calgary in the 1980’s (Canadian association of oil and gas producers, 2012) and it consisted in the drainage of two parallel horizontal in-ground wells: the top well is for steam injection and the bottom one is for oil and water collection. Zooming into the physical process, high-pressure steam loses its latent heat of vaporization to oil sands particles. Steam condenses and transfers heat to the mixture, leading to a decrease in the viscosity of its oil content. In turn, this will cause the liquefaction of the bitumen. Liquid bitumen slurry will drain to the bottom well where it will be collected and pumped, along with condensed steam, into an oil-water separation facility.

Afterwards, oil is sent to an upgrading facility and processed water is piped to a water treatment plant to remove oil, clays, organics and minerals (Deutsch and al., 2005).

In-situ techniques, particularly SAGD, have gained importance over open mining techniques in areas where the overburden depth is significant. SAGD recovery rates have exceeded all other oil extraction techniques (up to 80%); however, a series of challenges need to be overcome to ensure the method's maximum extraction efficiency.

Environmental and economic factors define the feasibility of the steam injection process. Steam generation entails the usage of significant amounts of energy, the release of proportional quantities of Syngas and Greenhouse gases, and the usage of large quantities of fresh water (Allen, 2010). These factors dictate an in-depth study to define an optimum for operating a steam generation process, especially with the rise of natural gas prices.

The large quantities of fresh water required for the SAGD process raise major environmental concerns. On one hand, the water used in the SAGD process is surface water, considered to be the cleanest type of water present in nature, and on the other hand, the large amount of process water to be disposed causes significant challenges to the surrounding environment. Although the ratio of steam usage over oil produced has improved (from 3 to 0.6 (IHS CERA inc.)), the amount of water required to extract the oil is still high. A key solution to limit fresh water usage is to treat processed water and recycle it back into the SAGD process for re-use as steam.

Effluent treatment remains a major challenge for recycling; condensed steam contaminated with pollutants is to be filtered and rerouted to steam generation units.

Cyclic Steam Stimulation

Another in-situ technique is Cyclic Steam Stimulation (CSS). This method consists of the injection of steam in a well in order to raise the temperature of the deposit and its surroundings. After the injection of a sufficient amount of water vapor, the latter is contained in the well for an extended period of time where it starts condensing. During this process known as “soaking”, the latent heat of vaporization is transferred to the oil, rendering it more liquid. The increase of pressure in ground due to steam injection will displace the oil outside the deposit well by natural flow. This cycle is repeated until an economic benchmark has been attained. Often, CSS is used for multiple cycles, after which the system is switched to SAGD for economic reasons since the latter exhibits a high- recovery rate for small volumes (20 % CSS, 50 % SAGD of the total oil volume).

Other Techniques

While using the same set-ups of SAGD, solvents can be used instead of the steam in in-situ techniques to separate sand particles from oil, which causes the latter to flow to the lower well prior to being pumped to the surface (www.oilsandsdevelopers.ca).

VAPEX is a method that injects vaporized hydrocarbons into the upper well, causing bitumen deposits to drain into the lower well. This method allows partial upgrading of the bitumen into crude oil and eliminates a processing step in the upgrading plant.

Toe-to-heal is an in-situ extraction method that combines the usage of a vertical well, into which air is pumped, and a horizontal production well. A volume of oil is ignited, creating a vertical wall of fire. The flame will burn the deposit and crack heavy components in the bitumen into lighter molecules, collected in the horizontal well. Although this method mitigates the need for steam, it is hard to control the fire inside the deposit well. The feasibility of the Toe-to-heal method depends on the ability to control fire propagation.

Cold Flow is also another method employed to recover oil and it simply implies the pumping of oil from the deposit area to the plant using progressive cavity pumps. This method recovers only up to 6% of the oil in place and requires minimum oil fluidity. Canadian companies improved this method by removing sand filters from the well and pumping out as much sand as possible. This technique improved oil recovery rates to as high as 10% but raised the problem of processed sand disposal (www.suncor.com).

Researchers are focusing mainly on methods to avoid extraction of sands from the oil sites in order to reduce operation cost as well as avoiding problems that will occur from the disposal of processed sands. This goal is achieved primarily by in-situ techniques, where oil is separated from the sand in-ground and is pumped out for processing.

Extraction processes are not necessarily mutually exclusive and are often used in combination to maximize efficiency; however, the main obstacle is to find routes to separate oil, sands and water by physical and chemical means. The feasibility of these routes depends on the geographical area, the depth and composition of oil deposits.

Extraction processes are continuously being studied on the technical and economical scale to improve the recovery rates of petroleum from oil sands.

2.3. <u>Oil -Water processing</u>

After the extraction of oil sands, the mixture is piped to a separation plant whose effluents are an aqueous and an organic phase. Similarly to the separation techniques for surface mining, and inside the separation vessel in which gas is pumped, a froth of bitumen is formed on top of the water layer due to density difference. Later, a centrifuge is employed to remove water traces in the oil.

The oil is channelled to a refining facility and water, known as processed water, undergoes a filtration process for safe disposal or reuse. The process that refines bitumen and separates its components is known as the upgrading process. As for the water filtration, several processes are being used and sought to remove contaminant particles.

2.3.1. Oil upgrading process

After the separation of bitumen from the rest of the oil sands constituents, oil is sent to an upgrading unit to be converted into crude oil to feed the classical oil refineries. The upgrading process starts by adding diluents to the bitumen enabling it to flow to the upgrading facility. Diluents used in oil sands are naphtha from natural gas condensate, or synthetic crude oil, to form Dilbit and Synbit respectively. Diluents are recovered and recycled by distillation. The ratio of diluents to bitumen is determined by the viscosity and pumping requirements of the pipelines.

The upgrading process consists of thermally cracking large molecules of oil into smaller ones. To do so, the temperature is raised until the mixture’s flashpoint is attained. The blend separates into gas phases and carbon-rich coke. This stage is called hydrocracking, where atoms of carbon are removed and large molecules are broken into lighter ones. Hydrotreating is another refining process, known to produce a superior quality of oil and maintain a high octane rating. It consists of exposing the fuel, in the presence of a catalyst, to a hydrogen-rich environment so the hydrogen can bond to the carbon chains. Nowadays, hydrotreating gains more importance due to its ability to deliver fuel products with lower sulfur and nitrogen contents without generating coke as a by-product.

The objective of hydrocracking and hydrotreating is to remove impurities, and increase the hydrogen to carbon ratio to produce lighter molecules. The effluent gases from the hydroprocess are routed to a fractionation tower to produce naphtha, gas oil and diesel. The three effluent streams are combined in a specific ratio to produce blends of synthetic crude oil or further processed into other finished product streams.

In Alberta, five upgraders treat 206 000 m^3 of bitumen per day. Syncrude and Suncor employ on-site upgraders, for surface mining and SAGD (www.canadianenergyadvantage.com).

2.3.2. Water treatment processes

The objective of water treatment is to reach a purity that allows the recycling of SAGD processed water back to the process to feed the steam boilers. The water treatment process is the cornerstone for any recycling activity since elevated levels of contaminants compromise the boiler’s integrity. This is manifested by scale formation on boiler surfaces, reduction in heat transfer and an increase in pipeline and equipment corrosion (the contaminants present in the SAGD processed water are listed in Appendix “A”).

The concentration levels of minerals, ions and organic materials that a water boiler can tolerate without risking the vessels' integrity, are dictated by the working pressure, steam temperature and boiler material. However, general guidelines exist for the maximum allowable contaminant concentrations in a boiler (values presented in appendix "A").

Up until the late 1980's, separation activities were limited to liquid-solid separations; but, this changed soon after the awareness of the effects of soluble toxins, such as organic acids in tailing ponds. This called for the development of water filtration techniques to reduce the environmental hazards and risks of the processed water disposal.

Adsorption

Adsorbents are substances used to remove contaminants from waste water streams. Adsorbents extract soluble organic compounds, oil and grease as well as heavy metals.

Activated carbon, one of the most common adsorbents in filtration, demonstrates effectiveness in removing naphthenic acid in acidified oil sands but shows poor results in adsorbing BTEX. In the same manner, activated carbon is effective in lowering organic carbon concentration but is ineffective in the removal of toxic naphthenic acid which continues to be a difficult substance to eliminate from oil sands processed waters.

These issues are solved by utilizing alternatives such as inorganic adsorbents. In fact, Zeolites showed positive results in removing BTEX from the oilfields waters. Adding amines and organic groups to Zeolite has further shown significant results in the elimination of emulsified oils from the contaminated waters.

Biological treatment

Biological treatment implies the use of microbes to remove organics from process waters. This method is widely used in municipal wastewater treatment plants. The microbes in the stream feed on soluble organic compounds and in the presence of oxygen multiply and further consume organic molecules. The limitation of this method is the salinity of the water, the existence of toxic organic chemicals as well as the effect of the processed waters' temperature on the microbes' performance and growth. Levels of these three factors should be closely monitored and controlled. Inconvenient chemical and temperature conditions can cause the depletion of microbes and death of the culture, lowering the removal rate of organics. In general, biological treatment is employed in series with other treatments in a way to create a safe environment for microbial activities.

All biological based processes share the same principles (microbes growing in presence of nutrient); however, physical and chemical properties change the selectivity and yields.

Biological treatments are applied in fluidized beds, bioreactors and biofilm reactors.

In membrane bioreactors, biological solids are filtered out and routed back to the process after undergoing membrane filtration. This cancels the need for a settling clarifier and protects microbes in the reactors from fluctuations in the feed water quality (Allen, 2008).

Advanced oxidation

Chemical oxidation is a process that utilizes oxidants to degrade chemical pollutants present in a stream. The dominant chemical reactions in this process are ionic and radical reactions that are initiated and propagated by a redox reaction.

The most common oxidants are Chlorine, Hydrogen Peroxide, Ozone and Permanganate. These oxidants are generally used for compounds that are not removed by biological treatments or adsorption due to high toxicity or aromaticity. Two-sub categories are present under the oxidation processes: photocatalytic and sonochemical oxidation.

Photocatalytic oxidation consists of the usage of radicals that are produced by photo-excitation of peripheral electrons on the surface of a catalyst. The high reactivity of radicals degrades high molecular weight components and toxic compounds. Moreover, radicals are effective on both organic and inorganic compounds in processed water.

The sonochemical treatment entails the usage of high frequency waves to promote the creation and collapse of air bubbles in a medium. This produces high temperature and pressure cavitation that break the pollutant molecules. This method is not economically viable given the high energy needed to treat large water quantities.

Treatment wetlands

This method is widely applied in municipal wastewater treatments as well as in industrial water treatments including refineries and petro-chemical plants. This method removes suspended solids, organic and nitrogen compounds by trapping the pollutant particles in physical and chemical agents. The phenomena used in wetlands treatments are adsorption, filtration and sedimentation. Research focuses on the ability of optimizing the surface of contact to minimize space and energy usage needed to achieve separation.

Wetlands are very effective at removing oil, as well as removing BTEX pollutants. The downfall of this method is that its performance is vulnerable to changes such as pH, and can be inhibited by low temperatures present in the Canadian oil fields.

Research in the water treatment field focuses on identifying an optimum between water quality and operation costs for the water filtration processes (Allen, 2008).

Currently, water filtration techniques (described above) are limited to reduce contaminant levels for disposal and are unable to reach purity levels required for steam generation in SAGD operations. This calls for the development of a filtration technique that provides high-purity water while maintaining feasibility. Ultrafiltration membranes are considered to be promising elements in finding an optimum between treatment feasibility and performance, but limitations and difficulties are to be overcome to ensure membrane filtration efficiency.

3. Filtration membrane and fouling description

3.1. <u>Filtration membrane</u>

A membrane is a physical layer formed by a chemical or mixture of chemicals whose main function is to separate stream components into permeate and retentate. The mixture to be separated comes into contact with a semipermeable membrane which, selectively, allows the permeation of specific mixture components to the other side of the membrane (Sethi and al., 1995), known as the permeate side. The remainder of the solution, containing non-permeating species, remains on the feed side and is often recirculated.

3.1.1. Separation models

A membrane separation process is governed by the pore size or a concentration gradient.

Under a hydrodynamic model, the membrane is size selective, where molecules smaller than membrane pores reach the opposite side of the filtration membrane to form the permeate stream.

Filtration membranes characterized by the hydrodynamic model, are divided into three categories: microfilters, ultrafilters and nanofilters, and remove compounds with particles as small as 0.1 um, 0.005 um and 1nm, respectively.

The transport of solutes in a diffusion model, across the membrane, occurs in the presence of a concentration gradient. The diffusion model is favorable for small molecular particle separation. Reverse osmosis (RO) is an example where separation is a pressure-driven process controlled by a concentration gradient. In oil sands' water filtration applications, reverse osmosis separates low molecular organics by targeting soluble organic compounds. Reverse osmosis is under investigation for applications requiring high-purity water; however, its technical and economic feasibility are in question since it delivers a permeate quality of very high purity level, deemed to be unnecessary for recycling.

3.1.2. Membrane material

Filtration membranes are produced from organic and inorganic-based materials.

Polymeric membranes are formed of organic polymer chains that are synthesized to have selective affinity to specific group of components. Polymeric membranes are widely used in industry due to their efficiency and low cost (www.membranespecialists.com.php).

Inorganic membranes are formed from inorganic components. The commonly known types are ceramic membranes such as Alumina (aluminum oxide), Titania (titanium dioxide) and Zirconia (zinc dioxide). Ceramic membranes are known for their stability under harsh physical and chemical conditions (Dafinov, 2001): ceramics are less vulnerable to the surrounding media than polymeric membranes.

Although literature indicates that both types of membranes show promising results in the removal of suspended solids and pollutants from the water stream, ceramic membranes are able to keep their chemical and thermal stability over a wide range of temperatures and pH. A noteworthy candidate for membrane processes is the ceramic supported polymer (CSP). The CSP membrane targets bitumen and oil-water emulsions, and is subject to intense research in the oil industry in order to enhance performance and adaptability.

3.1.3. Membrane synthesis

Two types of filtration membranes exist: porous membranes and dense membranes.

Porous membranes operate under the hydrodynamic model and are divided into symmetric, where the pores have an identical size, and asymmetric having various pore sizes throughout the membrane surface. A porous membrane is formed of a porous layer mounted by a layer with smaller pores, known as top layer. Often, the top layer is a dense layer, depleted of pores, to increase the membrane selectivity (Ahmed and al., 2010).

Dense membranes operate in the presence of a concentration gradient, creating a driving force, between the feed and the permeate side. The dominant fabrication material of a dense membrane is a pure component, but can also be composed of a mixture of metal alloys such as silver and palladium or an electrolyte such as zirconia.

The fabrication process differs between polymeric and inorganic membranes: polymeric membrane fabrication starts by drying a polymer. The material is then dissolved in a homogenous solution followed by spinning and phase inversion.

Ceramic membranes are prepared by either dip coating (Gu, 1999), anodic oxidation, chemical vapour deposition (CVD) (Xomeritakis, 1994), co-pressing or co-sintering.

3.2. <u>Fouling</u>

Membrane separation is considered a highly efficient technique in particle separation to produce high water quality. However, the main impediment for filtration is fouling occurring on the membrane surface, reducing the permeate flux and compromising its quality (Awad, 2011).

Fouling is a physical phenomenon translated by the deposition of non-diffusing substances on the membrane. Fouling clogs membrane pores and halts flux permeation.

There are four major types of fouling: crystallization fouling, biological fouling, particulate fouling and chemical fouling. The first usually occurs in water systems and involves the formation of crystals on the surface also known as scaling. Biological fouling is caused by the growth of bacteria on surfaces forming a fouling layer. Particulate fouling occurs when retentate particles deposit on the separation surface, impeding the flux passage. There is also chemical fouling, generated by a chemical reaction, at high temperature, occurring on the membrane at the separating surface.

