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Preliminary Study of Nanofiltration for Production of Smart Water from Produced Water

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Abstract

Production of smart water from produced water is the focus of the thesis. Smart water performance is regulated by the concentration of ions such as Ca^{2+} , Mg^{2+} and SO_4^{2-} . Choosing produced water as the source for smart water is a wise step as it reduces produced water discharge making it suitable for pressure support in EOR.

Experimental setup of the project consists of a nanofiltration (NF) membrane coupled with ion exchange for barium removal. NF membrane separation was designated to increase the concentration of Ca^{2+} and Mg^{2+} while ion exchange was used for barium removal in order to prevent BaSO_4 scaling. These experiments were carried out using synthetic produced water sample from Tor Field.

EM-NF-1812-50 and NANO-BW-4040 NF modules were used. Concentrate from NF was selected as the source of smart water. NF membrane separations were able to increase the concentrations of Ca^{2+} and Mg^{2+} by 24 – 85 %. EM-NF-1812-50 gave higher retention while NANO-BW-4040 was more preferable due to its ability in changing the pressure. Ion exchange removed 99 % of barium.

According to the experiments, a combination of separation processes by NF and ion exchange is proposed as a potential solution to increase the quality of produced water as smart water.

Keywords: Enhanced Oil Recovery, Nanofiltration, Produced Water, Barium Removal, Ion Exchange, Smart Water

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Abbreviations

<i>AWWA – American Water Works Association</i>	<i>NCS – Norwegian Continental Shelf</i>
<i>AN – Acid Number</i>	<i>NF – Nanofiltration</i>
<i>BaC– Barium (solution) Concentrate</i>	<i>NPD – Norwegian Petroleum Directorate</i>
<i>BaF – Barium (solution) Feed</i>	<i>NSW – Normal Seawater</i>
<i>BaP – Barium (solution) Permeate</i>	<i>PW – Produced Water</i>
<i>CA – Cellulose Acetate</i>	<i>PWRI – PW Reinjection</i>
<i>CBR – Crude oil, brine, rock</i>	<i>RO – Reverse Osmosis</i>
<i>CP – Concentration Polarization</i>	<i>SDI – Silt Density Index</i>
<i>EDR – Electro Dialysis Reversal</i>	<i>SPW – Synthetic PW</i>
<i>EOR – Enhanced Oil Recovery</i>	<i>SPWF – Synthetic Produced Water Feed</i>
<i>IC – Ionic Chromatography</i>	<i>SPWC – Synthetic Produced Water Concentrate</i>
<i>ICP – Inductively Coupled Plasma</i>	<i>SPWP – Synthetic Produced Water Permeate</i>
<i>IOR – Improved Oil Recovery</i>	<i>SW – Seawater</i>
<i>Ksp – Coefficient of Solubility Product</i>	<i>TDS – Total Dissolved Solid</i>
<i>MF – Microfiltration</i>	<i>UF - Ultrafiltration</i>
<i>MW – Molecular Weight</i>	
<i>MWCO – Molecular Weight Cut-Off</i>	

Nomenclatures

$^{\circ}\text{C}$ – degree Celcius

C_c – Concentration of retentate

C_f – Concentration Factor

C_p – Concentration of Permeate

P_c – Concentrate's Pressure

P_f – Feed's Pressure

P_p – Permeate's Pressure

Q_c – Concentrate Flow Rate

Q_f – Feed Flow Rate

Q_p – Permeate Flow Rate

Part 1 – General Overview

Chapter 1 - Introduction

Water flooding has been done for years in oil reservoir to maintain pressure and displace the oil remaining using untreated seawater (SW) and produced water (PW). Since 1990's researchers discovered that ionic composition of the injected water can change the wetting¹ properties of reservoir, thus giving enormous effect on oil recovery. The engineered water discovered is well known as smart water.

1.1. Background Information

There are three types of oil recovery in petroleum extraction process: primary, secondary and tertiary recovery. Primary recovery is when oil is extracted using the natural force of the reservoir to push crude oil to the surface. When the pressure is not sufficient to force oil to the surface, secondary recovery methods are applied by supplying external energy into reservoir in the form of injecting fluid (e.g. water or gas) to maintain pressure. Another way to increase the oil production is through tertiary recovery or known as enhanced oil recovery (EOR).

During the production life of the reservoir, water was produced along the extraction of oil that is called produced water (PW). PW is the biggest volume of waste stream in hydrocarbon exploration and production phases, which can exceed by ten times the volume of hydrocarbon produced (Stephenson, 1992). Huge volume of streams and complexity of the compounds have been the main issues in handling PW. PW discharge has been done over a century as the easiest way in managing PW but it can cause acute or long-term effects for marine environment. Figure 1-1 was released by the Norwegian Petroleum Directorate (NPD) to show the historical of PW discharges in Norwegian Continental Shelf (NCS) as well as their future forecast of PW discharges (NPD, 2014). NPD targeting the decrease of PW discharge on 2020.

In order to reach the target, discharge has to be chosen as the last option to get rid of PW. To avoid direct discharge, PW is also used as pressure support (secondary recovery) in produced water reinjection (PWRI) or water flooding. Technically, PWRI is considered as

¹the ability of liquids to form interfaces with solid surfaces in crude oil, brine, rock (CBR) system example of wetting property is the contact between the rock surface and the two fluids, oil and brine (Austad, 2012)

conservative way in discharging the PW by giving less impact towards the environment without getting more benefits of it.

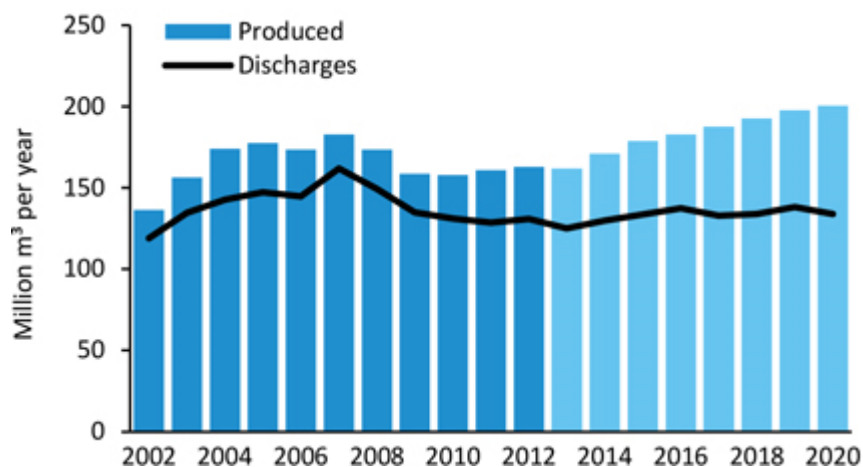


Figure 1-1 Historical Figures and Forecast for PW Discharges in Norwegian Continental Shelf (NPD, 2014)

Over the years researchers have carried out studies on the use of wettability² alteration in the injected water using SW to improve the displacement of oil by changing the ionic composition of the injection fluid (Austad, 2012). The altered quality of water is called smart water. While water flooding or PWRI is considered as secondary recovery of oil, smart water injection is considered as EOR because it not only helps maintaining the pressure; the injected fluid also changes the wettability of the reservoir. Austad (2012) reported that by using smart water as injected fluid, the oil recovery is predicted to increase up to more than 30%.

Smart water performance is based on some important determining ions: Ca^{2+} , Mg^{2+} and SO_4^{2-} (Strand et al., 2008). With high concentration of SO_4^{2-} in SW and high concentration of Ca^{2+} and Mg^{2+} in PW, both fluids have been used as the source of smart water (Puntervold, 2008; Puntervold & Austad, 2007; Ravari, 2011). In order to make PW a 'smarter' source for injection, some experiment in treating it was done.

This research was done as a groundwork idea to see whether nanofiltration (NF) membrane separation could be a proper treatment to change the ionic composition in PW so that it

²relative adhesion of two fluids to a solid surface. Associated with oil and water in pore's rock as immiscible fluid in porous media, wettability can be described as the preferred tendency measurement of one of the fluid to wet (spread or adhere to) the interstitial surface of the porous medium in the presence of other fluid

could give a better quality of smart water source. The project reviewed the available information from recent studies of membrane separation and smart water technology and combined them in order to identify the obstacles to the successful implementation of this technology merged together. It also defined the key technical areas where future works should be focused.

Two NF modules were used in this experiment: EM-NF-1812-50 and NANO-BW-4040. NF membranes were chosen because it has been known to separate small solute in forms of ions. It also offers additional advantage in separation process in terms of space and weight. It works on pure separation basis so it involves no chemicals in the operation process. This project were completed using synthetic produced water (SPW) sample which contained only all interesting determining ions in smart water. Theoretically, source of the smart water comes from the rejection flow of NF membrane where the ions are concentrated.