Particulate fouling is caused by particle build-up at the entrance of membrane pores (Porter, 1972) leading to the formation of a layer known as a filtration cake on top of the membrane (Wigmans, 1984). Both forms of particulate fouling create significant hydraulic resistance and lead to a flux decline. Also, the accumulation of particles on the feed side increases the concentration of non-diffusing particles on the membrane surface. The growing difference in particle concentration between the surface of the membrane and the permeate side creates a concentration gradient between both sides, affecting the permeate quality by forcing contaminant particles to the permeate side (Bott, 1995).

Although a porous filtration membrane separates stream components based on particle size, the creation of a concentration gradient plays a role in moving contaminant particles that have a slightly larger size than the pores to the permeate side of the membrane.

As filtration progresses, particle accumulation promotes filtration cake growth and leads to a filtration process that is increasingly independent of the pressure gradient. At this point, the permeation rate is controlled by mass diffusion and if the pressure is increased, the cake growth rate increases, causing more resistance to the permeation flux (Porter, 1972).

The evaluation of membrane performance is determined, in general, by the permeation flux of the permeating specie, the filtrate contaminants' concentration and by the type of fouling occurring on the membrane surface. Affinity to oil and membrane hydrophilicity are also factors taken into account to evaluate membrane behaviour.

3.2.1. Fouling cake formation

Mathematical and analytical models are proposed to describe phenomena occurring inside the membrane body and on its surface. During filtration, the deposition of non-permeating particles on the membrane creates a concentration gradient between the filter cake and the stream. This causes foulant diffusion from the cake to the feed stream.

" The film theory" model states that the transport of particles, by advection, (convection due to liquid flow) to a polarized layer, known as the filtration cake, is equalized by the diffusion of particles in the opposite direction due to Brownian movement (Sethi, 1995).

Later on, the concepts of "shear-induced diffusion" and "inertial lift" were introduced to explain the phenomena observed in cross-flow feed channels related to the convection of particles away from the membrane surface (Eckstein, 1977). As their names indicate, both phenomena are caused by the flow of a fluid passing across the surface of the membrane and generating shear stress on the polarized layer of particles. The shear force applied on the particles causes them to move away from the membrane, entraining a reduction in the thickness of the cake. Therefore, shear-induced diffusion in addition to the Brownian diffusion (inertial lift is neglected due to its small magnitude compared to shear force) counters the deposition of particles on the membrane and equalizes it under steady-state.

3.2.2. Particulate fouling models

The understanding of the fouling phenomena occurring on the membrane surface will help develop mathematical models to quantify the flux through the membrane.

Four mathematical models describe the fouling types that can occur on the membrane surface. The models show the effect of the fouling type on the permeation flux.

The first model is *complete blocking*, assumes that particles that reach the membranes clog and block the pores entirely. The second model, *intermediate blocking*, assumes that the particles settle into each other, block the pores but channels remain open.

The third model, the *standard blocking* model suggests that the particles deposit on the pore walls and cause a proportional decrease in flux volume.

The fourth model, the *cake filtration* model, assumes that there is no pore blocking, but only cake formation due to particles' accumulation on the membrane surface.

All four models respect the following equations (Ho and Zydney, 2000):

$$\frac{dJ}{dt} = -kJ(JA)^{2-n} \tag{3.1}$$

For complete blocking n = 2; for intermediate blocking n = 1; for standard blocking or pore constriction n = 1.5; for cake filtration n = 0.

For each fouling model, with the corresponding n value, equation 3.1 is integrated and the following results are obtained (Peng and Tremblay, 2008) in Table 3.1:

Table 3.1: Permeate flux variation as a function of time

Model	**Constant**	**Analytical Form**
Complete Blocking	$K_{Block} = \frac{\alpha_{block} A J_0 C_b}{N_0}$	$\frac{J}{J_o} = \exp(-K_{Block} t)$
Intermediate Blocking	$K_{Inter} = \frac{\sigma_{inter} \Delta P}{\mu R_{inter} J_0}$	$\frac{J}{J_o} = (1 + K_{Inter} t)^{-1}$
Standard Blocking	$K_{constriction} = \frac{\alpha_{pore} A J_0 C_b}{\pi r_p^2 \delta_m}$	$\frac{J}{J_o} = (1 + K_{constriction} t)^{-2}$
Cake Filtration	$K_{cake} = \frac{2\alpha_{cake} J_0 C_b}{R_m}$	$\frac{J}{J_o} = (1 + K_{cake} t)^{-1/2}$
Combined Model	$K_1 = \frac{\alpha \Delta P C_b}{\mu R_m}$	$\frac{J}{J_o} = \exp(-K_1 \mathrm{t}) + (1 + K_3)^{-1}$ $\times [1 + K_2 t (1 + K_3)^{-2}]^{-\frac{1}{2}} \times [1 - \exp(-K_1 t)]$
	$K_2 = \frac{2 f' R' \Delta P C_b}{\mu R_m^2}$	
	$K_3 = \frac{R_{p0}}{R_m}$	

During the membrane filtration process, both pore clogging and cake formation are likely to occur on the membrane surface.

The combined model (presented in Table 3.1) is developed to predict the behaviour of the permeate flux with both types of fouling occurring on the membrane surface. The model developed assumes that the blocking of the pores of the membrane occurs at first.

Subsequently, the deposits of particles start to form a cake. Although their contribution to the flux decline is unequal, both fouling phenomena are pooled in the combined model in a way to predict the flux decline as a function of time. Based on the combined model, the impact of cake formation on the flux decline increases as time progresses.

The mathematical modeling allows the identification of the fouling type occurring on the membrane surface and the quantification of the permeate flux. This will be determined by the coefficients K_1, K_2, K_3 via curve fitting using the analytical forms in the Table 3.1.

3.3. Process economics

In industry, the largest portion of energy consumed is put into drying and concentrating operations (Muralidhara, 2010). This gives membranes an economic advantage and reduces energy consumption drastically since filtration membranes require minor utilities to operate. In addition, the ability of the membrane to produce high-quality water allows the usage of a portion of the permeate to regenerate the membrane, contributing to operational cost savings (Hang, 2001).

However, the membrane process itself is an expensive practice: it requires continuous cleaning, due to fouling, in order to maintain an acceptable membrane performance. This entails solvent and chemical usage in order to flush the system after an operation period. In addition, although cleaning is essential, restoring the full integrity of the membrane is difficult, which forces the replacement of the membrane after a period of time.

The permeate flux and membrane integrity are benchmarks during the evaluation of the membrane performance to determine the optimum operation time before replacement. The declining integrity is characterized by the deteriorating membrane selectivity and permeate quality.

In many applications, membranes are used in a hybrid process consisting of a membrane along with other units in order to perform drying or concentration while lowering operational costs. Example, pre-concentration by reverse osmosis prior to evaporation reduces energy savings by 78% if only evaporators were used (Muralidhara, 2010).

3.4. Fouling mitigation techniques

Fouling occurring on the membrane surface is the primary complication when employing a membrane-based filtration system to purify large quantities of oil sands water effluents.

As aforementioned, fouling is the physical deposition of particles on the membrane. This covers the pores, obstructs the flow of permeate and creates a significant solute concentration gradient between the feed and the permeate side. Fouling impedes the filtration process by increasing operation costs and causing disturbance in other process units.

Fouling can be mitigated by applying physical and chemical modifications to the membrane, to the feed water and to the direction of permeate flow to overcome fouling.

Pre-treatment is an upstream technique employed to modify the conditions of the contaminated stream before coming in contact with the membrane. This technique will be examined in order to enhance membrane separation efficiency and fouling reduction.

The second technique of interest is the cleaning or backflushing process to regenerate the membrane in order to increase its operational life and improve its performance. Emphasis will be put on backwashing of the membrane using a strong shear force to loosen contaminants from the membrane surface (Peng and Tremblay, 2008).

The last technique of interest is the application of chemical compounds and physical modifications to the filtration membrane surface. In this study, emphasis is put on this specific technique and surface modification will be discussed in length.

3.4.1. Coagulation and flocculation

Pre-treatment is a fouling reduction technique employed on the water feed. Pre-treatment of the solution consists of the addition of chemicals and the control of the physical conditions of the contaminated solution prior to feeding it to the membrane system.

The principles of coagulation, flocculation and sedimentation are key for pre-treatment.

Suspended solids are common components in the waste water stream whose removal requires physical and chemical manipulation of their own properties. These particles are stable in the solution due to the interaction of the physical forces applied to them, mainly the repulsion forces due to similar surface charges (Parastoo and al., 2011).

Coagulants or coagulation agents, dissociate when added to water. As a result, ionic compounds are formed. Their charges destabilize contaminant particle charges, reduce repulsion among the suspended solids and allow them to form flocks. Coagulation is achieved through the compression of the double layer surrounding the contaminant particles. The selection of coagulants depends on the nature of the solids in suspension to be removed, the feed water condition and the quality of effluent required. The most common types of coagulation agents are inorganic compounds: they are known for being effective and practical for large water quantities.

The following step is flocculation and consists of growing the flock size and driving more particles to the flocculation region. This stage typically requires a longer contact time than coagulation. Polymeric molecules are used as flocculants to enhance flock formation and growth by forming a platform to which contaminant particles bond.

Inorganic and polymeric compounds are used as coagulants and flocculants, respectively, and they effectively neutralize, attract and flocculate solid particles (Torres, 2009).

The next step is typically sedimentation, where gravity comes into play due to the increase of flocks' size and mass. This stage requires the addition of a settling tank in the process to maximize the gravity effect and sedimentation efficiency. However, a common industrial application, called direct-filtration process, skips the sedimentation step and proceeds to the removal of microflocs during the downstream filtration process.

Pre-treatments are found to be the most cost-effective techniques to extend the membrane life (Kim and al., 2012): they allow to easily clean the membrane for regeneration by minimizing the amount of foulant coming into contact with the membrane surface.

In an example where contaminated water is treated with an inorganic coagulants, pre-treating the solution with alum, $Al_2(SO_3)_2.18H_2O$, has increased filtration flux by 98.5% at the membrane stage (Kim, 2011). Alum causes salt precipitation, reducing the quantity of salt that could potentially trigger cake formation once it reaches the membrane.

Jar tests conducted by G.A Specken (Specken, 1975) suggested that potassium permanganate used along with a polyelectrolyte (aquafloc 466) is an effective combination of coagulant and flocculent for the treatment of clay water. Results showed that it performs better than an ionized salt, such as alum or calcium chloride that leads to the accumulation of polyvalent ions in the stream. Specken also showed that aeration of the processed water, consisting of adding oxygen, does not enhance flocculation.

On an industrial-scale, the usage of chemicals, either in the solution or on the membrane surface, requires a delicate feasibility analysis to define an optimum between operation costs and membrane performance.

3.4.2. Cleaning

Physical and chemical cleaning techniques are under research to minimize fouling and render the membrane separation process sustainable on a scientific and economic level. The build-up of particles and the formation of a cake pose a significant challenge in developing efficient cleaning procedures and techniques (Wang and al., 2006).

The chemical treatment utilizes fairly concentrated chemical solutions to clean the membrane surface. Often, the solution is formed of compounds that have strong alkalinity, acidity or toxicity to be able to dissolve fouling particles. This increases the operation costs and presents a waste disposal problem for produced streams especially when very strong particle attachment, known as irreversible fouling, is occurring.

The physical methods for fouling reduction consist in the application of pressurized air, vibration, sponge ball cleaning and backflushing to regenerate the filtration efficiency. Water, steam, air cleaners are the most common cleaning agents and consist of applying a

flux in the opposite direction of the permeation flux to detach fouling particles from membranes. Raising the temperature of the cleaning fluid enhances foulant removal by reducing the viscosity of the particles, which eases their detachment from the membrane. Physical techniques can be inefficient if strong fouling is occurring on the membrane.
A combination of both chemical and physical techniques is often performed and involves cyclically alternating between a sequence of chemicals and physical treatments for a set period of time to achieve a desired level of regeneration.

In conclusion, results indicate that membrane recovery quality is a direct result of the regeneration techniques. Backflushing improves membrane performance; however, the regeneration technique’s efficiency calls for an in-depth study for industrial volumes.

3.4.3. Surface modification

A well-known technique for fouling mitigation is achieved by modifying the surface properties of the membrane to reduce foulant accumulation. This is achieved by reducing attractive forces or increasing repulsive forces between contaminant particles and membrane surface (Belfort and al., 1994). The modification of the surface properties involves physical or chemical treatments to increase membranes’ oil rejection feature.

3.4.4. Plasma modification

Plasma is a proposed modification applied to the membrane surface to enhance anti-organic fouling and increase contaminant rejection to assure high-quality permeates.

Experiments conducted on two smooth hydrophilic (NF270 and TFC-SR2) and two rough hydrophobic (NF90 and TFC-S) membranes concluded that the plasma treatment of the membrane surface, with $NH_{3,}$ reduced fouling on the membrane. The decrease in fouling is attained by reducing attraction forces between membrane and foulants. The experiment also showed that treatment is more effective on rough surfaces and the contact angle decreased by 75 % in comparison to smooth surfaces. However, the smallest value of contact angle is observed on membranes with smooth surfaces (12.8°). Increasing time for plasma increased membrane polarity, hence, decreased the contact angle and increased zeta potential. No change in membrane behaviour has been observed for treatment time exceeding ten minutes (Kim and al., 2012).

The experiment also concluded that severe fouling occurred on hydrophobic surfaces due to hydrophobic-hydrophobic interactions between particles and membrane surfaces. Hydroxyl groups present in hydrophilic membranes decreased the amount of fouling occurring on the surface and enhanced water permeation through the membrane. This is a result of a formation of a water layer on top of the membrane surface, reducing affinity between contaminant particles and membrane surface.

3.4.5. Polymer modification

Positive results are achieved by modifying the ceramic surface with polymeric molecules. The addition of a silyl group, known as silylation, though graft polymerization, consisting of the addition of a polymer chain to the main polymer chain, are used to generate a top layer of poly-vinylpyrrolidone, PVP, to form a hybrid polymeric-ceramic membrane

(Castro and al., 1996). The addition of polymer chains of different densities and length to the membrane surface is achieved by radiation or by plasma. It was observed that the flux through modified membranes is higher than the flux through unmodified ones.

Chemical cleaning was required when using a polyamide composite layer and it is due to irreversible fouling occurring on the surface of both modified and unmodified membranes. For the permeation flux, the polyamide modified membrane showed a significant improvement (of 63 %) over the unmodified membrane (Chu and al., 2005).

3.4.6. Nanoparticles

The treatment of the membrane with nanoparticles is proposed to modify the surface of the membrane. Nanoparticles tend to increase the polarity of the membrane, enhancing water affinity to the membrane surface. Metal oxides such as (Al_2O_3 or TiO_2) and silver are the most common nanoparticle materials utilized for membrane surface modification.

Nanoparticles are deposited by dip-coating consisting of dipping the membrane into a solution containing nanoparticles in suspension. An organic binder such as phytic acid is used to deposit metal oxide nanoparticles onto the membrane surface (Karnik, 2006). Conversely, the membrane enhanced with silver nanoparticle requires dipping into Ag-TiO2 solution and sintered at high temperature (Ma and al., 2009). Coating conditions, such as the number of layers and sintering temperatures, affect directly the performance and efficiency of the nanoparticles on the membrane-coated surface (Jeonghwan, 2010).

Nanoparticle application significantly improved the regeneration of the membrane. The ability of easily removing the fouling cake, by backflushing, from a modified membrane has been noted in comparison to unmodified membrane where irreversible fouling impeded the full recuperation of the membrane's performance (Faibish, 2001).

Also, nanoparticles enhanced the permeation flux through the membrane and reduced contaminant accumulation; however, their application in an industrial-scale filtration system raises the need for an economic and environmental impact assessment.

Although promising results are found using several modification techniques, the eventual objective of this work is to find a method to be applied to a tubular membrane in a full scale industrial process. Therefore, membrane modifications requiring plasma treatment, nanoparticles or vapour deposition applications will be extremely difficult to implement to the interior of the membrane, hence, such modifications will be discarded from testing. In the light of all these restrictions, dipping is the main technique to be applied to attach chemical molecules to the membrane surface.

With literature being poor in regards to the usage of modification agents for ceramic membranes dip-coating, several modification molecules are selected, using theoretical principles, to modify the ceramic membranes' surfaces tested in this work. Dipping and modification agents are discussed with the laboratory system components in section 4.

4. Experimental filtration system

4.1. Laboratory system

As previously mentioned, filtration membranes separate the feed stream into two other streams: retentate and permeate. The retentate stream contains dissolved solids, oil, organic and inorganic particles that are retained by the membrane, and, the permeate is mainly formed of an aqueous phase containing particles smaller than membrane pores.

For this project, a pilot plan scale system is developed to filter SAGD processed water. The system employs industrial scale membranes having a tubular shape with a hollow center for flux passage. However, the operational and economic challenges ensuing from applying modifications to a pilot plan scale process highlight the need to conceive a smaller filtration system. The laboratory system is installed and operated to mimic the pilot plant process. The laboratory system allows the manipulation of the process variables flexibly and feasibly.

For this work, on a laboratory scale, the membranes have the shape of a disk and are placed in a circular cross-flow cell with a channel height of 2 mm. For cleaning and regeneration purposes backflushing is performed, in cycles, using a volume of distilled water. To note, pure water is used for backflushing since the permeate is to be conserved for weighing.

The scope of this system is to delve into the filtration process occurring at the laboratory scale, in a way to analyze the membrane's behaviour and efficiency. The laboratory system runs processed water filtration experiments to test and identify chemicals and physical conditions that show fouling mitigation. The ability to reach conclusive results that could be applied to a pilot plan scale is an ultimate goal of this project.

4.2. Equipment and apparatus

The laboratory system (fig 4.2) consists of a feed tank containing the bitumen solution. The feed mixture is formed of sea-water and oil and is continuously stirred by a mixer to inhibit oil droplets from coagulating on the liquid’s surface or on the tank’s walls.

A gear pump circulates the solution from the feed tank to the membrane cell. The tank is jacketed by a water compartment through which passes hot water from a heater.

A pressure gauge is installed to control the pressure on the feed side of the membrane.

The core of the set-up is the membrane, sealed tightly in a cell. Solution from the tank is continuously fed to the feed side of the cell housing the membrane. The permeate side of the cell is split into two, and valves are present on each line. The main valve feeds the permeate recipient (V-101 in fig 4.2) and another valve (V-102) serves for backflushing. During filtration, the main valve opens and the permeate is collected in a tank placed on a scale to determine its weight. In backflushing mode, the main valve closes and the backflush valve opens. The diaphragm pump pushes distilled water, back to the permeate side through the membrane cell for cleaning.

Labview software is employed to control the experimental parameters by computer. The valves’ sequences, the operation and backflushing periods are monitored and controlled electronically. Values of weight measurements are recorded on an Excel spreadsheet.

4.3. Feed solution

In the pilot filtration process, the membrane system is preceded by a hydrocyclone, in a way that the underflow of the latter, rich in water, constitutes the membrane feed.

The solution used is prepared in a way as to mimic the effluent's processed water from the hydrocyclone process. Bitumen is added to distilled water at a concentration of 2 g/L. The solution is heated in order to reduce viscosity of the dispersed bitumen particles. As for salt content, salts are added to the solution. To obtain representative salt mixtures contained in SAGD process water, a salt composition containing the same proportion of salts as found in seawater is used in all experiments (on a few occasions, sea levels rose and flooded the continental basins of northern Alberta and Saskatchewan where oil sands are found in Canada (Meijer Drees, 1990, van Hees, 1956; Norris 1963; Rice, 1967)). Minerals are added to the solution in the following values:

Table 4.1: Concentration of salts in processed water

Chemical	Concentration (g/L)
NaCl	73.6
$Na_2SO_4.10H_2O$	12.3
$MgCl_2.6H_2O$	33.3
$CaCl_2$	24.3
KCl	2.1
$NaHCO_3$	0.6

Calculations are made based on brine containing half seawater and can be found in appendix "A" (Burnett, 2006).

4.4. Membrane type

At the membrane level, bitumen will be in direct contact with the membrane surface. The high temperature forms the main challenge for the membrane application. The processed water emerges from the SAGD process at a temperature ranging between 90 and 95° C. This elevated temperature is the reason behind selecting inorganic ceramic membrane for oil sands water filtration given its stability at a wide range of temperatures and pH.

Ceramic membranes employed in the filtration experiments are formed from metal oxides molecules: Alumina (Al_2O_3), Zirconia (ZrO_2) and Titania (TiO_2) with an Alumina-Zirconia support layer. Their model follows the hydrodynamic or exclusion model, which separates stream components based on particles' sizes.

The ceramic membranes have molecular weight cut-offs of 50 kDa, 150 kDa, 300 kDa, 1250 kDa. To note that the molecular weight cut-off (MWCO) is defined as the molecular weight of the smallest molecule of which 90% is retained by the membrane. The membranes with the highest MWCO (1250 kDa) are TiO_2-based, and the lower MWCO are made of Al_2O_3 or ZrO_2.

In addition to their stability, the chemical morphology of the ceramic membranes is the other reason for their selection. Zooming on the chemistry aspect, the oxygen atom in the metal oxides captures a hydrogen atom from the process water to create a hydroxyl group, generating a hydrophilic feature. The hydrophilicity of the membrane increases the wettability of the surface, boosting the affinity of the latter to water molecules (Buekenhoudt, 2008). Due to oil's high viscosity, hydrophilic membranes are more fit for water filtration given their ability to repel oil molecules and prevent pore clogging.

Although polymeric membranes are relatively unstable at high temperatures due to their weak thermal resistance, two polymeric membranes were tested.

A hydrophilic polyacrylonitrile (PAN) polymer membrane with a polyester (PET) non-woven support layer was tested (Manufacturer Sterlitech). PAN is a polymer formed by a $(C_3H_3N)_n$ monomer and can remain fairly stable at relatively high temperatures (Rahaman, 2007) . The PAN membrane used has a MWCO of approximately 500 kDa.

The high hydrophilicity of the PAN caused by the presence of the functional group CN forms hydrogen bonds with water molecules increasing water permeation.

A Polyethersulfone membrane (PES) with a MWCO of 100 kDa is also tested with processed water to study its performance (Manufacturer GE Osmonics). Even though, PES membranes can be chemically and thermally stable at relatively high temperature, fouling on this type of membrane is expected to be significant due to membrane hydrophobicity (Chu and al., 2005). However, the chemistry of a compound containing sulfur groups and cyclic molecules hinders the secondary forces between the foulants particles and the membrane surface which can promote water permeation.

4.5. Modified membranes

Reducing fouling is achieved by weakening the interaction forces between contaminant particles and the membrane surface. In this regard, the goal is to add specific functional groups to the ceramic membrane with the ability of reducing attraction forces or creating repulsion between foulant particles and membrane surface. The effects of modification agents on membrane permeability, stability and fouling reduction are investigated.

Chemical substances, known as modifying agents, are applied to the membrane surface to modify its morphology in order to enhance its resistance to fouling. Inorganic agents with a hydrophilic feature enhance the permeation of water through the membrane by creating a water layer on the surface (Wong, 2012) and reducing secondary chemical bonds between foulants and surface. Modification agents applied in-lab are deposited on ceramic membranes via dipping.

Although polymers have shown promising results in literature (Chu and al., 2005 & Castro and al., 1996) in reducing fouling on membrane surfaces, the high temperature of the effluent SAGD processed water (95 °C) causes the deformation of polymeric chains. This leads to the polymeric membrane exhibiting creep flow and, the overall MWCO of the membrane to decrease. These two events will directly contribute to reduction of flux. Moreover, the modification of a polymeric membrane requires special and more complex techniques that are difficult to perform in-lab. Henceforth, the use of polymeric molecules in the experiments is limited to the prefabricated PAN and PES membranes.

MSTFA (*N*-Methyl-*N*-trimethylsilyltrifluoroacetamide) is an organic molecule, employed as a modification agent and deposited via in-lab dipping onto a ceramic membrane.

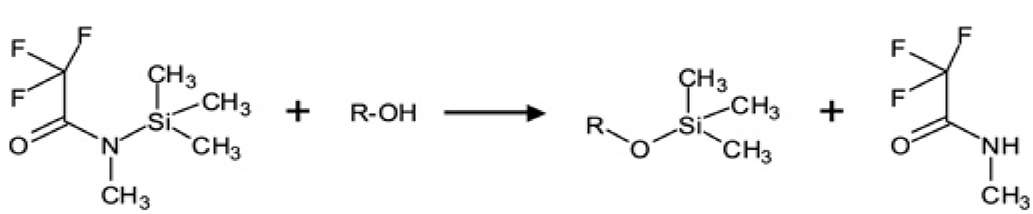

Figure 4.1: MSTFA silylation on the membrane surface (www.sigmaaldrich.com**)**

Having slight hydrophobic features, MSTFA tends to lower the water flux; but, the molecule's functional groups block the chemical groups present on the membrane surface and neutralize the attraction force between surface and foulants. This phenomenon is expected to overshadow the hydrophobic properties of the membrane.

Chemically, the silyl group, present in the MSTFA molecule, creates a covalent bond, via silylation, with the (OH^-) groups (figure 4.1) and neutralizes their activity. Although hydroxyl groups attract water molecules, silylation hinders the attraction forces between the membrane and the foulants which can improve permeation.

Other (undisclosed) modifications were performed on selected ceramic membranes and are listed as A, B, C, D, E and Z.

4.6. <u>Experimental parameters</u>

For consistency and results comparison, the study of the factors' effect on the water flux dictates the variation of a single experimental parameter at a time.

Five factors are tested at different states of physical and chemical conditions (Table 4.2):

The MWCO is varied to understand its influence on the filtration process.

The membrane material is also probed to observe its behaviour under diverse conditions. This includes the modification agents and the modified membrane surface.

The temperature is a major challenge for the membrane; hence, varying the temperature of the solution and studying its consequences is crucial to test the membrane stability.

The pH of the solution directly affects the interaction between membrane and solution. Therefore, the pH influence is examined since chemical interactions between the oil and the surface's functional group defines the fouling type and permeation rate.

Finally, backflushing efficiency is tested to grasp its effect on membrane regeneration.
To note, the pressure will remain constant throughout all experiments (25 psig).
To reduce the amount of resources used, not all combinations of parameters are tested; experiments to be conducted (Table 4.2) are chosen based on results of prior tests.

4.7. <u>Experimental design</u>

Experimental tests are grouped based on the pH value of the feed processed water and results are reported in five sections (Table 4.2).
In the first two sections, the pH of the solution is not altered and is slightly acidic at 5.6. In these sections, the effect of the temperature on permeates flux is studied in a way that the temperature is set at two levels: The lower level at 45 °C and the higher one at 80 °C. Membranes of different MWCO are tested at both temperature levels and compared.
The effect of backflushing on membrane regeneration is tested in the first section.

In section three, the pH of the solution is at 7.5, the temperature is set at 80 °C and ceramic membranes of different MWCO, as well as polymeric PES are put to test.
In section four, the alkalinity of the solution is increased to a pH of 9 and unmodified membranes are tested at 80 °C and compared with results obtained at previous pH values. In the same section, MSTFA modified ceramic membranes are tested.

Ceramic membranes that underwent other modifications with the undisclosed agents are tested in section five at a temperature of 80 °C and a pH of 9.

Table 4.2: Conditions of laboratory experiments

	pH	**Temperature (°C)**	**Membrane tested (polymerics are in italic)**	**Modification agent**
Section 1	5.6	45	50 kDa, 150 kDa, 300 kDa,1250 kDa , *PAN*	MSTFA
Section 2	5.6	80	50 kDa, 150 kDa, 300 kDa,1250 kDa , *PAN*, *PES*	-
Section 3	7.5	80	50 kDa, 150 kDa ,1250 kDa, *PES*	-
Section 4	9	80	50 kDa, 150 kDa ,1250 kDa, *PES*	MSTFA
Section 5	9	80	50 kDa,1250 kDa	A,B,C,D,E,Z

Table 4.3: Laboratory scale filtration system parameters

Parameter	Value or characteristic
Backflushing pump	Hydraulic
Backflushing solvent	Distilled water
Backflushing time	8 seconds
Ceramic membranes MWCO	50 kDa, 150 kDa, 300 kDa, 1250 kDa
Diameter of actual filtration area	38 mm
Feed pump type	Gear pump
Feed tube	3/8 inch Teflon
Filtration cycle	300 seconds
Filtration type	Ultrafiltration
Heater	Water bath coil heater
Membrane diameter	47 mm
Membrane type	Ceramic (Alumina, Titania, Zirconia), Polymeric.
Oil concentration	2g/L
Permeate tube type	¼ inch Polyethylene
Polymeric membranes MWCO	100 kDa (PES), 500 kDa (PAN)
Pressure	25 psi
Software	Labview, Excel
Temperature	45 °C and 80°C
Water pH	5.6, 7.5 , 9

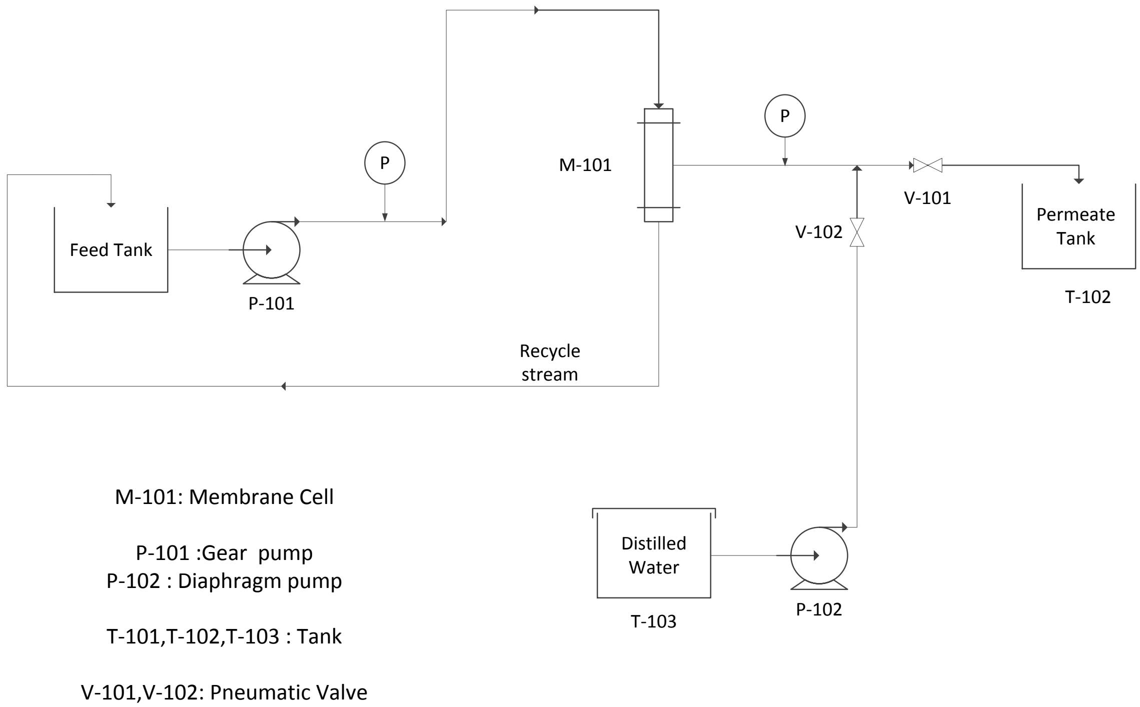

Figure 4.2: Membrane-based filtration laboratory system

5. Experimental findings

5.1. <u>Flux calculation</u>

The permeate flux is an indicator of membrane performance. The drop in the value of the permeation flux is a direct result of fouling occurring on the membrane surface.