The project was also combined with barium removal experiments to overcome barium sulfate (BaSO_4) precipitation which may occur if PW is mixed with SO_4^{2-} rich SW. Barium is present in low concentration in the PW and the reaction of it with SO_4^{2-} can cause a serious scaling problem. As NF membrane separation is not selective, there is a possibility of barium being retained along with other ions in the rejection flow; hence barium removal is a necessary treatment.

1.2. Objectives

The objectives of this project are:

- To discover the potential of NF membrane separation as treatment technology for altering the ionic composition of PW in designing smart water
- To determine the ability of NF membrane to concentrate divalent cations (Mg^{2+} and Ca^{2+}) in the absence of divalent anions
- To determine the effect of pressure in separation efficiency of NF membrane in SPW
- To figure out other parameters affecting the ions separation in NF membrane throughout the experiment
- To establish the most efficient way of barium removal techniques

- To check the compatibility between NF membrane separation and chosen barium removal technique as solid PW post-treatment system

1.3. Thesis Outline

This paper is divided into 3 parts: *General Overview*, *Theoretical Background and Experiments and Observations*. *General Overview* focuses on the information regarding background and objectives of this project. Base lines of the theory together with detailed information related to the research are presented in the *Theoretical Background* part, which is divided into 3 chapters: *Produced Water and Barium*, *Fundamentals of NF Membrane Separation and Enhanced Oil Recovery and Smart Water*. The last part – *Experiment and Observations* – presents the *Methodology* of the experiment, *Results and Discussions* as well as *Conclusions and Recommendations* for further research. *Appendices* are included in the last part to give comprehensive results from the whole experiments and supporting data.

Part 2 – Theoretical Background

Chapter 2 - Produced Water and Barium

In terms of volume generated and permit, PW is one of the main waste discharges from oil and gas production facilities, besides drilling fluids (Neff & Sauer, 1995; Veil & Clark, 2010; Veil et al., 2007). For years, it was seen as a pollution source but throughout the time oil and gas industry found a way to get its advantages from a proper PW management options but still within the regulations. Characteristic of PW varies from one reservoir to another. Barium is included in most of its common component. In oil and gas operation, the chemical reaction from barium with sulfate (e.g. in PW and SW mixing) can cause a serious BaSO_4 scaling problem.

2.1. Produced Water Characteristics

For millions of years, water is trapped with liquids and gases, between impermeable rocks and porous sediments. The water, which comes out at the same time when the oil is extracted, during production period is called PW. Boesch and Rabalais reported that PW is a very complex mixture consisting of non-polar and polar organic substances, inorganic cations and anions, and combinations of these diverse chemical categories (Higashi et al., 1997). Armstrong et al. (1979) explained that it is known to be an important source of hydrocarbon and metal pollution but little is currently known about the composition of other major categories of PW constituents (e.g. polar organic compounds and inorganic anions) and even less is known about the fate and transport of these substances in marine environment. Neff et al. (2011) described a comprehensive characteristic of PW. Some common inorganic components are summarized in Table 2-1.

PW contains various kinds of organic chemicals and the most abundant organic chemicals are low molecular weight organic acids, saturated and aromatic hydrocarbons. Hydrocarbon and organic acids represent more than 90 % of the organic compounds in PW. The properties of PW are not similar from one reservoir to another. This depends on parameters like field's geographic location, geological formation where the PW has been in contact for long time, type of hydrocarbon being produced (Veil et al., 2007) and also chemicals being added during production including inorganic salts, metals, radioisotopes and various kind of organic chemical.

Table 2-1 Common Inorganic Components in Produced Water (Neff et al., 2011)

Element/ion	Seawater (mg/l)	Average Produced Water (mg/l)
Salinity	35000	<5000 → 300000000
Sodium	10760	23000 - 57300
Chloride	19353	46100 - 141000
Calcium	416	2530 - 25800
Magnesium	1294	530 - 4300
Potassium	387	130 - 3100
Sulfate	2712	0 - 1170
Bromide	87	46 - 1200
Strontium	0,008	7 - 1000
Barium	3 – 34 (ppb)	0 - 342
Ammonium	-	23 - 300
Bicarbonate	142	77 - 560
Iodide	167	3 - 210
Boron	4,45	8,0 - 40
Carbonate	-	30 - 450
Lithium	0,17	3.0 - 50

Salt and inorganic ions in PW can vary from a low concentration in the range of a few permil (‰) to high concentration of saturated brine (Neff et al., 2011) compared to a salinity of 32-35 % for seawater as reported by Rittenhouse. According to Collins (1975), salinity of PW is usually higher than seawater which makes it denser.

Chemical analysis of PW composition is useful to identify source of intrusive water, water flood planning and saltwater disposal project and corrosion prevention problem in the recovery stages. It is also useful for the company to make further management on reusing PW by looking at desired properties. In terms of inorganic constituents, sodium, calcium and magnesium are major cations while chloride being the major anion. Veil and Clark (2010) mentioned that oil and grease and organic and inorganic compounds using as chemical

additives and naturally occurring radioactive material are also considered as major constituent in PW.

2.2. Management of Produced Water

During 1992 Statfjord discharged 30.9 million l/d (± 195000 bbl/d) treated PW to the Norwegian sector of the North Sea (Neff & Sauer, 1996). As reported by Veil et al. (2007) 77 billion bbl of PW are generated around the world every year or 210 million bbl daily in 1999. Its volume is changing over time. Neff et. al., (2011) shown an estimation of 667 million metric tons (± 800 million m^3) of PW discharged offshore worldwide and 358 – 419 million tons to offshore waters of Europe, mostly the North Sea, in 2003.

In term of quantity, the amount of PW often increases as the amount of oil production decreases. According to Figure 2-1, approximately 163 million m^3 of PW was being discharged on the NCS in 2007 and 13.6 million m^3 of it was on the Norwegian Sea. Volume of discharge PW to the Norwegian Sea is increasing until 2014 up to 28.5 million m^3 and later on, as the oil field getting mature and shut down, total volume of discharged PW will be decreased. On the year of 2015, its volume is expected to be 7 million m^3 (Environment, 2009)



Figure 2-1 Fluctuating Prediction of Produced Water Discharges (Environment, 2009)

In managing PW first priority is to minimize the production of produced water which can save money during production processes by several approaches for example by managing PW at the surface by remote separation (Veil et al., 2007). When this is not feasible, operator moves to another option - reuse or recycle, usually by re-injecting it to the formation as secondary recovery.

Later, if PW cannot be managed through the options mentioned, it has to be disposed after being treated properly. Farajzadeh (2004) mentioned that there are several methods in disposing PW; some of them are through evaporation pits, surface discharge and deep aquifer injection, irrigation, industrial use, desert flooding and PW reinjection. Several technologies are used to treat PW in order to remove some parameters like salt content or oil and grease. Disposing PW onto open water is considerably concerning as it is a continuous process over the production time. Moreover, higher concentration of solutes and other chemicals in PW compared to the receiving water may harm the environment.

PW is categorized as wastewater and when it is decided to be disposed, it must be disposed with certain manner. It should be noted that the choice of disposing PW depends on many factors such as site location, regulation, technical feasibility, cost and also the availability of infrastructure and equipment (Farajzadeh, 2004). But over the time, PWRI has become a potential way on discharging PW.

PWRI is getting more attention because it gives 3 purposes:

1. Secondary recovery to produce additional oil,
2. Utilizes a potential pollutant
3. In some areas, it controls land subsidence.

To be injected, some parameters like suspended solids and oil have to be removed first to prevent formation plugging and some system like separators or bacteria control equipment is needed. An attractive strategy for dealing with this obstacle is to reduce the complexity of the problem by first defining the properties of interest in PW (Higashi et al., 1997). In the present case, the properties of chief interest are the separation of monovalent and divalent ion. This approach is used for the research in smart water production.

2.3. Barium and Scaling Problem

Barium (Ba^{2+}) is a divalent ion belong the alkaline earth group on periodic table along with beryllium (Be^{2+}), Magnesium (Mg^{2+}), Calcium (Ca^{2+}) and Strontium (Sr^{2+}). Compared to other elements in IIA group, Ba^{2+} has the largest radius and heaviest molecular weight. It is a strong reducing agent compare to other elements in the group (Neff & Sauer, 1995). Because of its relatively low ionic potential, Ba^{2+} goes to the aqueous solution as the hydrated ion. Compared to other lower molecular elements in IIA group, its adsorption to clay particles and organic matters is stronger. The adsorption is caused by its smaller hydratic ionic radius. Detailed comparison of physical and chemical properties of barium compared to elements in IIA groups shown in Table 2-2 and Figure 2-2.