In the experiments, the permeation flux value is deduced from the permeate weight measured as a function of time. According to the following formula, the permeate flux volume (litre/m^2.h or lmh) is calculated using the slope of the permeate's weight with respect to time, the density of the solution and the active surface diameter.

$$Flux = (Slope)\ \frac{g}{s} \times 3600\ \frac{s}{h} \times \frac{1}{1000}\ \frac{kg}{g} \times \frac{1}{\rho}\ \frac{L}{kg} \times \frac{1}{\pi(\frac{d'}{2})^2}\ \frac{1}{m^2} \qquad 5.1$$

with: ρ (density) = 1.02 kg/L.
d' (active filtration surface diameter) = 0.038 m

5. 2. <u>Results and discussion</u>

A graph of permeate flux as a function of time is employed as an analysis tool to monitor flux variation throughout the filtration process.

As the permeate is collected and weighed on a digital scale, the weight slope is calculated for each interval (300 s) between backflushing cycles. Using the calculated slope, the corresponding permeate flux is calculated with equation 5.1. To note, there is no backflushing for polymeric membranes but an interval of 300s is used for consistency.

After calculating the flux of all intervals during filtration, values of fluxes are plotted against time to form a graph to analyze the membrane's permeation and fouling.

It is important to note that sections 5.2 and 5.3 are directly related. In fact, results' analysis in both sections help with understanding the type of fouling and the effects that the latter can have on the permeation flux.

Section 5.2 reports and compares the flux values observed for the membranes tested. This section is divided into five sub-sections based on the pH value of the feed solution.
Membranes' individual fluxes throughout the experiment are plotted against time and are grouped in summary charts at the end of each sub-section. Certain charts are split into two for the sole reason of enhancing the clarity and visibility of the individual curves.
It is essential to mention that tests are stopped either when the membrane stability starts fading leading to creep flux behaviour or when the flux has reached a steady-state value for a long time. In both cases, the last value observed and registered is referred to as the final flux value.

Section 5.3 characterizes experimental observations based on chemical and physical phenomena occurring at the membrane surface. Mathematical models are employed to explain results and behaviours observed in section 5.2. The fouling models (Table 3.1) are used to identify the type of fouling occurring on the filtration membrane surface. Along with the flux behaviour, the type of fouling occurring on the surface determines the optimum operation conditions to enhance the filtration process's performance.

All experiments were subject to noise interference with different magnitude. Although some noise interferences are significant, they did not affect the evaluation of the membrane performance since the permeation trends were consistent and the noises formed destructive interferences. This allowed drawing pertinent conclusions. The source of such noises could be equipment error, erroneous read or lack of stability.

Additionally, several membranes witnessed an increasing permeation flux during early stages of the filtration. This phenomenon is simply due to the hot feed mixture raising the temperature of the membrane and its housing.

5.2.1: Results for membranes tested at a pH of 5.6 and a temperature of 45 °C

In figure 5.1-b, the flux of the 1250 kDa MWCO membrane declined and reached a steady-state plateau after 170 minutes. The steady-state flux (129 lmh) indicates that the rate of particle deposition on the membrane surface is equal to the particle diffusion from cake back to the feed solution.

Although it had a steep decline in permeate flux during the early stage of filtration, the flux of the ceramic membrane of 300 kDa showed a slightly higher final flux than that of the 1250 kDa membrane (193 lmh). Both membranes had similar flux behaviours throughout the filtration tests and both fluxes started declining notably after 150 minutes.

A possible interest for future research would be to assess the membrane composition, since 1250 kDa is composed of Titania unlike the 300 kDa fabricated from Alumina and Zirconia.

The ceramic membrane of 150 kDa showed more fouling than membrane with higher MWCO given that the flux was significantly lower than the flux obtained with 300 kDa and 1250 kDa after 100 minutes. The final flux passing through the 300 kDa membrane is 3 folds greater (193 to 48 lmh) than the value of the flux for the 150 kDa.

In figure 5.1-a the ceramic membrane of 50 kDa showed more fouling than that of 300 kDa and 1250 kDa, but was performing very similarly to the 150 kDa ceramic membrane since both showed similar flux values consistently throughout filtration. At the 200 minute mark, the fluxes for the 50 kDa and the 150 kDa were the same, after which the 50 kDa started to illustrate creep flow and the 150 kDa continued the filtration process to reach a final flux at 48 lmh.

The Polyacrylonitrile (PAN) membrane had a final flux of 166 lmh. This flux did not vary significantly during the process, indicating that the polymeric membrane was capable of maintaining its stability at this temperature (45 °C). At any point, the PAN flux was higher than the fluxes of the ceramic membranes. This is due to the superhydrophilicity of the PAN polymeric membrane and its affinity for water.

A 300 kDa membrane was tested without backflushing cycles to examine the effectiveness of backflushing on the permeate flux and the regeneration of the membrane. As seen in Figure 5.1-a below, the ceramic membrane of 300 kDa without backflush showed a fall in the permeation flux value after a short period of time (50 min).

The low value of the permeate flux along with early flux decrease indicate that fouling has severely affected the membrane performance in a way that the flux through 300 kDa, with backflush, is more than 7 fold (193 to 27 lmh) the value of the flux for the 300 kDa membrane without backflushing. This demonstrates that backflushing significantly regenerates the performance of the membrane by removing foulant particles off the surface.

Ideally, one would expect to witness peaks in the flux curve when applying backflushing; however, the characteristics of the foulants and the membrane, especially the bitumen viscosity and the thickness of the ceramic membrane, force the water used for backflushing to permeate slowly through the membrane to clean it. Hence, the backflushing effects on regenerating the membrane performance are not observed spontaneously when backflushing is applied but are translated in reducing the permeate flux decline throughout the ultrafiltration experiment.

Despite the positive effects of backflushing on the permeation flux, when fouling starts to severely accumulate on the membrane surface as filtration progresses, the efficiency of regenerating the membrane by backflushing diminishes and the permeation flux decreases to nil. If the crossflow and the backflushing are able to counter the rate of foulant deposition on specific membranes, a steady state flux value will be reached.

The results for the ceramic membrane of 1250 kDa modified with MSTFA are shown in figure 5.1-b. The membrane had a flux behaviour and final value similar to that of the unmodified membrane (123 to 129 lmh).

The modification with MSFTA was also done on a 300 kDa membrane; though, no water permeated through the membrane. The membrane had become completely non water wetting.

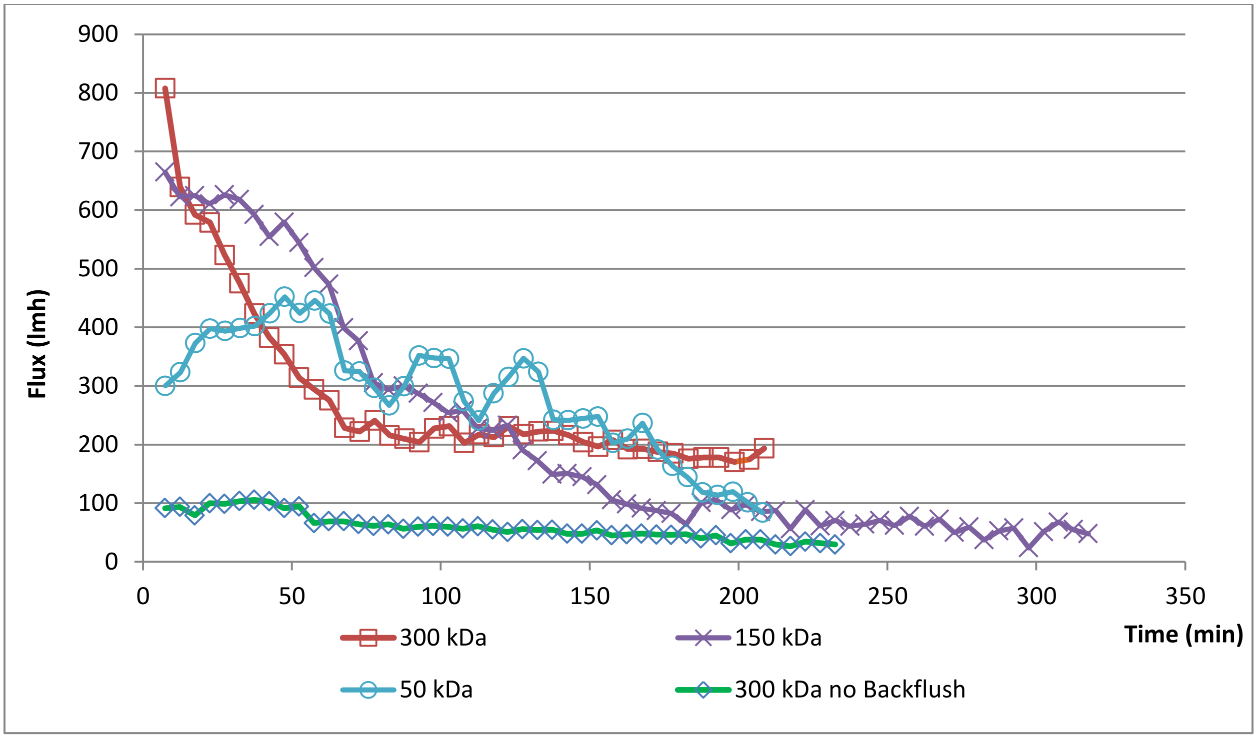

Figure 5.1-a: Fluxes for membranes at a pH of 5.6 and 45°C

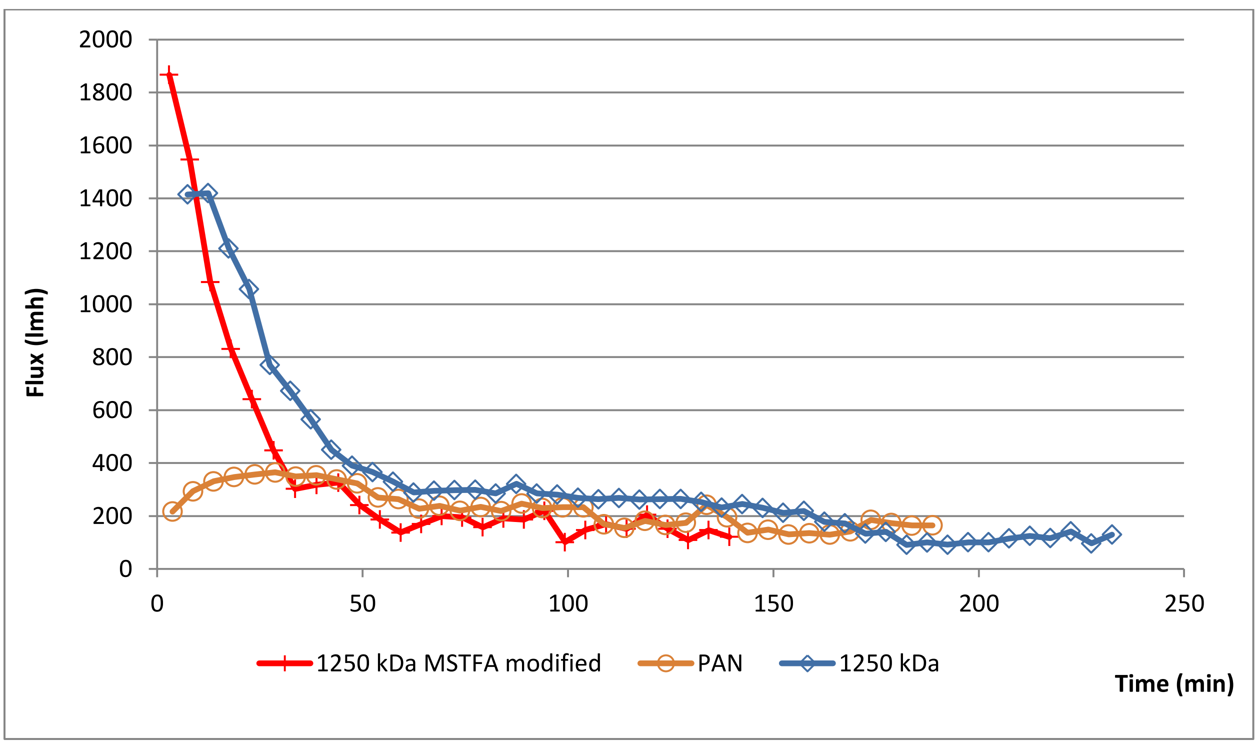

Figure 5.1-b: Fluxes for membranes at a pH of 5.6 and 45°C

5.2.2: Results for membranes tested at a pH of 5.6 and a temperature of 80 °C

The same set of ceramic membranes were studied at a higher temperature of 80° C. For all membranes, the decrease in permeation flux was accelerated at high temperature, indicating a rapid deposition of foulants on the membrane surface.

The flux of the 1250 kDa membrane as a function of time is shown in figure 5.2-a. The membrane showed very low water flux permeation (final flux at 11 lmh) in comparison with the same pore size membrane at a lower temperature. The 1250 kDa ceramic membrane had the lowest permeate flux among all ceramic membranes.
The 300 kDa showed a slightly superior performance than the 1250 kDa (fig 5.2-a), with an abrupt reduction in flux permeation during the early stages of the filtration experiment. The 300 kDa membrane also had a lower permeation flux value at a higher temperature.
The ceramic membrane of 150 kDa showed a better performance than larger pore size membranes at high temperature (53 lmh). This is due to the type of fouling occurring (section 5.3) which can be less severe for smaller pore size.
The ceramic membrane of 50 kDa had the best performance at high temperature, and the longest running time before reaching a final flux (63 lmh), although it had a significant amount of noises. The general trend shows that at high temperature the membranes with smaller pores size had less fouling.

The Polyacrylonitrile (PAN) membrane (fabricated by Sterlitech), at high temperature, has exhibited a flux significantly lower than the flux obtained at lower temperature (166 to 63 lmh). In addition to fouling increase, this discrepancy is predictable since the polymeric membrane was expected to lose, at high temperatures, the polymeric layer that provides it with the hydrophilic feature. In comparision with the ceramic membrane, the polymeric PAN membrane lost its performance superiority due to its lower stability.

The PES, another polymeric membrane, showed a very low permeation flux, in fig 5.2-b. Decreased stability may also have been a reason for the low permeation flux value for the PES.

The PES hydrophobic feature contributes mainly to the low flux permeation; its effect is obvious during the early stages of the experiment where the permeation flux was low.

It can be concluded that at high temperatures, the smaller the pore size, the better the performance of the membrane. This is due to the change in oil droplet viscosity, and possibly size, in a way that the former is allowing the oil to be driven by the permeating specie (water) to enter the membranes with large pore sizes, leading to its blockage. For the smaller pores, the oil droplets were unable to penetrate the pores and only deposited on top of the membrane surface. In turn, the filtration cake, formed by the accumulation of the oil droplets, is reduced by the cross flow pattern or by a backflush.

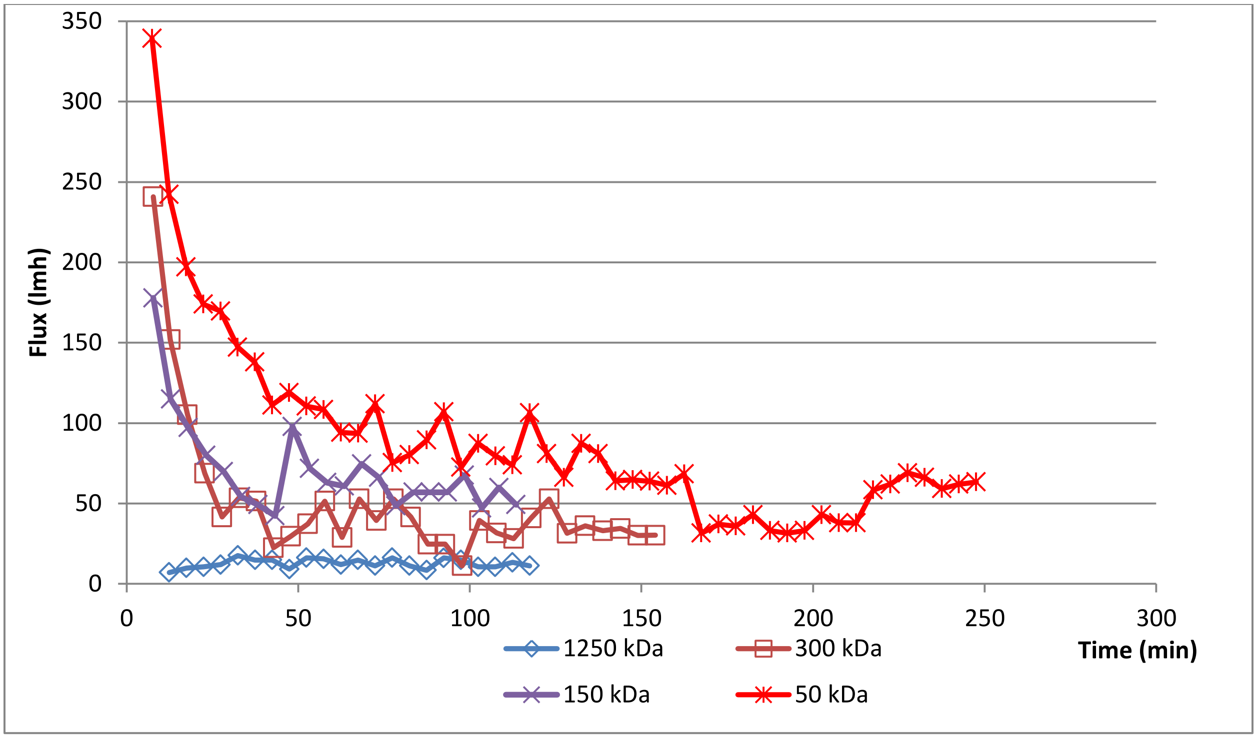

Figure 5.2-a: Fluxes for membranes at a pH of 5.6 and 80°C

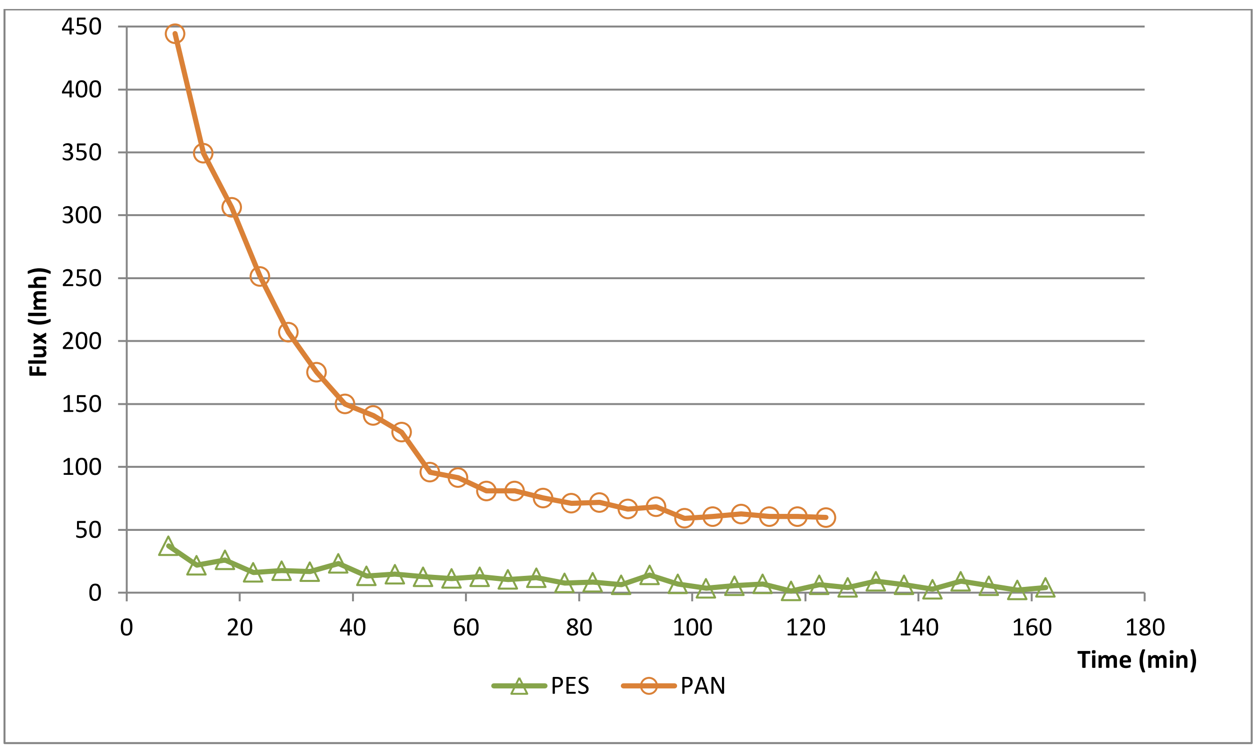

Figure 5.2-b: Fluxes for membranes at a pH of 5.6 and 80°C

5.2.3: Results for membranes tested at a pH of 7.5 and a temperature of 80 °C

All membranes in this section are tested at a temperature of 80 °C and results are shown in figure 5.3. Results are discussed further in section 5.3 but it is clear that the rise in pH augments the flux value during filtration, indicating a reduction in foulant accumulation. From a chemical point of view, the presence of OH^- ions in the solution increases the hydrophilicity of the membrane surface allowing water to penetrate easily (Mantari, 2006).

Fluxes observed in this section have reached a quasi-steady state, as shown in figure 5.3.

Marked by a significant early flux reduction, the 1250 kDa membrane showed a final flux of 28 lmh. This value is an improvement over the previously observed rate at a lower pH, where the flux reached zero. This amelioration was due to the rise in the solution pH.

The 150 kDa membrane showed a similar behaviour to the 1250 kDa and is denoted by a flux increase due to the solution pH rise. The final flux for the 150 kDa is at 84 lmh.

The 50 kDa membrane reached a plateau at 360 lmh. The flux decline is fairly low during the early stages in comparison with other membranes although the steady-state was reached more rapidly. The 50 kDa exhibited the best performance among all membranes at a pH of 7.5.

The 50 kDa and 150 kDa ceramic membranes showed the same flux at 100 minutes; yet, the membrane with the smallest pores size (50 kDa) maintained a higher flux afterwards.

The hydrophobic polymeric PES membrane exhibited poor performance in this test. The rate of decline in permeation flux was consistent over time and reached a value of zero. This poor performance raises the question of polymeric membranes' stability at high temperatures. In addition to thermal stability, the PES is expected to furthermore lose its performance with rising pH due to its hydrophobic and water repelling characteristics.

It was clear that the increase in the solution's pH had a direct effect on water permeation through ceramic membranes. The relatively high flux through the membranes is a direct result of hydrophilicity increase due to the OH^- ions. Although it is discussed in the fouling modeling (section 5.3), it is noteworthy to mention that hydroxyl ions in the solution create hydrogen bonds with the membrane surface, attracting water molecules and reducing fouling accumulating on the surface. Moreover, the flux value trend at high temperatures persisted as the flux values increased with decreasing pore size.

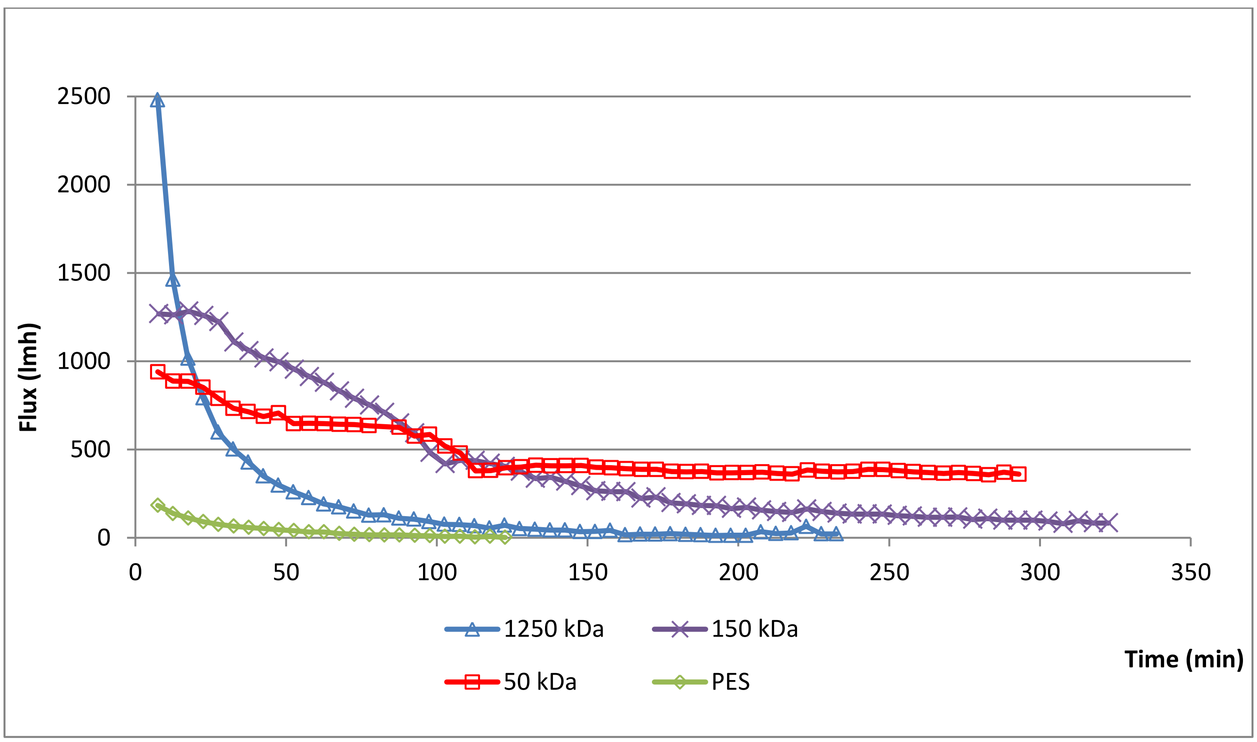

Figure 5.3: Fluxes for membranes at a pH of 7.5 and 80°C

5.2.4: Results for membranes tested at a pH of 9 and a temperature of 80 °C

The 1250 kDa ceramic membrane showed a small variation in data points as seen in figure 5.4-b. At a level of pH 9, the membrane showed a slightly higher flux than that observed at a pH of 7.5 (33 to 28 lmh). The permeation flux is considerably lower during the filtration process and no significant volume permeated during the experiment.

The 150 kDa membrane clearly follows the trend in which the permeate flux increases with rising pH. The flux almost doubled in comparison with that observed at a pH of 7.5. The 150 kDa membrane also continued to show superiority over 1250 kDa at the same temperature and pH level.

The 50 kDa membrane exhibited a final flux of 249 lmh, in figure 5.4-a. In this section, the 50 kDa membrane showed small variation in permeation flux during filtration, as opposed to the decline observed for the 150 kDa membrane. Both membranes had the same flux at minute 150; subsequently, the 50 kDa maintained a relatively high and stable flux whereas the 150 kDa membrane flux continued to decline.

The polymeric polysulfone membrane (PES) exhibited poor permeability at a high pH and high temperature (15 lmh). In addition to low flux being caused by the instability at high temperatures.

The MSTFA modified membrane did not show any noticeable improvement in figure 5.4-b. The final flux through the modified membrane was slightly lower than the flux through the unmodified 1250 kDa membrane. This signifies that the MSTFA molecules narrowed the pore size without significantly mitigating fouling accumulation on the membrane surface.