Table 2-2 Physical/Chemical Properties of Alkaline Earth Elements (IIA)
(Neff & Sauer, 1995)

Ion	Molecular Weight	Crystal Radius (Å)	Hydrated Radius (Å)	Charge Density	Ksp [M][SO ₄] at 25°C
Be^{2+}	9.01	0.31	4.59	6.45	-
Mg^{2+}	24.32	0.65	4.28	3.01	-
Ca^{2+}	40.08	0.99	4.12	2.02	3.75×10^{-5}
Sr^{2+}	87.63	1.13	4.12	1.77	3.42×10^{-7}
Ba^{2+}	137.36	1.35	4.04	1.48	1.05×10^{-10}
Ra^{2+}	226.05	1.52	3.98	1.32	4.3×10^{-11}

The least soluble barium salt is barium sulfate ($BaSO_4$) in atmospheric pressure and temperature of 25 °C. According to Table 2-2, it has solubility product (Ksp) of approximately 1.05×10^{-10} .

According to Burton et. al, (1969) solubility of $BaSO_4$ is low in fresh water and seawater at 20 °C, consecutively 2300 µg/l (1360 µg Ba/l) and 81 µg/l (48 µg Ba/l) (Neff & Sauer, 1995). The solubility will increase with temperature and increasing ionic strength of water. Haarberg et al. observed that at 25°C, solubility of $BaSO_4$ in deionized water increase from 2450 µg/l

(1441 $\mu\text{g Ba/l}$) to 25680 $\mu\text{g/L}$ (15100 $\mu\text{g Ba/l}$) in water with 1.4 molal ionic strength as various inorganic chlorides (Neff & Sauer, 1995).

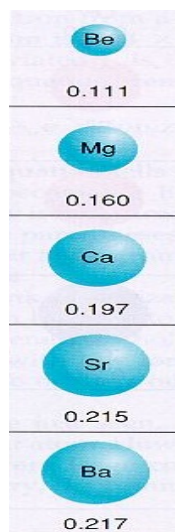


Figure 2-2 Ionic Radius Comparison among IIA Elements

At the ionic strength of seawater with 0.66 M with respect to NaCl, solubility of BaSO_4 will be 15400 $\mu\text{g/l}$ (9060 $\mu\text{g Ba/l}$), in the absence of sulfate. However, inorganic sulfate concentration in SW is high thus it will regulate the solubility of BaSO_4 and the saturation concentration of dissolved barium at much lower level. In PW, dissolved barium's concentration ranges from less than 1000 to more than 2000000 ppb ($\mu\text{g/l}$), while in the seawater it ranges from 4 to 20 $\mu\text{g/l}$ (Neff & Sauer, 1995).

Partitioning of barium and its complexes in the environment depends on several conditions such as pH, Eh (Oxidation-reduction potential), cation exchange capacity, and the presence of sulfate, carbonate, and metal oxides (oxides of aluminum, manganese, silicon and titanium). It has various solubility in water in relatively low temperature (0 – 20 °C) as described in Table 2-3. In aquatic media, barium is likely to precipitate out of solution as insoluble salt (i.e. as BaSO_4 or BaCO_3).

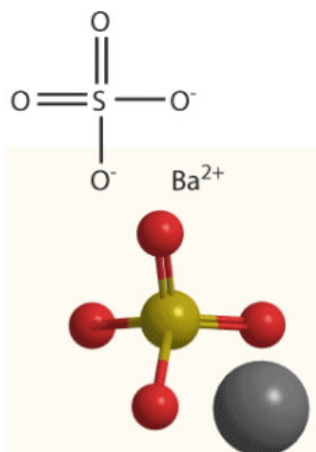
Solubility of barium sulfate increases considerably in the presence of chloride (Cl^-) and other anions (e.g. NO_3^- and CO_3^{2-}) and at pH levels of 9.3 or below, the barium ion is the dominant species. As pH level increase above 9.3 and in the presence of carbonate, barium carbonate becomes the dominant species.

Table 2-3 Solubility of Barium in Water (Barium Data Sheet, 2010)

Barium Combined Form	Solubility (water)
Carbonate	22 mg/L at 18 °C
Chloride	310 g/L at 0 °C
Chromate	3.4 mg/L at 16 °C
Cyanide	800 g/L at 14 °C
Hydroxide	Soluble in diluted acid
Nitrate	87 g/L at 20 °C
Permanganate	625 mg/L at 11 °C
Peroxide	Soluble in diluted acid
Sulfate	2.2mg/L at 18 °C

2.3.1. Barium Sulfate Scaling in Oil Production

Barium sulfate (BaSO_4), also known as barite, is a dense (4.48 g/cm^3), insoluble salt that has many uses. Chemical structure of BaSO_4 can be seen in Figure 2-3. BaSO_4 is an insoluble salt and has the density of 4.48 g/cm^3 .


Figure 2-3 Barium Sulfate Chemical Structure (ACS, 2008)

There are many issues in field operations and BaSO_4 scaling is one of the most troublesome and pricey among all. The occurrence, mechanism of deposition, and most importantly chemical properties of BaSO_4 scale are important to solve the problem. BaSO_4 scaling can be a major flow assurance problem. The buildup of BaSO_4 scale can also result in plugging the

pipe and can cause million dollar damage in oil and gas production. Figure 2-4 shows how BaSO_4 scaling looks like after some times.

When PW containing barium disposes directly to the ocean, barium is predicted to precipitate rapidly as BaSO_4 because of the high sulfate concentration (Neff & Sauer, 1995). However, organic acid anions, sometimes present in PW at concentrations as high as 10×10^6 $\mu\text{g/l}$, may complex with barium and slow its precipitation upon mixing of PW with seawater. Barium concentration in PW is roughly inversely proportional to the concentration of sulfate, indicating that the barium is in equilibrium with barium sulfate in the formation.

In order to precipitate as BaSO_4 , molal concentration of barium and sulfate must exceed the solubility product for barite (1.05×10^{-10} at 25°C) which can easily be obtained when the highly concentrated sulfate in seawater meets barium. According to Hanor (1969) barium made complex with sulfate but some can be complexed with chloride and bicarbonate (HCO_3^-) which sometimes are present at high concentration (Neff & Sauer, 1995).

Granbakken (1999) showed that 95% of the barium in 9:1 mixture of PW with seawater precipitates as barium sulfate within 10 – 15 minute at 91.4°C and pressure of 312 atm. However, he also showed that the precipitation process extended from 2 to 4 hours at 25°C and 1 atm pressure.



Figure 2-4 BaSO_4 Scale in Haynesville Shale Flow Line after One Month (Meehan, 2010)

Vetter (1975) mentioned that there are two common practice ways to determine BaSO_4 scaling tendencies in oilfield, analyzing the scale material and water samples analysis for Ba^{2+} and SO_4^{2-} constituents. Direct analysis of the solid scale material has main disadvantage

as the damage has already been there. It is too late for prevention and removal procedure is important. The analysis also cost a lot of money and cannot rejuvenate the initial productivity of the oilfield. On the second test, tendencies of scaling can be considered when the product of Ba^{2+} and SO_4^{2-} ion concentrations comes close to the solubility product of $BaSO_4$. Water analysis is a necessary tool in figuring out the scaling tendencies of $BaSO_4$. This test often fails by indicating that there is no scaling tendency thus, the interpretation of the analytical data has to be performed more carefully. All important thermodynamics conditions and their changes have to be evaluated as well as additional factors like precipitation kinetics and hydrodynamic conditions.

2.3.2. Barium Removal

Barium presents in water as divalent cations with similar chemical behavior with Ca^{2+} and Mg^{2+} , main component of hardness in water. Thus, processes used to soften water are very useful to remove these contaminants. There are several best available technologies (BAT) in removing soluble barium. Ion exchange, precipitation, reverse osmosis and electro dialysis have been proven for removing barium which has less than 2 mg/L concentration (Jurenka, 2010). In this research, two methods of barium removal were chosen: ion exchange and precipitation. Details provided in methodology section.

Reverse Osmosis

The RO semipermeable membrane is used to remove barium with the application of pressure to the concentrated solution. This will give water as permeate without any suspended and dissolved solid will be passing through the membrane. This method is effective and gives high quality water as the outcome but on the contrary, it needs high capital cost and also pretreatment prior to the RO separation. In terms of energy requirement, RO method needs high pressure, thus feed pumping is required. In using this method, all the soluble material is removed.

Electro Dialysis Reversal (EDR)

EDR method also uses membrane, but it uses semipermeable membranes in which ions migrate through the membrane from a less concentrated to a more concentrated solution as the result of ions' representative attraction to the applied direct current. This method can

remove specific contaminant but it has the limitation on the electrical requirement and concentrate disposal.

Ion Exchange

Ion exchange for soluble barium uses a charged resin to exchange acceptable ions from the resin for undesirable forms of barium in water. It is an effective and well-developed method, but it needs restocking of salt or acid supplies and regular regeneration of resin. Ion exchange using hydrogen form resins must be followed by a carbon dioxide stripping process and pH adjustment step. A portion of raw water can bypass the ion exchange and carbon dioxide removal process. Figure 2-5 depicted a configuration of barium removal using hydrogen-form resin (Snoeyink et al., 1987).

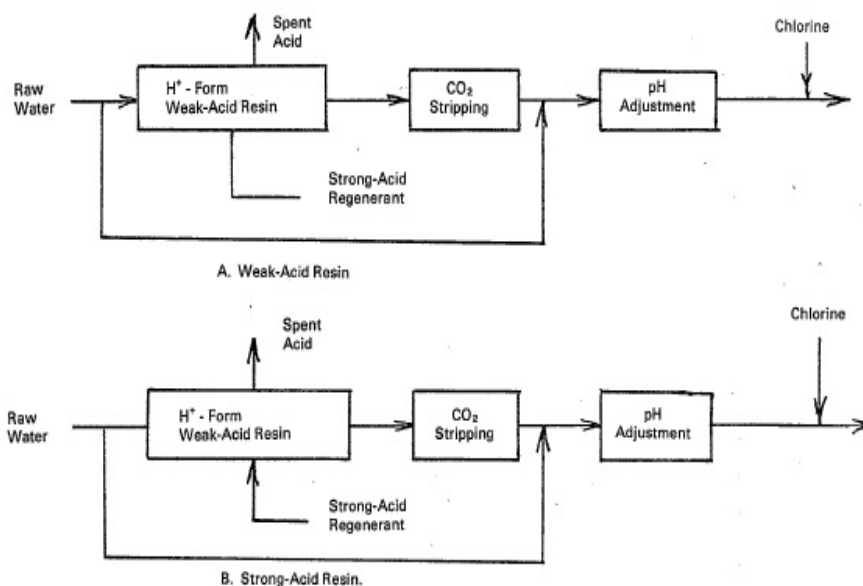


Figure 2-5 Configuration of Ion Exchange Process in Barium Removal (Snoeyink et al., 1987)

Precipitation

Precipitation for soluble barium, hydroxide or sulfide is used in sufficient quantity to raise the pH to about 10 in order to make it settle. This method requires quite low capital cost and has been proven reliable. However, it has some limitations such as care of the chemical usage, sludge disposal and insoluble barium compounds may be formed at low carbonate levels and it requires coagulation and flocculation resulting in wider footprint.

Chapter 3 - Fundamentals of NF Membrane Separation

Membrane separation technology is used in many kinds of engineering and industries process and approaches for transporting substances between two fractions using the help of permeable membranes. The choice of membrane is based on which solute is intended to be separated. NF membrane in general is a negatively charged membrane which reject divalent anions leaving the permeate rich in monovalent ions.

3.1. Concept of Membrane Separation

Membrane technology works based on separation of molecules and can remove both organic and inorganic components. There are 4 commons types of membrane used in the separation processes: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) membranes. Those types are divided into two groups with similar membrane process: MF/UF and NF/RO. The essential factors that differentiate those groups were type of membrane, removal mechanism, process driving force and primary application. In its simplest form as depicted in Figure 3-1, membrane separation required only pumping of the feed solution on certain pressure through the surface of membrane of the proper chemical nature and physical configuration (Cheryan, 1998).

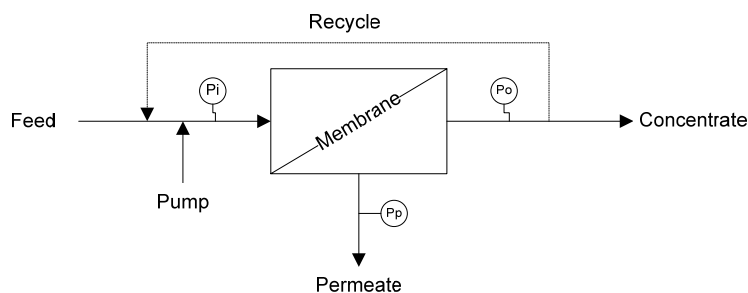


Figure 3-1 Schematic Diagram of Membrane Concept

Based on Figure 3-1, the feed stream is divided into two streams: concentrate and permeate. Concentrate (or usually referred to as 'retentate') is the retained stream and it is the side where fluid will be rich of retained macromolecules while permeate (referred to as 'fraction') is the stream which permeates or passes through the membrane and has lower concentration of macromolecules. The permeable solutes also show in the concentrate. Cheryan (1998) wrote that the permeate solutes might be in the similar concentration or

even higher than in the permeate stream. That depends on separation process or rejection rate of the membrane.

Figure 3-2 shows the characteristic of membrane on controlling which components are going to the permeate side and which are being concentrated in the retentate³. RO and NF are operating based on pressure-driven processes. Nonetheless semipermeable membrane, which can foul easily when exposed to significant particulate loading (AWWA, 2007), is used for targeting dissolved components removal through diffusion-controlled separation process. NF membrane retains only sugar, divalent salt and dissociated acid (Cheryan, 1998) and its process utilizes charged membrane with larger pores, compared to RO, but still able to repel many organic compounds.

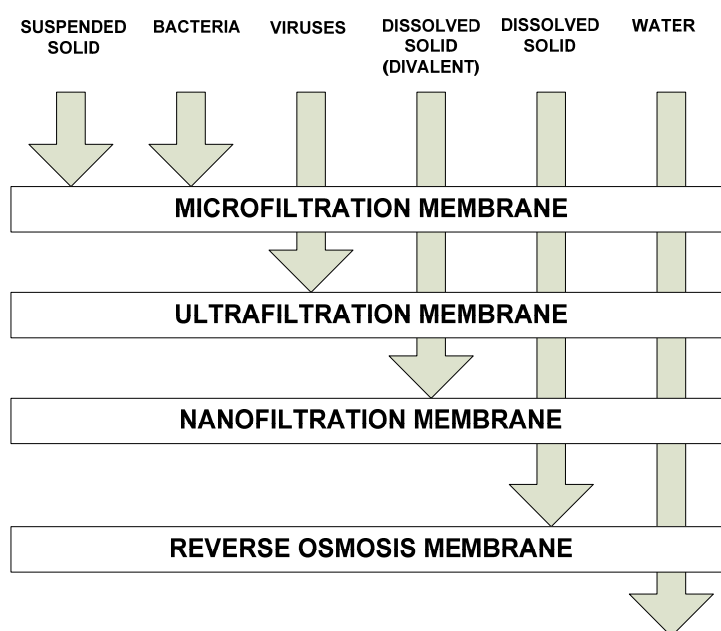


Figure 3-2 Membrane Process and Their Separation Characteristics
(Cheryan, 1998; Schafer et al., 2005; Wagner, 2001)

RO permeate's product is water because it retains all components other than the solvent in its conceptual description. UF furthermore, is made to retain particles larger than 10 – 200 Å ($\pm 0.001 - 0.02 \mu\text{m}$) and macromolecules, while MF is designed to retain suspended particles in the micron range of 0.1 – 5 μm . However, in UF instead of using particle size alone it is

³The term <<retentate>> is synonymous to <<concentrate>> in this paper

more accustomed to refer to the 'molecular weight cut-off'⁴ (MWCO) (AWWA, 2007). UF membrane can handle molecules that range from ± 1000 in molecular weight to ± 500000 Daltons. If there is any particle larger than micron size of MF, clarification and filtration is more desirable (Cheryan, 1998; Schafer et al., 2005).

The osmotic pressure required for MF/UF processes is low compared to NF/RO process. In comparison, RO involves fairly high pressure about 35 – 100 bar to overcome the high osmotic pressure of the small solutes while NF needs lower pressures of 10 – 30 bar. When high pressure is applied to the feed side of the membrane, water is forced to flow through the pores of the membrane surface, then solutes and dissolved solid are being retained in the concentrate side. Because of this, the permeate water contains less dissolved solid than the feed. More differences on the characteristic of four type of membrane are elaborated on Table E1 in Appendix E.

3.2. NF Membrane Characteristics

For membrane process in this project, NF membrane was chosen. Its characteristics have not been well defined as many authors described NF membrane as any loose RO membrane with less rejection on salt (Eriksson et al., 2005; Schafer et al., 2005). While RO is the tightest membrane process for liquid separation (pore size around 0,0001 micron), NF is sometimes confused with it. NF membrane has the MWCO in the range of 150 – 300 Daltons (Schafer et al., 2005). During its operation, charge gives big impact on the separation process. **True NF rejects ions more than one negative charge** (e.g. divalent) ions like SO_4^{2-} or PO_4^{2-} , while monovalent negative ions passed through. **NF also rejects uncharged dissolved materials and positively charged ions according to their shapes and size.** Table 3-1 shows the rejection values NF compared to other membrane.