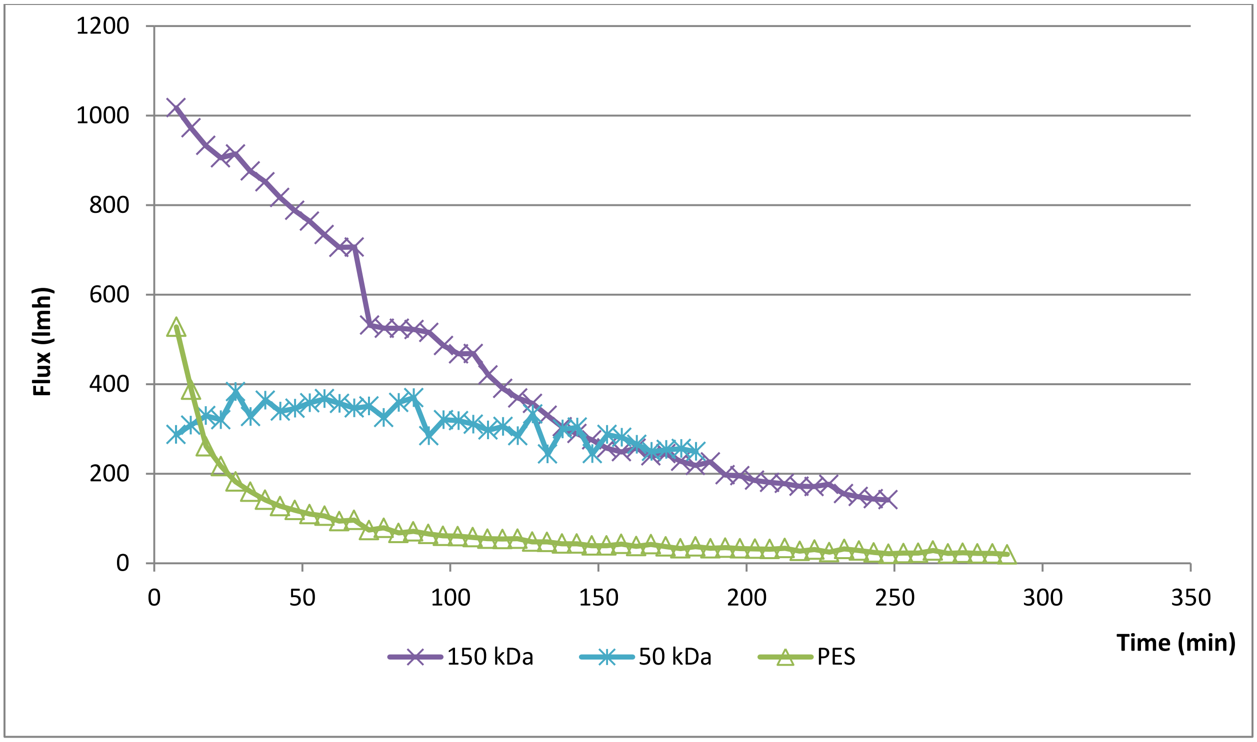

Figure 5.4-a: Fluxes for membranes at a pH of 9 and 80°C

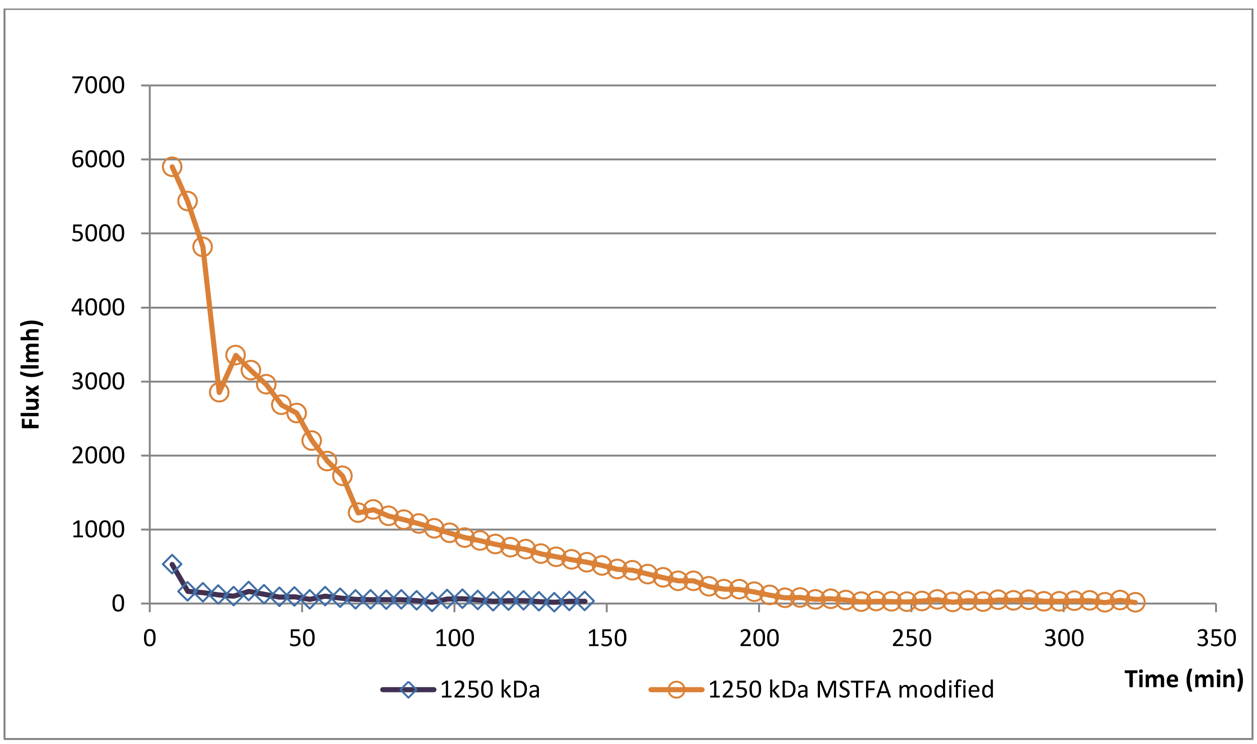

Figure 5.4-b: Fluxes for membranes at a pH of 9 and 80°C

5.2.5: Results for modified membranes at a pH of 9 and a temperature of 80 °C

A series of modification agents was applied to 50 kDa and 1250 kDa membranes. The molecules in use for the modification are undisclosed due to intellectual property issues. For this thesis, these agents are arbitrarily named A, B, C, D, Z and E : the first five modification agents are employed on 50 kDa ceramic membranes and agent E is applied to a 1250 kDa membrane. Filtration results are shown in figure 5.5-a and 5.5-b.

A started to decline during early stages of filtration, as seen in figure 5.5-a. Agent A and Z had a same flux at minute 60 ,then, A started to show a steeper decline than Z. The latter did not vary from the flux observed on the unmodified 50 kDa.

The permeation flux through the 50 kDa membrane modified with a slightly hydrophilic agent B was almost nil. The 50 kDa membrane modified with hydrophobic agents C and D showed a very low permeation flux. The observed flux value was mostly due to the noise caused by the laboratory equipment since no permeation volume was collected during the experiment.

Although the flux for the modified 1250 kDa exhibited a quick drop initially, a steady-state was reached during the experiment and the final flux observed, in figure 5.5-b, for the modification E was 387 lmh. This is 10 fold higher than the flux of the unmodified 1250 kDa membrane and 1.5 times higher than the unmodified 50 kDa membrane, at a pH of 9 and 80°C.

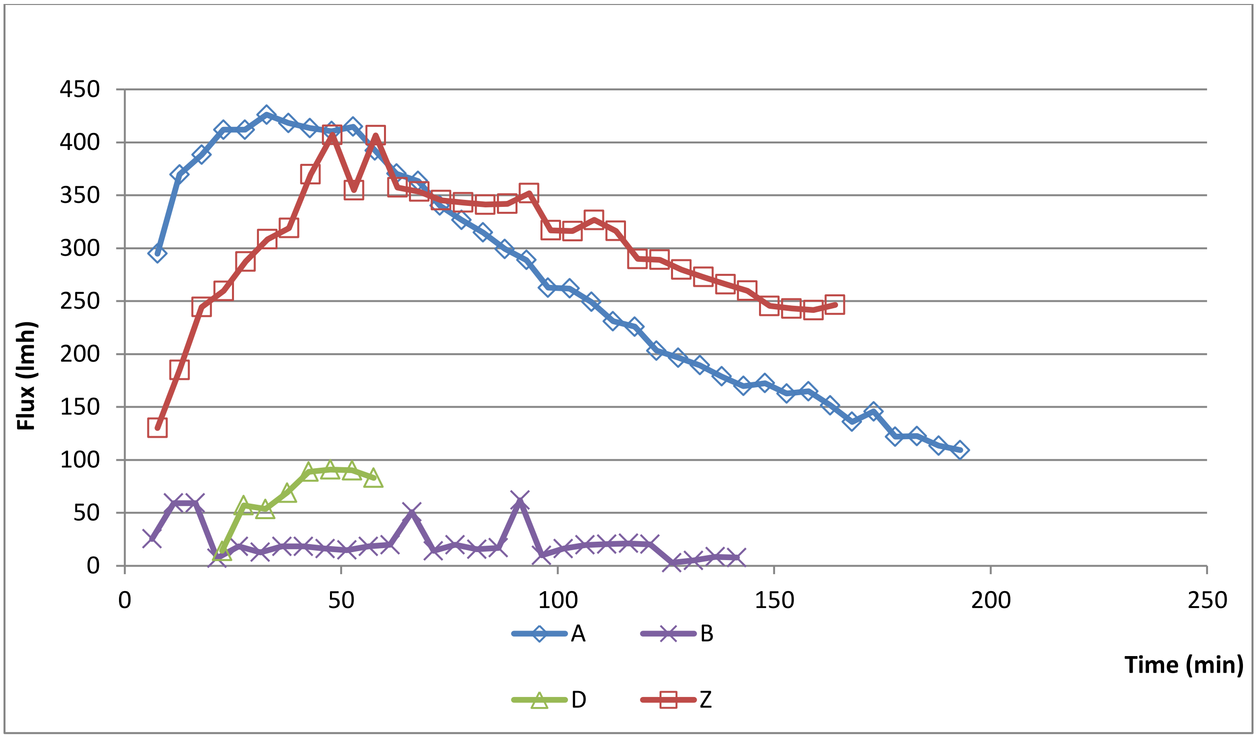

Figure 5.5-a: Fluxes for modified membranes at a pH of 9 and 80°C

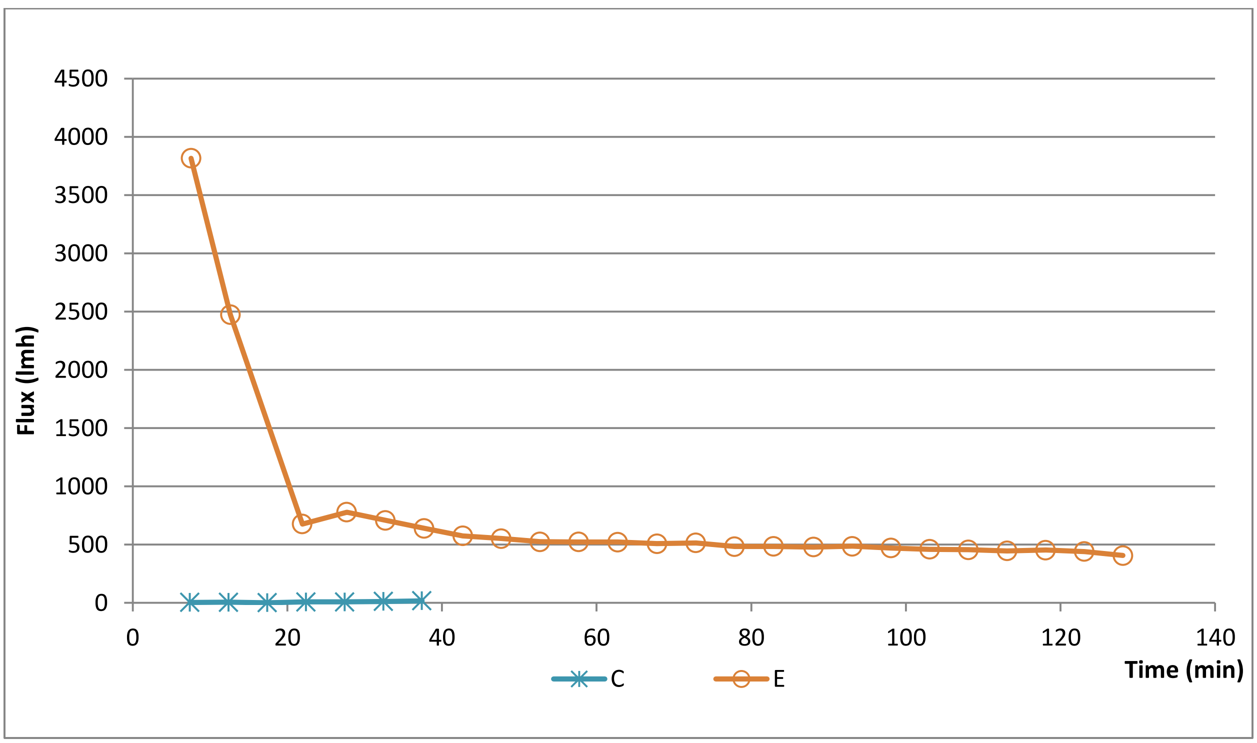

Figure 5.5-b: Fluxes for modified membranes at a pH of 9 and 80°C

Table 5.1: Final Fluxes for membranes tested at different temperatures and pH

At 45 °C and a pH of 5.6	
1250 kDa	129
300 kDa	193
150 kDa	48
50 kDa	84
PAN	166
1250 kDa (MSTFA)	123
300 kDa (No Backflush)	27
At 80 °C and a pH of 5.6	
1250 kDa	11
300 kDa	29
150 kDa	53
50 kDa	63
PAN	63
PES	16
At 80 °C and a pH of 7.5	
1250 kDa	28
150 kDa	84
50 kDa	360
PES	0
At 80 °C and a pH of 9	
1250 kDa	33
150 kDa	141
50 kDa	249
PES	15
1250 kDa (MSTFA)	19
A	109
B	21
C	0
D	0
E	387
Z	247

5.3. Fouling modeling

In light of the data presented in section 5.2, the flux observed through the membranes is analyzed along with the fouling phenomena in order to understand the physical and chemical events taking place on the surface of the membrane. The objective is to be able to determine the optimum experimental conditions that lead to an increase in permeation flux by the reduction of fouling accumulation on the membrane surface. Experimental conditions tested consist of the factors that are under investigation, presented in Table 4.2: membrane type, membrane MWCO, solution pH, temperature and modification agent.

In addition to analysing the performance of the membrane as function of the experimental conditions, the type of fouling occurring on the membrane surface is of critical importance in order to explain fouling accumulation and the subsequent reduction in permeation flux.

For fouling analysis, collected data is fitted in mathematical models to determine the type of fouling taking place during filtration. It is not possible to understand the fouling phenomena without studying the chemical events occurring at the membrane surface. Chemistry principles are visited in the fouling characterization simply because the fouling taking place on the membrane surface is due to chemical bonds and interactions.

The analytical forms presented in Table 3.1 are employed to conduct fouling analysis. Fouling model expressions (right hand side of the equation in Table 3.1) are compared with the normalised flux $\frac{J_v}{J_o}$, which is the actual flux value (in lmh) divided by the permeation flux of pure water through an unfouled membrane.

Using a statistical package (in Excel), the Root Mean Square Error (RMSE) is minimized by adjusting the values of the coefficients (K) in the analytical forms. The main feature of the fouling modelling is the presence of a combined model that lumps cake fouling and pore clogging in one expression containing three coefficients $K_{1,}$ $K_{2,}$ K_3. It is expected that the combined model will be able to best model the fouling occurring on the membrane. On one hand, since the model contains three coefficients, it is obvious that the later will have an edge over other models to minimize the error. On the other hand, it is also predicted that on the membrane surface, both fouling types will be occurring in different proportions. Therefore, it is important to probe the second lowest RMSE value in order to identify the contribution of each fouling type to the combined fouling model.

This section follows the same division as section 5.2, where membrane tests are performed based on solution pH level. Experimental results and analysis are presented in the sub-sections. In every sub-section, for each filtration membrane, a detailed analysis of the fouling type is given, followed by a table summarizing the RMSE values for membranes tested.

The smallest RMSE value corresponds to the fouling model occurring dominantly on the membrane. The second lowest RMSE corresponds to the second best model.

To note, the smallest RMSE value will be in bold, the second smallest will be underlined. For purposes of consistency, the water flux through the clean membrane J_o is assumed to be the permeation flux during the first seconds of the experiment, before fouling starts taking effect. By doing so instead of performing full water runs, the actual flux and the clean membrane flux would be generated during the same experiment and any discrepancy that might result from experimental settings variation are eliminated.

5.3.1: <u>RMSE at a pH of 5.6 and a temperature of 45 °C</u>

For the 1250 kDa ceramic membrane, pore constriction is indicative of the oil droplets entering the pores and depositing on the sides of the membrane's pores, thus, reducing the water flux permeation. This is proven by assessing flux values obtained with the 300 kDa membrane. Although the 300 kDa has smaller pores than 1250 kDa, it had a higher permeation flux. This can be explained by the intermediate blocking occurring on the 300 kDa membranes in which oil droplets form bridges amongst each other. This phenomenon blocks a portion of the pore but keeps void channels for water permeation.

The fouling occurring on the 150 kDa membrane had an important portion of complete pore blocking caused by the oil particles hindering significantly the water permeation. The complete blocking fouling is the most severe type of particulate fouling and is the reason behind the 150 kDa membrane having the lowest final permeation flux.

The 50 kDa membrane performance was similar to that of the 150 kDa but had a lower flux than the 1250 kDa and 300 kDa membranes during filtration. Based on data in Table 5.2, complete blocking is occurring on the 50 kDa, although all RMSE are very close in value which indicates that pore clogging and cake accumulation are occurring simultaneously on the membrane and have a similar weight in the combined model.

The effect of the backflushing was studied to determine the efficiency of applying cleaning techniques for membrane regeneration. A 300 kDa ceramic membrane experimented without backflushing witnessed a flux decline of more than 7 fold in comparison with a membrane of the same pore size undergoing a cleaning cycle. This clearly showed that the backflushing contributes directly to the membrane regeneration. Fouling modeling has showed that the partial blocking observed on a 300 kDa membrane undergoing cleaning cycles has become a complete blocking model in a system without backflushing. The lodging of oil on the membrane surface for an extended period of time has caused the total blockage of the pores and reduction of water permeation flux.

The polymeric membrane (PAN) showed exceptional performance at this temperature. The results revealed a high permeate flux with a small amount of fouling. Based on RMSE analysis, fouling on the PAN membrane did not take a specific form and RMSE was not conclusive.