The effect of the removal has proven preferable to applications where moderate salt removal is acceptable since pressure and power are significantly lowered. In exchange for less than complete salt removal, cost is reduced. Bjarne Nicholaisen characterized three different rejection phenomena of NF (Wagner, 2001):

⁴A term used to describe the potential separating capabilities of UF membrane. Molecular weight of a theoretical solute with a 90% rejection of that membrane (Cheryan, 1998)

1. Multivalent ions (e.g. SO_4^- and PO_4^{3-}) rejection rate,
2. Sodium chloride (NaCl) rejection rate which varies from 0 – 70% or even negative in mixed system,
3. Uncharged, dissolved materials and positively charged ions rejection rate in the solution which relate mostly to the size and shape of the molecule.

Table 3-1 Comparative Rejection Values for RO, Loose RO, NF and UF (Schafer et al., 2005)

Species	RO	Loose RO	NF	UF
Sodium Chloride	99%	70 - 95 %	0 ⁵ - 70 %	0%
Sodium Sulfate	99%	80 - 95 %	99%	0%
Calcium Chloride	99%	80 - 95 %	0 - 90%	0%
Magnesium Sulfate	>99%	95 - 98 %	>99%	0%

During NF membrane operation, proper system design is needed to optimize the process. The membrane system includes an inlet for feed water and outlet for concentrate and permeates. Dissolved matter, colloids, suspended particles and microorganism presents in the feed water can accumulates on the membrane surface and cause the membrane to decrease its performance and may even damage the membrane (Mortensen et al., 2007). That is why Abdel Jawad stated that feed water quality is critically necessary when membrane technology is chosen for treatment option (Mortensen et al., 2007). Feed water for NF necessarily has to go through certain degree of pretreatment, which may involve the addition of acid, scale inhibitor, or both to prevent precipitation of soluble salts as the increasing concentration of the rejected ion in the concentrate to protect the NF membrane from particulate fouling.

In preparing the feed water, feed source, quality and flow have to be taken into consideration. NF can treat very low salinity water up to high-salinity brackish waters with

⁵“0% rejection is valid for a 30.000 ppm NaCl solution in mixtures with other ions. The rejection for a pure 30.000 ppm NaCl solution is ranged from 20 – 30 %. Loose RO membrane exhibits rejections for salts which generally fall in the range between 70 – 95 %. A standard RO membrane will generally show 99% or higher rejection for dissolved salts.” (Schafer et al., 2005)

TDS in the range of 5000 – 15000 mg/l (Dow, 2010). Figure 3-3 represents major water types that being treated using NF membrane.

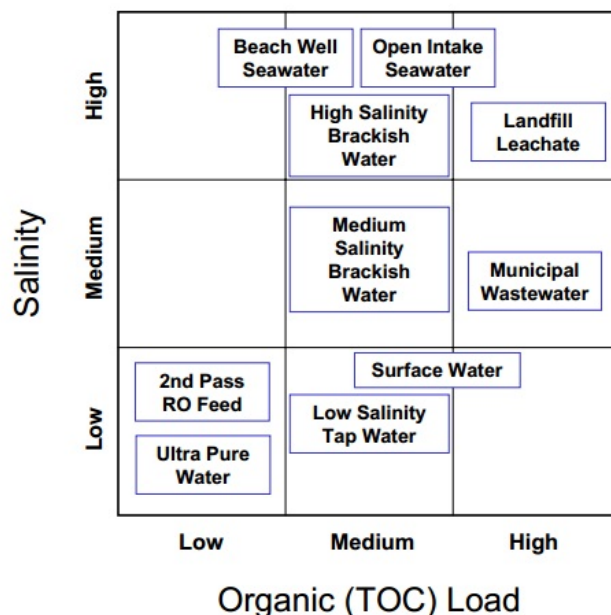


Figure 3-3 Major Water Types Treated by NF (Dow, 2010)

Besides TDS, Silt Density Index (SDI) is an important parameter. Dow (2010) mentioned that SDI value of the pretreated feed water has a direct correlation with the amount of fouling material present. For membrane separation, the SDI value should be below 5. The concentration of fouling materials at membrane surface increases with increasing permeates flux.

Other important parameters are: applied pressure, osmotic pressure, feed concentration, temperature and turbulence in the feed channel which is expressed in term of flux (Cheryan, 1998). Flux (J) is the rate of solvent transport per unit area per unit time. With Q_p as permeate flow rate (l/hr) and A as membrane area (m^2), flux (J) is expressed in l/m^2hr and calculated as:

$$J = \frac{Q_p}{A} (1)$$

Flux decreases exponentially with the increase of feed concentration while an increase in temperature leads to increase in flux. All these factors give significant effect towards rejection value (R). For example, high pressure will raise the possibility of a situation called

concentration polarization (CP⁶) which can increase the rejection rate. CP usually happens in situation of high pressure, lower velocity, and other conditions which bring solute to the membrane very rapidly (Cheryan, 1998). Rejection rate (R) in the membrane can be calculated based on the assumption that the probability of particles passing through the membrane is highest for solutes with 0% rejection. R is defined as

$$R = 1 - \frac{C_p}{C_c} \quad (2)$$

Where C_p is the concentration of solute in the permeate side and C_c is the concentration of solute in the retentate³.

3.2.1. NF Membrane Operating System

There are two ways to operate a membrane, dead-end and cross flow filtration. In dead-end filtration, feed is pumped directly towards the membrane and there is one stream entering the membrane module and leaving the membrane. But most of NF membranes operate in crossflow mode. In this mode, feed is pumped across or tangentially to the membrane surface and one stream enters the module and two streams leaves the module as permeate and concentrate.

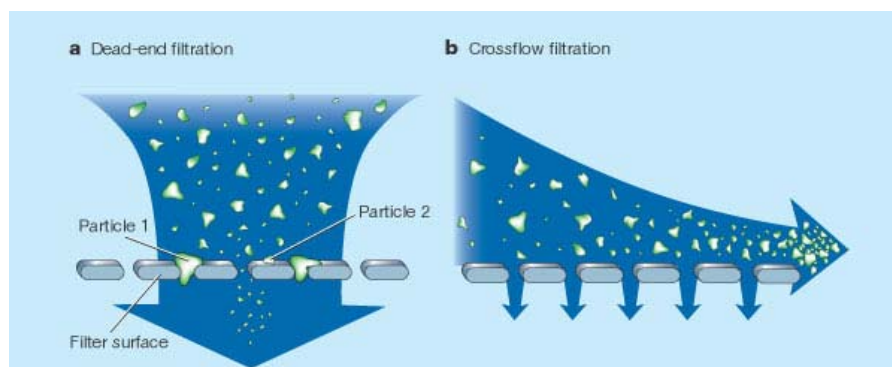


Figure 3-4 Difference between Dead-End and Crossflow Filtration (Brainerd, 2001)

Figure 3-4 shows the difference between those two modes. Dead-end filtration operation make fluid flow vertical to the membrane surface that can make the membrane clogged with particles easily. However, crossflow filtration operation is more desirable because according to Cheryan (1998):

⁶CP is solid build up close to or on the membrane surface (Cheryan, 1998).

- it limits the solid build up on the membrane surface,
- it has less membrane resistance,
- it has higher average flux during operation,
- it will give less solid cake builds up on the membrane surface resulting in higher permeate flux over time

Approaching system in operating NF membrane are also various, some of them are: batch, single pass, feed and bleed and multistage recycle operation. Feed and bleed mode of operation, shown schematically in Figure 3-5, is commonly used for continuous full scale operation. It is a combination of batch and single pass operation. This system works with two pumps: feed pump to provide system pressure and recirculation pump to provide cross-flow.

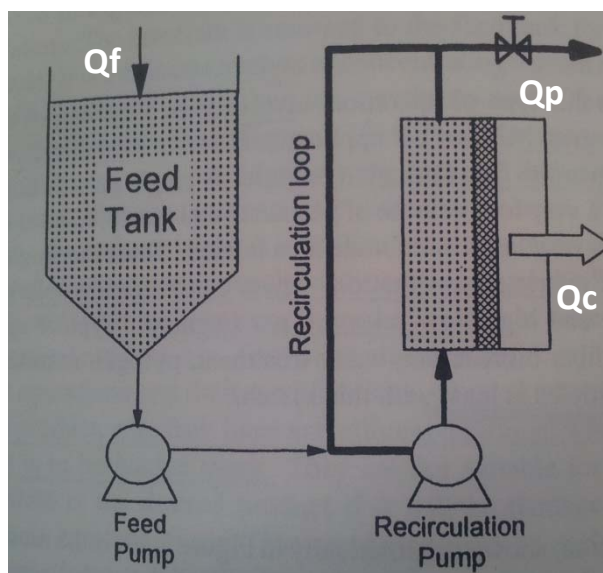


Figure 3-5 Illustration of Feed and Bleed Operation (Cheryan, 1998)

During startup, feed pump is used to fill the recirculation loop after the recirculation pump is started. To stabilize pressure, after a few seconds concentrate is bled off the recirculation loop at a flow rate (Q_c) such that:

$$C_f = \frac{Q_f}{Q_c} = \frac{Q_p + Q_c}{Q_c} \quad (3)$$

Where Q_f , Q_p and Q_c are volumetric flow rate of feed, permeate and concentrate respectively. C_f is the concentration factor.

Cheryan (1998) describes that feed and bleed operation gives immediate final concentration as the feed is pumped into the loop. On the other hand, the process loop is continuously operating at C_f equivalent to the final concentration of a batch system. This makes the flux lower than average flux in batch mode, thus requiring larger membrane area. When fouling occurs, Q_p in equation C_f will decrease with time. In order to keep C_f value constant during operation, Q_r have to be decreased.

3.2.2. NF Materials and Modules

According to AWWA (2007), two basic types of membrane currently used are asymmetric homogenous and composite membrane while the materials used to manufacture the membrane itself are varies from both organic (e.g. Cellulose acetate, polyamide) and inorganic (ceramic) materials. Cellulose acetate (CA) and its derivative and diverse kind of polyamide are widely used in manufacturing NF membrane. Polyamide is used in thin-film composite membrane even though it has worse resistance to chlorine compared to CA.

Table 3-2 compares the performance of CA and thin-film as two organic materials for membrane. Influence of pH and temperature in CA can cause a decrease of rejection rate over a period and can lead to the deterioration of the membrane when microorganism is present and produces cellulose enzyme. Composite membranes, also called thin-film composite membrane, were made to replace CA. It has a thin dense polymer skin formed over a microporous support. Many of the inorganic additives used in the membrane to make it able to operate at higher temperature (Fathima et al., 2007).

Membrane is manufactured in different types of modules: flat sheets, tubes, hollow fiber or spiral wound (Cheryan, 1998). Modules give support to the membrane and also help to provide an effective management of fluid (Schafer et al., 2005). Effective fluid management is needed in membrane processing to determine the extent of CP, manage permeate side⁷ and avoid leakage from feed to permeate. Detailed comparison of NF modules is presented in Table E2 in Appendix E.

⁷“Fluid management is important on the downstream, permeate side of the membrane. Permeate usually flows through the membrane support material and the porosity of this material and the length of the flow path determine downstream pressure losses which influence the net trans-membrane pressure. “ (Schafer et al., 2005)

Table 3-2 Comparison between Cellulose Acetate and Thin-Film Composite as Two Organic Materials of Membrane (AWWA, 2007; Cheryan, 1998; Wagner, 2001)

Conditions	Cellulose Acetate	Thin-Film Composite
Usage	UF, NF, RO	RO and NF
Advantages	Less fouling due to its hydrophobicity Cheaper Easier to manufacture	Higher flux and salt rejection Good resistance towards pH and temperature Stable pressure
Disadvantages	Can hydrolyze Influenced by pH and temperature	Not good with oxidizing environment Greater biofouling tendency

The most compact and inexpensive configuration of all is spiral wound, which make it popular especially in NF operation usage. Spiral wound has low footprint because more membrane area can be packed into the pressure vessel due to its narrow channel height as schematically shown in Figure 3-6.

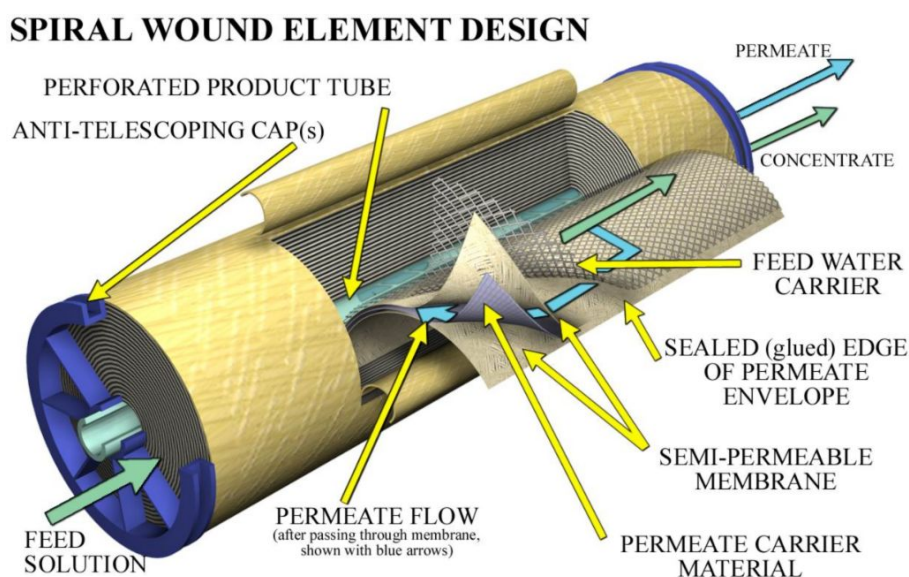


Figure 3-6 Spiral Wound Membrane Configuration (TTP, 1999)

Spiral wound module also comes in various length of individual membrane. In terms of energy, it requires low energy consumption which makes this configuration is the most

economical configuration. Unfortunately, due to the vast number of the permeate outlet tube sizes and design available from different manufacturers, the substitute of one spiral is hard except it comes from the same manufacturer.

3.2.3. NF Membrane Separation System

The separation method in NF membrane results from a complex mechanism; various parameters are involved not only based on the size of solutes or the sizes or pores. Paugam et. al. stated that the behavior of NF membrane in rejecting single components (e.g. salts, pesticides, microorganisms) has been fully understandable while on multi-component systems it becomes complex and cannot be predicted (Krieg et al., 2005). Rejection of charged solutes is determined by the solutes characteristics (size and polarity) and membrane properties (pore size, membrane material and membrane charge).

In rejecting the ions, the electroneutrality of the membrane has to be ensured. Negatively charged membrane is built to reject negative divalent ions. For example, in the presence of sulfate ions, high rejection of divalent cations will be improved (Krieg et al., 2005). Since NF membrane is manufactured with fixed charges, separation mechanism is related with steric and electrostatic partitioning effect between membrane and the external solutions. Upon separation on negatively charged membrane, besides its characteristic of having high water permeability, Donnan exclusion⁸ (charge effect) and steric hindrance⁹ combination have an important role during the separation.

Not only Donnan exclusion, NF mechanism on ion transfer is build based on the extended Nernst-Planck equation (accounting for ionic diffusion, electromigration and convection in the membrane pores) written below:

$$j_i = K_{i,d} D_i \frac{dc_i}{dx} - \frac{z_i K_{i,d} D_i F}{RT} \frac{d\Psi}{dx} + K_{i,c} c_i V \quad (4)$$

Details of the equation are given in Appendix E. This equation describes the mass transfer and an equilibrium partitioning relation to describe the ion distribution after separation (Szymczyk & Fievet, 2006). However, Donnan exclusion theory cannot successfully predict divalent ions rejection behavior on NF membrane (Vezzani & Bandini, 2002). It means that

⁸the result of electrostatic interaction between ions and the fixed charges of the membrane

⁹accounts for the sieve effect due to the intrinsic porosity of the membrane

Donnan equilibrium is not enough in giving an explanation on rejecting divalent ions even if ion size effect is taken into account. (Szymczyk & Fievet, 2005) suggested that dielectric exclusion has to be added into account to explain the phenomena between membrane and external solution. Dielectric exclusion mechanism is a combination of image forces¹⁰ and Born effect¹¹.

3.3. NF Utilization in Petrochemical Industry

Membranes have been used widely in petrochemical industries: for solvent lube dewaxing, removal of contaminants, deacidifying crude oil, secondary oil recovery and PW treatment. In dewaxing process, up to 50% of cold solvent is recovered from the filtrate. The solvent recovered is recycled directly to the dewaxing process so that energy consumption will be reduced. Gould & Nitsch reported that membrane used was polyamide with MWCO around 300 Da with spiral wound configuration (Schafer et al., 2005). According to this usage, the rejection rate of the lube oil using NF membrane is above 95% resulting less than 1 wt % oil in the permeate.

Other usage of membrane in petrochemical industry is to remove contaminants. Cossee et al. (2001) claimed that hydrophobic NF membrane can be used to remove contaminants with high molecular weight (ca. 400 Da and higher) from liquid hydrocarbon products. NF membrane can also be used for deacidifying crude oil (Livingston & Osborne, 2002). The permeate stream contains methanol and the concentrate is naphthenic acid and some residual methanol with the feed stream of polar solvent. In secondary oil recovery, an NF installation membrane of Dow Filmtec SR-90-400 is being used to produce low-sulfate seawater for injection (Mellor et al., 2000).