The flux of the MSTFA modified membrane was similar to that of the unmodified membrane of equal pore size. Pore constriction occurred on both modified and unmodified membrane. The experiment indicates that the MSTFA molecules were able to neutralize the OH^- groups on the membrane surface leading to fouling reduction; however, the MSTFA molecules have reduced pores' width causing no significant improvement in the permeation flux.

Table 5.2: RMSE for fouling models at a pH of 5.6 and 45 °C

Membrane	Complete Blocking	Intermediate Blocking	Pore Constriction	Cake Filtration	Combined Model	Final Flux (lmh)
1250 kDa	0.085	0.0853	<u>0.0729</u>	0.124	**0.058**	129
300 kDa	0.106	<u>0.0512</u>	0.0669	0.060	**0.031**	193
150 kDa	<u>0.074</u>	0.117	0.097	0.140	**0.024**	48
50 kDa	<u>0.296</u>	0.300	0.298	0.303	**0.192**	84
300 kDa No Backflush	<u>0.095</u>	0.108	0.101	0.122	**0.0001**	27
PAN	0.332	0.333	0.333	0.333	**0.219**	166
1250 kDa MSTFA	0.065	0.076	<u>0.058</u>	0.121	**0.118**	123

5.3.2: <u>RMSE at a pH of 5.6 and a temperature of 80 °C</u>

RMSE data did not determine the type of fouling occurring on the 1250 kDa membrane, but the flux value reached zero at the final stages, showing that a significant amount of fouling is occurring on the 1250 kDa membrane surface.

At 300 kDa, although fouling was taking place under the intermediate type, the foulants' accumulation started to become more severe due to the ability of a larger amount of foulant particles to enter the pores of a 300 kDa when temperature is raised. Fouling type for 300 kDa was not a function of temperature (remained intermediate), but led to a notably decreased permeation flux.

At 150 kDa, water flux increased in comparison with larger pore sizes. This increase is explained by the intermediate blocking model under which fouling is occurring. Although the penetration of particles inside the pores must decrease the water flux, this form of fouling is less harmful to the permeation flux. This is due to particle build-up inside the pores which leaves open channels between oil droplets and creates voids for water permeation.

At 50 kDa, RMSE showed that cake filtration was occurring dominantly. The high flux through the 50 kDa membrane is the result of a cake fouling model occurring in which the cake thickness is reduced by the crossflow, easing the permeation of water.

The polymeric PAN membrane lost the clear advantage observed at low temperatures. Even though the flux through the PAN membrane is still relatively high due to partially active hydrophilic groups on its surface, RMSE showed that the complete blocking model took place on the PAN membrane. This is a result of polymeric chains losing their chemical stability and exceeding their plastic temperature (~ 75°C), defined as the temperature after which the polymeric chain loses their chemical forms and features beyond recuperation. The significant difference in the flux values between low and high temperatures suggests that PAN's performance will deteriorate furthermore with longer filtration times (Mitsu, inc.).

The PES membrane showed a low flux at high temperatures with slight pore restriction. The low flux can be the result of the polymeric chains losing stability and the MWCO of 100 kDa being too small for a hydrophobic membrane. Although RMSE showed a pore constriction, the permeation flux was low throughout the whole filtration process.

While membranes with hydrophilic features are more favourable for water filtration, the behaviour of both polymeric membranes, PAN and PES, showed that the membrane stability is a main player at high temperatures regardless of the polymeric chain nature.

At elevated temperatures, flux increased with decreasing pore sizes; hence, smaller pore size membranes are apt to less fouling. This is due to the viscosity of oil droplets in the solution. At high temperatures, bitumen droplets' viscosity decreases allowing them to enter the pores of the high MWCO ceramic membranes, along with water. Conversely, smaller pores retain oil droplets and limit their penetration to a shallow depth inside the pores.

Table 5.3: RMSE for fouling models at a pH of 5.6 and 80 °C

Membrane	Complete Blocking	Intermediate Blocking	Pore Constriction	Cake Filtration	Combined Model	Final Flux (lmh)
1250 kDa	0.233	0.233	0.233	0.235	**6.9E-05**	11
300 kDa	0.124	0.093	0.100	0.110	**0.026**	29
150 kDa	0.102	0.051	0.128	0.099	**0.0013**	53
50 kDa	0.188	0.189	0.068	0.064	**0.007**	63
PAN	0.061	0.087	0.065	0.129	**0.009**	63
PES	0.086	0.077	0.072	0.107	**0.010**	16

5.3.3: RMSE at a pH of 7.5 and a temperature of 80 °C

At a temperature of 80° C and a pH of 7.5, the complete blocking model was still dominant for high MWCO membranes (there was no need to test a 300 kDa). However, the permeation fluxes for all membranes were higher than fluxes observed at a lower pH.

For smaller pore size membranes, 150 kDa and 50 kDa, the fluxes were also higher than the fluxes observed at a lower pH. The 150 kDa witnessed pore constriction model as opposed to complete blocking observed at a 5.6 pH, and the 50 kDa underwent an intermediate blocking model. The change from a cake model to intermediate blocking model is due to the increase in electrostatic attractive charges between the oil droplets and the membrane induced by the addition of hydroxyl ions (OH^-). Even though cake fouling is less harmful to the permeation flux than the intermediate model, the addition of (OH^-) increases the hydrophilicity of the membrane surface and reduce the effect of the foulant accumulation by creating a water layer on top of the filtration membrane surface.

Delving into chemistry, the hydroxyl groups added to the solution interact with the hydroxyl groups present on the membrane surface, in a way that an attraction hydrogen bonding is formed. When attracted by the membrane surface, hydrogen bonds formed between OH^- and water molecules, will drag the latter towards the membrane. A water layer is formed on top of the membrane reducing foulant adherence to its surface. This eases the passage of water molecule through the membrane to the permeate side.

The attraction forces strength on the membrane surface are directly proportional to the concentration of OH^- groups in the solution. In fact, by raising the pH and increasing the concentration of hydroxyl groups, the activity of the attraction process described above will increase as well, leading to a higher permeation flux and fouling reduction.

The flux of the PES filtration membrane has reached zero with a complete fouling model. This is due to the plasticization of the membrane by bitumen.

Table 5.4: RMSE for fouling models at a pH of 7.5 and 80 °C

Membrane	Complete Blocking	Intermediate Blocking	Pore Constriction	Cake Filtration	Combined Model	Final Flux (lmh)
1250 kDa	<u>0.014</u>	0.183	0.193	0.209	**9.03E-07**	28
150 kDa	0.536	0.111	<u>0.090</u>	0.143	**4.4E-06**	84
50 kDa	0.050	<u>0.039</u>	0.040	0.049	**0.00033**	360
PES	<u>0.038</u>	0.099	0.066	0.148	**0.0197**	0

5.3.4: <u>RMSE at a pH of 9 and a temperature of 80 °C</u>

The trend at a pH of 9 followed the same flux trends observed in previous sections: the increase in pH leads to the increase in permeation the flux. Moreover, the flux increases with decreasing pore size due to the reduction of oil droplets' viscosity at higher temperatures.

For the 1250 kDa, the pore constriction model had a slight advantage over other models. Compared to the same membrane at a pH of 7.5, the final flux was slightly higher at a pH of 9. This is the effect of passing from complete blocking to pore constriction.

At 150 kDa, a form of pore constriction takes place at the surface level. This membrane followed the same trend that is observed for a lower pH and continues to have a higher flux with increasing pH. The 150 kDa showed an improvement in water permeation when the pH is increased from 7.5 to 9 although the fouling model is invariable.

RMSE for 50 kDa was not conclusive and did not determine the type of fouling occurring on the membrane. Nevertheless, the high flux value indicates that low fouling is occurring on the membrane surface. The data established that the small pores inhibit the penetration of oil droplets in the membrane, reducing the fouling effect. The 50 kDa kept its advantage over all other membranes at high temperature. The 50 kDa at a pH of 9 had a lower flux than the membrane at 7.5. This is mainly due to the high quantity of hydrogen bonds forming in a small volume inside the pores, in a way to form high density electron area. This area forms a barrier inside the pores impeding the permeation of water molecules.

PES and MSTFA modified membrane showed a weak permeation flux. For the polymeric membrane, the small permeation flux was due to the hydrophobic nature of the molecule and high temperature compromising the membrane's stability.

Table 5.5: RMSE for fouling models at a pH of 9 and 80 °C

Membrane	Complete Blocking	Intermediate Blocking	Pore Constriction	Cake Filtration	Combined Model	Flux (lmh)
1250 kDa	0.108	0.094	<u>0.091</u>	0.120	**0.0095**	33
150 kDa	0.084	0.093	<u>0.071</u>	0.128	**4.54E-06**	141
50 kDa	0.188	0.189	0.188	0.189	**2.34E-05**	249
PES	0.061	0.051	<u>0.042</u>	0.088	**0.007**	15
1250 kDa MSTFA	<u>0.037</u>	0.076	0.051	0.117	**0.003**	19

5.3.5: RMSE at a pH of 9 and a temperature of 80 °C for modified membranes

The modified membranes A and Z did not show any enhancement of the permeate flux value in comparison with the unmodified 50 kDa. The type of modifying agent A and Z helped maintaining a permeating flux even though fouling was complete.

The agents B, C and D exhibited poor and inconsistent results throughout the experiment. RMSE showed that cake fouling is occurring on C and complete fouling on B and D.

The modified membrane B showed a complete blocking model based on the RMSE value. A very low flux is observed throughout the process.

Modification agent C revealed weak permeation flux although the fouling is of the cake type and not complete. This can be due to the strong accumulation of polymerized layers of bitumen on top of the hydrophobic agent.

The membrane with modification agent D showed complete fouling and a permeation flux of zero.

The ceramic membrane of MWCO 1250 kDa modified with agent E showed a substantial enhancement in permeate flux and fouling mitigation. The permeation flux remained at a high level for an extended period of time, indicating that the modification agent is stable and that the agent remained active. RMSE showed pore constriction occurring in a way that the pores continued to have open channels throughout the filtration process.

The molecules of the modification agent E blocked the active groups on the membrane surface and reduced the attraction force between the membrane surface and fouling components.

Table 5.6: RMSE for fouling models at a pH of 9 and 80 °C for modified membranes

Membrane	Complete Blocking	Intermediate Blocking	Pore Constriction	Cake Filtration	Combined Model	Flux (lmh)
50 kDa (A)	<u>0.294</u>	0.301	0.297	0.314	**3.63E-05**	109
50 kDa (B)	<u>0.560</u>	0.563	0.562	0.566	**2.48E-05**	21
50 kDa (C)	0.664	0.519	0.591	<u>0.471</u>	**0.000225**	0
50 kDa (D)	<u>3.252</u>	3.258	3.258	3.258	**0.062973**	0
50 kDa (Z)	<u>0.948</u>	1.011	0.981	1.061	**0.948**	247
1250 kDa (E)	0.110	0.101	<u>0.096</u>	0.128	**0.093**	387

5.4. Permeate Quality

A TOC (Total Organic Carbon) was performed to quantify the organic matter concentration inside the collected water permeate. Although TOC determines the concentration, in ppm, of organic compounds present in the water as well as inorganic matters and salts, this method, does not determine the nature of the organic molecule. This being said, this method is unable to identify and quantify bitumen particles in solution and is limited to reporting the concentration of total organic compounds in the permeate.

However, in this experiment, and since the only organic matter present in the solution is bitumen, it is reasonable to assume that the fluctuation in the organic particles' concentration detected by the TOC comes solely from the variation in bitumen concentration in the filtration permeate.

For a permeate sample collected at 80 °C and a pH of 5.6, Table 5.7 shows a trend that indicates that organic concentration rises with increasing Molecular Weight Cut-Off (MWCO) . The results showed that the 50 kDa membranes is 3 times more efficient at retaining emulsified oils than the 1250 kDa membrane, indicating that the quality of filtrate water is a direct function of membrane pore size.

Results also indicate that the bitumen concentration is high for a membrane separation process, but considering that most of the membranes tested in this work are covered with at least 1 mm of bitumen due to the 2 mm channel height (low shear stress in the cell for the cross flow to be very efficient), the performance of the membrane was satisfactory, especially that the bitumen concentration in the initial feed solution was high (2g/l).

The high TOC might be due to the presence of phenols in the bitumen. Phenols are highly soluble in water and show up as dissolved organics.

Table 5.7: TOC for permeate at a pH of 5.6 and 80 °C

Membrane	Concentration of Organics (ppm)
1250 kDa	33
300 kDa	29
150 kDa	15
50 kDa	11
PAN	26

6. Conclusion and recommendations

Low Temperatures and MWCO

At low temperatures, the contaminants in the organic phase have a high viscosity. The droplets are unable to enter deep in the pores of any membrane, but rather stick to the surface or form a cake on the membrane's feed side. This hampers water penetration.

Membranes with relatively small pore size witness little water permeation rate due to the clogging of the membrane pores by oil accumulation on the membrane surface.

However, membranes with bigger pore size have larger empty spaces between contaminant particles that have accumulated on the membrane surface, and continue to have open channels which ease the penetration of water through the membrane.

The downfall of large pore size membranes is that a higher concentration of particles would pass through the membrane and might compromise the quality of the permeate.

The polymeric membranes PAN exhibited good performance due its hydrophilic nature and its capability of maintaining a relatively high stability during the filtration process.

High Temperature and MWCO

At high temperatures, the reverse phenomenon is observed. The permeation flux increases with decreasing pore size. At high temperatures, the oil droplets' viscosity decreases and, flowing by water drag, a bigger portion of bitumen droplets penetrate the membrane. This explains the lower permeation flux through the membranes at high temperatures in comparison with the same membranes at lower temperatures.

At high MWCO, the relatively small size of foulant particles allows oil droplets to enter the pores deeply resulting in pore clogging. This form of fouling (pore clogging) is a more severe form of fouling than cake formation occurring on top of the membrane.

For lower MWCO, the droplets form a shallow foulant layer that is swept or reduced by a crossflow, allowing a flux of water to penetrate the membrane.

The hydrophilic polymeric membrane showed average results but lost its clear superiority observed at low temperatures due to a decrease in their stability. The stability of polymeric membranes is at risk when exposed to high temperatures for an extended period of time.

Solution pH

Tests were conducted at three levels of pH. As a general trend, the permeation flux for all MWCO rises with increasing pH. At lower pH levels, the acidity of the solution could promote the polymerization of bitumen. This forms a layer of bitumen that adheres to the membrane surface and clogs its pores. In order to reduce such interactions between the solution and the membrane; the pH was increased using sodium hydroxide.

The added OH^- ions to the processed water interact and form strong hydrogen bonds with water molecules. Simultaneously, the OH^- groups form hydrogen bonds with the hydroxyl groups present on the membrane surface. This phenomenon eases the passage of water through the membrane and keeps a high permeation flux. Hence, with increasing alkality, the rising concentration of OH^- in the solution form additional bonds with hydroxyl group on the membrane surface, allowing a higher water quantity to penetrate.

Moreover, the interaction between hydrated hydroxyl groups and membrane surface forms a layer of water on the membrane surface. This layer contributes to fouling mitigation by weakening the bonds between foulant particles and membrane surface.
Hydrogen interaction is not effective when a hydrophobic modification agent is applied to the membrane surface. The reason is the neutralization of the functional groups leading to the diminishing of interactions between the membrane surface and water molecules. Therefore, when employing a hydrophobic agent such as MSTFA to modify the membrane surface, the effect of raising the solution pH on the membrane performance is eliminated.

Modifications and Prefabricated membranes

Chemical modification agents are employed to modify the membrane surface to mitigate fouling. Molecules with hydrophobic and hydrophilic features are deposited on the ceramic membrane surface to minimize fouling occurring on the membrane surface.