Figure 3-7 depicted in red box where in which stage membrane can be utilized for PW treatment. Some research has been done in the area of treating produced water using NF membrane (Alzahrani et al., 2013; Ozgun et al., 2013; Wickramasinghe & Mondal, 2008). In this project NF membrane is used for the treatment of previously treated PW to make smart water.

¹⁰interaction between ions and the polarization charges induced by ions themselves at the dielectric boundary between the pore solution and pore walls

¹¹the increase in ion solvation energy due to change in the solution dielectric constant between bulk and confined solution

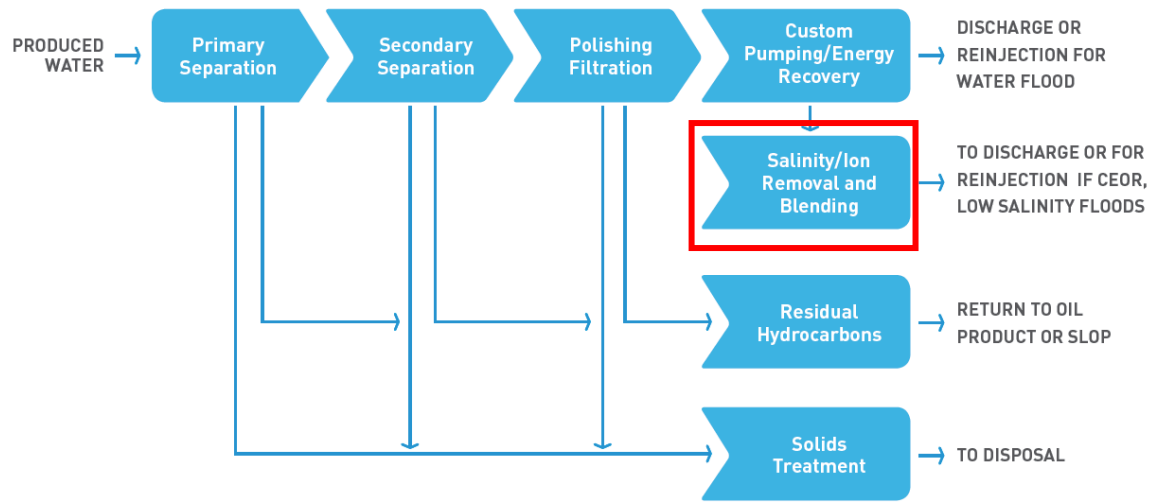


Figure 3-7 Nanofiltration Membrane Use for Produced Water Treatment (Standard, 2012)

Chapter 4 - Enhanced Oil Recovery and Smart Water

EOR is a tertiary recovery process in extracting oil. There are many ways in executing EOR process; some of them are thermal method, microbial or using chemical. Smart water is one EOR techniques by injecting specific low salinity fluid with certain ionic composition to alter the wettability¹² of crude oil, brine, rock system (CBR system). EOR techniques by wettability alteration are designed to overcome the capillarity forces that trap the oil in the reservoir.

4.1. Enhanced Oil Recovery

Crude oil production is distinctive into three different processes: primary, secondary and tertiary production as illustrated in Figure 4-1. During the lifetime of the reservoir, the reservoir natural pressure energy or forces carry primary hydrocarbon production on the earliest stage of its life. As the reservoir gets more mature, secondary recovery is applied by injecting fluid in order to maintain the reservoir pressure and produce more oil. The global average recovery factor for a typical oilfield is approximately 40% (Schlumberger, 2014). This results in a large amount of identified oil left behind so the need to improve the recovery factor and the accelerating of the associated production has made tertiary production or EOR being developed.

EOR is a stage of hydrocarbon production that involves usage of sophisticated techniques to recover more oil than would be possible by utilizing only primary production or waterflooding. Technology considered as EOR when it can result an additional production of oil from the introduction of artificial technology into the reservoir (Bondor et al., 2005). EOR encompasses a range of techniques used improve hydrocarbon displacement or fluid flow in the reservoir. EOR technologies can increase significant amount of oil from reservoir. By using this method, 30 – 60% of the remaining hydrocarbon in the reservoir can be displaced. There are many kinds of EOR method, namely some are water flooding, injection of miscible gas or miscible slug process, and thermal methods.

Water-based EOR or water flooding EOR has been chosen over century in increasing oil recovery because it gives pressure support to the reservoir to prevent gas production and it can displace the oil by its viscous forces (Austad, 2012). Injecting water into the reservoir

¹²The degree of wetting which determined by a force balance between adhesive and cohesive forces

has been classified as secondary oil recovery. However, during years of study, different ionic composition of injected water compared to the initial formation water can disturb the chemical equilibrium in the reservoir. Not only that, according to Austad (2012) wetting properties that changes along with the equilibrium may also give an improvement in the recovery rate of oil. Injecting similar water with the same composition as the initial formation water only give small effect in the chemical equilibrium but with the one with different composition, wetting properties change. Thus, that kind of injection acts as tertiary recovery process.

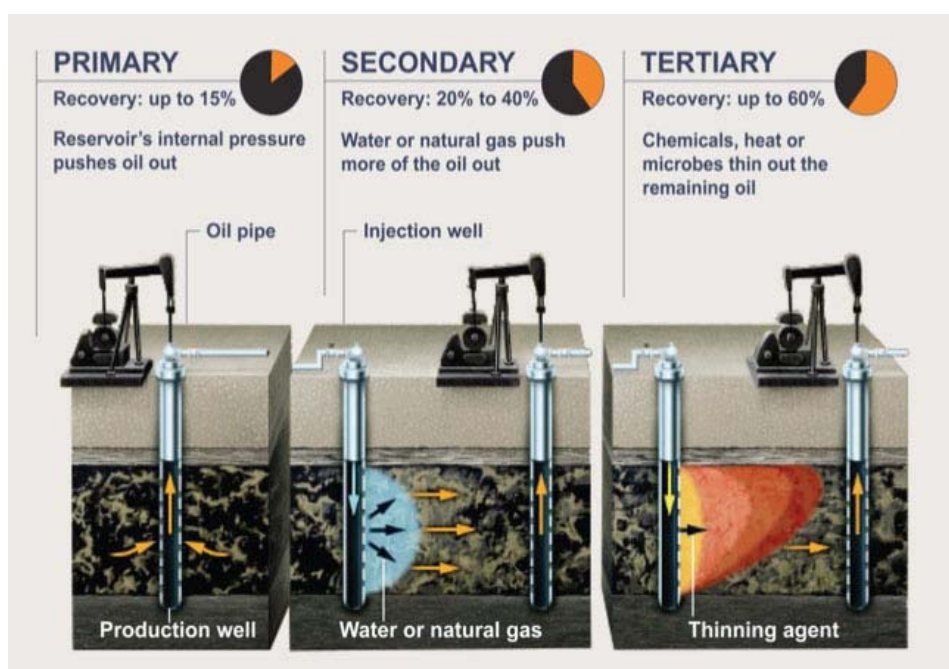


Figure 4-1 Conventional Recovery Stages in Petroleum Extraction (SUSRIS, 2014)

Application of EOR offshore fields is not as easy as onshore. Space and weight are known as the main restriction as well as the need for high reliability and the challenging economics of such projects impose constraints not present in onshore applications. Besides that, reservoir fluid and core samples should be obtained and analyzed as well as specific data for EOR must also be gathered. All these steps are necessary because the injected medium will be interacting with both reservoir fluids and reservoir rocks. According to Vai Yee et al. (2013), the usual injection water candidate is SW. But now, consideration is also given to whether PW can be recycled to reuse for EOR (Bondor et al., 2005).

4.2. Smart Water

During the last 30 years wetting properties of the reservoir was discovered to have an important role to increase the efficiency of water flood (Austad, 2012). It is found that different ionic composition in the injection fluid can give different impact on the oil recovery and efficiency of displacement. Smart water is classified as EOR because it has different properties on the injected fluid, which is able to change the wetting properties of the reservoir, thus improved the oil recovery.

4.2.1. General Overview on Smart Water

Smart Water is an injection fluid made by changing its ionic composition in order to change the equilibrium of the initial reservoir system that can modify the initial wetting conditions. By injecting smart water, oil is displaced easier from the rock porous as illustrated in Figure 4-2. Injection of smart water is characterized as tertiary recovery method unlike conventional water injection. It is because the extra oil was recovered after secondary water flood is performed using formation water.