As a general trend, hydrophobic modifications have shown superior performance on high MWCO ceramic membranes, in comparison to neutral agents and unmodified membranes. Although it can hinder interactions between membrane surface and water molecules, hydrophobic agents block the membrane's functional group, reducing interaction between membrane surface and foulant particles.

Also, extreme hydrophilic agents attached to the membrane promote the formation of a layer of water on the membrane which reduces fouling accumulation. This is the same phenomena previously explained, and observed when the pH of the solution is increased.

Although PES and PAN are known for their thermal stability, the process water high temperature exceeded their tolerance and weakened their performance.

Recommendation and Implementation

Employment of ceramic membranes for bitumen saline showed promising results. The stability of the ceramic membranes at high temperatures is the major feature that would allow the implementation of membrane-based systems in the oil industry. The ability of the hydrophilic ceramic membranes to reduce foulant adherence eases the application of cleaning and regeneration techniques when large quantities of process water are involved.

As well, the capability of applying modification agents to the membrane surface improves the membrane performance. Stability of the modification agent is key to maintain membrane performance and permeate flux. Hence, determining other possible compatible modification agents to firmly bond to the membrane surface preserves the membrane performance over a wide range of temperatures and pH, and reduces the operational costs for industrial systems should be studied

The modification of the feed solution conditions improves the permeation of the flux through the membrane. Increasing the alkalinity of the solution reduces foulant adherence to the membrane surface. This can be achieved simply by raising the pH of the solution. The low cost of sodium hydroxide allows increasing the pH of the solution without jeopardizing the feasibility of the filtration process. Other even less expensive agents such a lime should be tested as a neutralizing agent.

References

Allen, “Process water treatment in Canada’s Oil sands industry: II. A review of emerging technologies”, NrCan Press web, J.Environ.Eng.Sci 7, 499-524, 2008.

Allen, “Process water treatment in Canada’s Oil sands industry: I. Target pollutants and treatment objectives”, NrCan Press web, Environ.Eng.Sci 7,123-138, 2010.

Anton Dafinov, Ricard Garcia-Valls, Josep Font “ Modification of ceramic membranes by alcohol adsorption “Journal of Membrane Science 196 69–77, 2002.

Awad “Fouling of Heat Transfer Surfaces’’ , Mansoura University, faculty of Engineering, Mech. Power Eng. Dept.,Egypt, 2011

Bott, “Fouling of Heat Exchangers”, Elsevier, 55-223, 1995.

Buekenhoudt, “Inorganic Membranes synthesis characterization and application”, Elsevier, 2008.

Burnett, “Advanced Membrane Filtration Technology for cost effective recovery of Fresh water from oil & gas produced brine”, Texas A&M University, 2006.

Canadian Association of Oil and Gas Producers, “Water Use in Canada’s Oil sands”, CAP, 1-8, 2012.

Castro, R.P, Cohen and H Monbouquette, “Silica-supported polyvinylpurrolidone filtration membrane”, Journal Membrane of Science, 115,179-90, 1996.

Chu, L.Y, Wang and Chen “Surface Modification of Ceramic-Supported polyethersulfone membranes by interfacial polymerization for reduced membrane fouling.” Macromolecular Chemistry and Physics, 206, 1934-1940, 2005.

C.Ho and Andrew Zydney, “a combined pore blockage and cake filtration Model for protein fouling during microfiltration”, J. Colloid Interf. Sci., 232, 389-399, 2000.

Clark, K.A. “Bituminous sands of Alberta “, The oil weekly, 1945.

Deutsch and McLennan”Guide to SAGD, Steam Assisted Gravity Drainage, Reservoir Characterization Using Geostatistics “, CCG, 2005.

Engelhardt and Marius Todirescu “An Introduction to Development in Alberta’s Oil sands”, university of Alberta, 2005

Environment Canada “Athabasca Bitumen” Emergencies science and technology division.

Environment Canada “Cold Lake Bitumen” Emergencies science and technology division.

Elsevier Science Ltd “Microporous and Mesoporous Materials”, New York, Elsevier Science, 1998.

Faibish, R.S, and Cohen, “Fouling and rejection behavior of ceramic and polymer-modified ceramic membranes for ultrafiltration of oil-in-water emulsion and microemulsions”, Colloids and Surfaces A: Physicochemical and Engineering aspects, 191, 27-40, 2001.

Farnand, s. Coulombe, and h. Sawatzky “Production of Boiler-Feed Quality Water from Bitumen-Heavy Oil-Oil-in-Water Emulsions by Ultrafiltration” ,Energy Research Laboratories, Energy, Mines, and Resources Canada, Canada Center for Mineral and Energy Technology, Ottawa, Ontario, Canada ,1985.

Field, D. Wu , J.A Howell , B.B Gupta “Critical flux concept for microfiltration fouling” , Journal of membrane science , 100, 259-272 ,1995.

G.A Specken, “Clarification of wastewater from tar sands processing”, Wilson Service Limited, 1975.

Georges Belfort, Robert H. Davis and Andrew L. Zidney “The behavior of suspensions and macromolecular solutions in crossflow microfiltration”, Journal of Membrane Science 96, 1–58, 1994.

Glen Bolton, Dan LaCasse, Ralf Kuriyel “Combined models of membrane fouling: Development and application to microfiltration and ultrafiltration of biological fluids”, Journal of Membrane Science 277, 75–84, 2006.

Gu Y. Meng G. “A model for ceramic membrane formation by dip-coating” , Journal of the European Ceramic Society, Volume 19, Number 11 , pp. 1961-1966(6) , 1999.

Hamam, Mohamed Hamoda, Habib Shaban and Amal S. Kilani. “Crude Oil Dissolution in saline water”, College of engineering and petroleum, Kuwait University, 1987.

Hand, Yanfu, Chao “Oil adsorption measurement during filtration”, Journal of membrane science 214, 93-99, 2003.

Helen (Hongjing) Fu, Mohamed Gamal El-Din, Daniel W. Smith, Michael D. MacKinnon, and Warren Zubot, “Degradation of Naphthenic Acids in Athabasca Oil sands Process affected Water Using Ozone” University of Alberta, Edmonton, Alberta*Syncrude Canada Ltd: International Oil sands Tailings Conference Edmonton, Alberta, Canada December 7-10, 2008

Iqbal Ahmed, Zainal Abidin Mohd Yusof, “Fabrication of Polymer Based Mix Matrix Membrane - A Short Review” International Journal of Basic & Applied Sciences, vol 10, No: 02, 2010.

IHS CERA, inc “Oil sands Technology: Past, Present, and Future”, 2011.

Jeonghwan Kim , Bart Van der Bruggen” The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment”
Environmental Pollution, 158, 2335-2349 (2010)

Jo, Kinam Park , “Surface modification using silynated poly(ethylene glycol)s” ,Purdue University, School of Pharmacy, West Lafayette, Elsevier , Biomaterials 21 (2000) 605-616 ,1999

Karnik, B.S., Baumann, M.J., Masten, S.J., Davies “AFM and SEM characterization of iron oxide coated ceramic membranes.J.Mater.Sci.41, 6861-6870, 2006.

Kim, E.-S, Liu and El-Din, “Evaluation of Membrane Fouling for In-Line filtration of Oil sands process affected water: The effects of pre-treatment Conditions” Env. Science and tech, 46, 2877-84, 2012.

Kim, E.-S, Liu and El-Din, “Coagulation-flocculation- sedimentation treatment of Oil sands process affected water for high pressurized membrane filtration” 2011.

Lohokare, S. C. Kumbharkar, Y. S. Bhole, U. K. Kharul “Surface Modification of Polyacrylonitrile Based Ultrafiltration Membrane” , Polymer Science and Engineering Division, National Chemical Laboratory, Pune-411008, India, Wiley InterScience ,2005.

Ma, L., Fan, X., Quan, X., Zhang, Y., “Ag-TiO2/HAP/Al2O3 bioceramic composite membrane; fabrication, characterization and bactericidal activity” .J.Membr.Sci. 336, 109-117, 2009.

Meijer Drees, N.C. “Sedimentology and facies analysis of Devonian rocks”, southern District of Mackenzie, Northwest Territories, Canada. Geologica Ultraiectina No. 63, State University Utrecht, the Netherlands, 1990

Meyer and Emil D. Attanasi, “Heavy Oil and Natural Bitumen--Strategic Petroleum Resources”, U.S geological survey, 70-03, 2003.

Mika Mänttäri ,Arto Pihlajamäki ,Marianne Nyström “Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH”, Laboratory of Membrane Technology and Technical Polymer Chemistry, Department of Chemical Technology, Lappeenranta University of Technology, Finland, 2006.

Mitsu Chemical, Inc., “Polyethersulfone (PES) Technical Literature”.

Mochinaga ,S. Onozuka, Fumio Kono and Toyokazu Ogawa ,Akihisa Takahashi and Takahiro Torigoe "Properties of Oil sands and Bitumen in Athabasca "Japan Petroleum Exploration Co., Ltd. Shinagawa-ku, Tokyo,2006

Muralidhara, "challenges of membrane technology in the XXI century", Elsevier , 2010.

O.P Strausz, "chemistry of Alberta Oil sands bitumen" Hydrocarbon research center, department of chemistry, university of Alberta.

Parastoo, Przemyslaw, Yingnan, el-din, Perez, Martin, Anderson, Wiseman, Liber and Giesy," The impact of metallic coagulant on the removal of organic compounds from Oil sands process-affected water, Env. Science and tec, 45, 8452-8459, 2011.

Peng and Tremblay," Membrane Regeneration and filtration modeling in treating oily wastewaters", Journal of membrane science 324, 59-66, 2008.

Porter, "Concentration polarization with membrane ultrafiltration" ind. and engrg, chem, prod.research and develop 11(3), 234-248, 1972.

Sethi and Weisner, "Performance and cost modeling of ultrafiltration", Journal of Environmental Engineering, vol 121, No 12, 1995.

Strausz, Angelina Morales-Izquierdo, Najam Kazmi, Douglas S. Montgomery, John D. Payzant, Imre Safarik, and Juan Murgich "Chemical Composition of Athabasca Bitumen: The Saturate Fraction", Energy Fuels, 24, 5053–5072, 2010.

Rahaman, A.F. Ismail, A. Mustafa "A review of heat treatment on polyacrylonitrile fiber" Elsevier, 1421-1432, 2007.

Rice, D.D. Stratigraphy of the Chinchaga and older Paleozoic formations of the Great Slave Lake area, southern Northwest Territories and northern Alberta. Unpublished M.Sc. thesis, University of Alberta, Edmonton, 1967.

Torres, Belloc, Vaca, Iturbe, Bandala, "Coagulation-flocculation process applied to wastewaters generated in hydrocarbon-contaminated soil washing: Interactions among coagulant and flocculent concentrations and pH value", journal of environmental science and health *Part A* 44, 1449–1456, 2009.

Wang, Chu and Chen "Fouling-resistant composite membrane for separation of Oil-in-water microemulsions", Chinese J.Chem.Eng.14 (1) 37-45, 2006.

White Ralph E Pinaturo Peter N, "industrial membrane processes", American institute of chemical engineers (1986).

Wiesner, Clark and Mallevialle," Membrane filtration of coagulated suspension", Enviro.engrg, ASCE, 115(1), 20-40, 1989.

Wigmans, S Nakao and C.A Smolders "Flux limitation in ultrafiltration: osmotic pressure model and gel layer model", Elsevier, 0376-7388, 1984.

Wong, Brendan Liu, Serena McCalla , Benjamin Chu, and Benjamin Hsiao, “Analysis of PAN and PEGDA Coated Membranes for Filtering Water with Reduced Fouling and Increased Heavy Metal Adsorption” , Internship article, 2012.

Xomeritakis and Yue-Sheng Lin” Chemical Vapor Deposition of Solid Oxides in Porous Media for Ceramic Membrane Preparation. Comparison of Experimental Results with Semianalytical Solutions” Ind. Eng. Chem. Res., 33, 2607-2617, 1994.

Young, Liao-Ping Cheng , Dar-Jong Linb, Ling Fane, Wen-Yuan Chuang ,” Mechanisms of PVDF membrane formation by immersion-precipitation in soft (1-octanol) and harsh (water) nonsolvents , Elsevier 40, 5315–5323 , 1999.

http://www.altret.com/upload/article/boiler-water-treatment-guideline-20120705124824.pdf (visited August, 2013).

http://www.canadianenergyadvantage.com/bitumen-upgrading.php (visited February, 2013).

http://www.energy.gov.ab.ca/oilsands/793.asp (visited March, 2013).

http://www.gccoal.com/operations/surface-mining.html (visited November, 2013).

http://www.japex.co.jp/english/business/oversea/sadg.html (visited October, 2013).

http://www.membranespecialists.com/choosing-the-right-membrane.php (visited September, 2013).

http://www.nationalboard.org/SiteDocuments/Commissioned%20Inspectors/NB-410 (visited June, 2013).

http://www.oilsands.ualberta.ca/wqm/?page_id=230 (visited September, 2013)

http://www.oilsandsdevelopers.ca/index.php/oil-sands-technologies/in-situ/the-process-2/vapex- and-solvent-technology/ (visited February, 2013).

http://www.sigmaaldrich.com/analytical-chromatography/thereporter/2012/mstfa-derivatization.html (visited August, 2013).

http://www.suncor.com/en/about/272.aspx (visited February, 2013).

Appendix A

Table A.1: Maximum allowable contaminant concentration in boiler feed water

Component	Concentration
TDS (Total dissolved solids)	< 1000 ppm
Hardness	<0.3 ppm
Silica	<150 ppm
Alkalinity (ppm of $CaCO_3$)	<700 ppm
Oil	< 1 ppm

Values are for boilers operating from 0-300 psi from:

http://www.nationalboard.org/SiteDocuments/Commissioned%20Inspectors/NB-410.pdf

http://www.altret.com/upload/article/boiler-water-treatment-guideline-20120705124824.pdf (Farnand, 1985).

Table A.2: Contaminant concentration in oil sands processed water

Component	Concentration
pH	7.8-8.1
Dissolved solids (% by wt)	0.20-0.25
Suspended Solids (% by wt)	0.01-0.20
Conductivity	3000-4000 (µS/cm)
Alkalinity	600-800 (mg/L)
Naphthenic Acids	50-80 (mg/L)
Hardness (as CaCO3)	50-100 (mg/L)

It is important to note that the numerical values are from analysis of processed water in tailing ponds.

Values are from: Helen (Hongjing) Fu, Mohamed Gamal El-Din, Daniel W. Smith, Michael D. MacKinnon*, and Warren Zubot, “Degradation of Naphthenic Acids in Athabasca Oil sands Process affected Water Using Ozone”.

University of Alberta, Edmonton, Alberta*Syncrude Canada Ltd.

International Oil sands Tailings Conference Edmonton, Alberta, December 7-10, 2008.

Based on the work of David B Burnett the following values of mineral to be added to the oil – water solution are calculated below.

The solution is mixed in 10 L of water.

The volume need for the laboratory system is 3 L; hence by proportionality rules:

$$\frac{245.34}{10} \times 3 = 73.6 \text{ g of NaCl}$$

$$\frac{40.94}{10} \times 3 = 12.3 \text{ g of } Na_2SO_4.10H_2O$$

$$\frac{555.6 \times 0.2}{10} \times 3 = 33.3 \text{ g of } MgCl_2.6H_2O$$

$$\frac{57.9 \times 0.2}{10} \times 3 = 24.3 \text{ g of } CaCl_2$$

$$\frac{69.5 \times 0.1}{10} \times 3 = 2.1 \text{ g of KCl}$$

$$\frac{20.1 \times 0.1}{10} \times 3 = 0.6 \text{ g of } NaHCO_3$$