Main principle in smart water is changing the wetting properties of the system that give positive effect on the capillary pressure and relative permeability of oil and water regarding oil recovery. It is cheap, environmentally friendly, no expensive chemicals are added and no injection problems. From an economical point of view, the smartest water should be injected from the start of the water flooding process. In applying smart water injection, established initial wetting properties and the filling history of oil reservoir play important part in regards of wetting properties especially in carbonates reservoir. Smart Water will significantly increase the oil recovery from both carbonates and sandstones (Austad, 2012).

Austad (2012) claimed that several groups and oil companies have verified smart water's performance in laboratory scale and field scale during the past 20 years. By knowing the chemical mechanism for wettability modification, it is possible to optimize the ion composition in the injected water to maximize oil recovery.

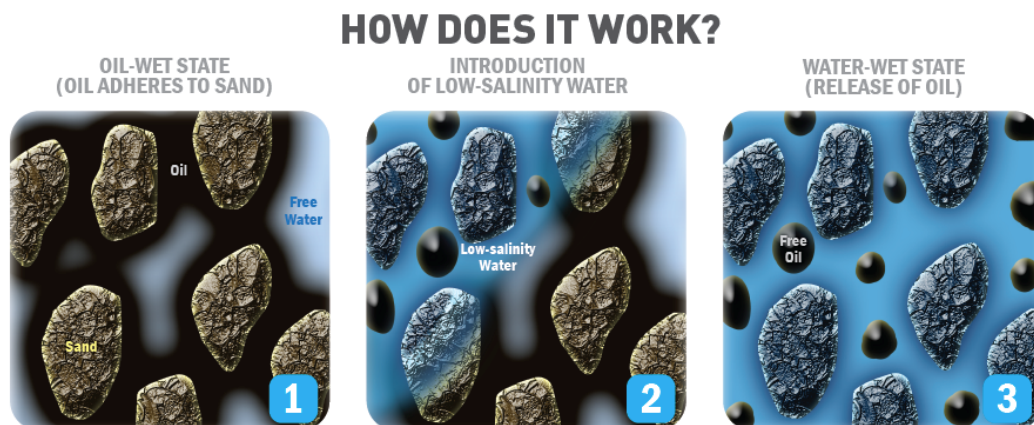


Figure 4-2 Low Salinity Injection Process (Standard, 2012)

4.2.2. Smart Water for Carbonate Reservoir

More than 50% of known oil reserves are trapped in carbonate reservoir: limestone, chalk and dolomite. Carbonate reservoir has high salinity and calcium rich formation water. Due to its low water wetness, natural fractures, low permeability and inhomogenous rock properties, oil recovery in carbonate reservoir is below 30% (Austad, 2012). In carbonate reservoir some important wetting parameters are:

- **Acid Number (AN)** (mg KOH/g) (Standnes and Austad, 2000) whereas the imbibitions rate and oil recovery decreased as the AN of oil increased,
- **Temperature** (Rao, 1996), high temperature carbonate reservoir is more water-wet compared to low temperature one and AN of the crude oil decrease as the reservoir temperature increases
- **Pressure** (Buckley, 1995) When pressure decreases towards the bubble point of the oil, solubility of asphaltenes in crude oil decrease and they will precipitate and adsorb onto the rock
- **Composition of the formation water**, for example: sulfate is the most active ion regarding wetting properties in carbonate reservoir. According to Sgariatpanahi, sulfate presence will increase the water wetness of the system

Smart water in carbonates must contain potential determining ions of Ca^{2+} and/or Mg^{2+} , SO_4^{2-} and the symbiotic interaction between ions and carbonate surface which is sensitive to temperature (above 70 °C). Not only that, Austad pointed out that SW depleted in NaCl will

be smarter than ordinary smart water from normal SW. An increase in NaCl concentration of SW decreased the oil recovery (Fathi et al., 2012).

With the variation of sulfate's concentration from 0 – 4 times of ordinary SW, oil recovery increased from less than 10% to about 50% of OOIP as pointed out in Austad (2012). Not only sulfate, Ca^{2+} ion gives positives effect when its concentration is increase into 0 – 4 times normal concentration of SW. Oil recovery increased from 27 to 60% after 30 days of imbibitions with normal sulfate concentration of SW. In the appearance of Mg^{2+} ions, its reactivity towards carbonate surface increases as temperature is more than 70°C . Mg^{2+} is less reactive in low temperature.

High concentration of Ca^{2+} and possible Mg^{2+} in formation water as well as positively charged rock due to high PH is noted while negatively charged potential determining ion is negligible (CO_3^{2-} and SO_4^{2-}). As SW injected to the fractured carbonate reservoir, SO_4^{2-} will adsorb onto the positively charged surface and lower the positives charge. Because of electrostatic repulsion, concentration of Ca^{2+} near the surface is increased and it binds to the negatively charged carboxylic group and releases it from the surface. As temperature increase, Ca^{2+} and SO_4^{2-} concentration increase and Mg^{2+} displaced Ca^{2+} from carbonate rock because of high temperature.

4.2.3. Smart Water in Sandstone Reservoir

Sandstones composed from many different minerals of the silica types that are negatively charged at relevant pH range of the formation water. The strongest component adsorbed by polar components from the crude oil is clay mineral (Austad, 2012). Clays are chemically unique due to the presence of permanent negative charges and therefore act as cation exchangers. H^{+} ion have largest affinity towards the clay surface followed by Ca^{2+} and Mg^{2+} ion. Lowest relative affinity on cations is regarded to be from lithium and sodium ion.

H^{+} or proton is the most reactive cation towards the clay even though the H^{+} concentration is low in pH range of 6 – 8 it will play an important role in cation exchange reactions at low salinities. According to the research of Burgos et al., Madsen and Lind, and Rezaei Doust et al., the adsorption of basic and acidic material onto the clay is very sensitive to the pH and it can change dramatically within the pH range $5 < \text{pH} < 8$ (Austad, 2012). The adsorption of both

acidic and basic material from crude oil appeared to increase as the pH is decreased to about 5. Since clays are not normally distributed uniformly on oil reservoir, certain area can be less water-wet than others. These areas can be bypassed in a water flood process, which will make both macroscopic and microscopic sweep efficiencies decrease.

While in carbonates SO_4^{2-} is being the determined ion and parameter, sandstone reservoir has more complicated conditions for its low salinity injections. The conditions that have to be fulfilled are:

- They have to be porous medium as sandstones containing clay mineral and oil must contain polar components.
- The formation water in the reservoir must be present and contain divalent cations (such as Ca^{2+} and Mg^{2+}).
- The injection fluid also has to be low salinity with the value ranged from 1000 – 2000 ppm and it appeared to be sensitive towards ionic composition.

Tang and Morrow reported that PW usually have pH of 1- 3 pH units and increase in pH value needs to be observed more compare to low salinity effects (Austad, 2012). Furthermore, they added that most reports said that the injection usually been performed at temperature below 100 °C.

4.2.4. Recent Study on PW and Sea Water Mixture for Smart Water

If PW is not reinjected into the reservoir, it can be an environmental problem. PW has many kinds of hazardous content especially aromatic carcinogenic material. PW from an offshore carbonate reservoir flooded with SW will contain low concentration of sulfate even after SW breakthrough due to adsorption/precipitation of sulfate in the reservoir (Austad, 2012; Puntervold & Austad, 2007, 2008). Thus, reinjection of PW will not be smart water causing wettability alteration and improved oil recovery. If however the PW is mixed with SW, good quality of injected fluid can be maintained (Austad, 2012).

Part 3 – Experiments and Observations

Chapter 5 - Methodology

In order to get representative results, proper methods were established for the whole project as shown in Figure 5-1. There were two main parts of experiments: membrane separation and barium removal. Details of the experiment were explained in sections below.

5.1. Sample Preparation

Two kinds of samples were prepared by diluting soluble salts into deionized water. Samples were used as the feed water for membrane separation or barium removal experiments.

5.1.1. Synthetic Produced Water

Synthetic produced water (SPW) was prepared specifically so that it mainly contains monovalent and divalent ions, which play an important role in smart water performance. It was intended to see the potential in manipulating ionic composition of PW for more optimum smart water through designated treatment. The ionic composition was prepared in accordance to the article of *'Injection of Seawater and Mixtures with Produced Water into North Sea Chalk Formation: Impact of Fluid-Rock Interactions on Wettability and Scale Formation'* (Puntervold & Austad, 2007). Experiments were aimed to see the performance of NF membrane separation as well as deal with barium removal by not taking into account the presence of divalent anions (SO_4^{2-}) in the feed. According to those criteria, **PW from Tor Field was chosen as the most representative and appropriate reference for this experiment.**

Besides the deficiency of SO_4^{2-} , PW usually contained some amounts of Ba^{2+} and often come with higher TDS (≥ 35000 mg/l). To highlight the ionic compositions, they were written in comparison to NSW to see the main difference composition in PW and NSW. Molar composition of Tor Field SPW can be seen in Table 5-1.

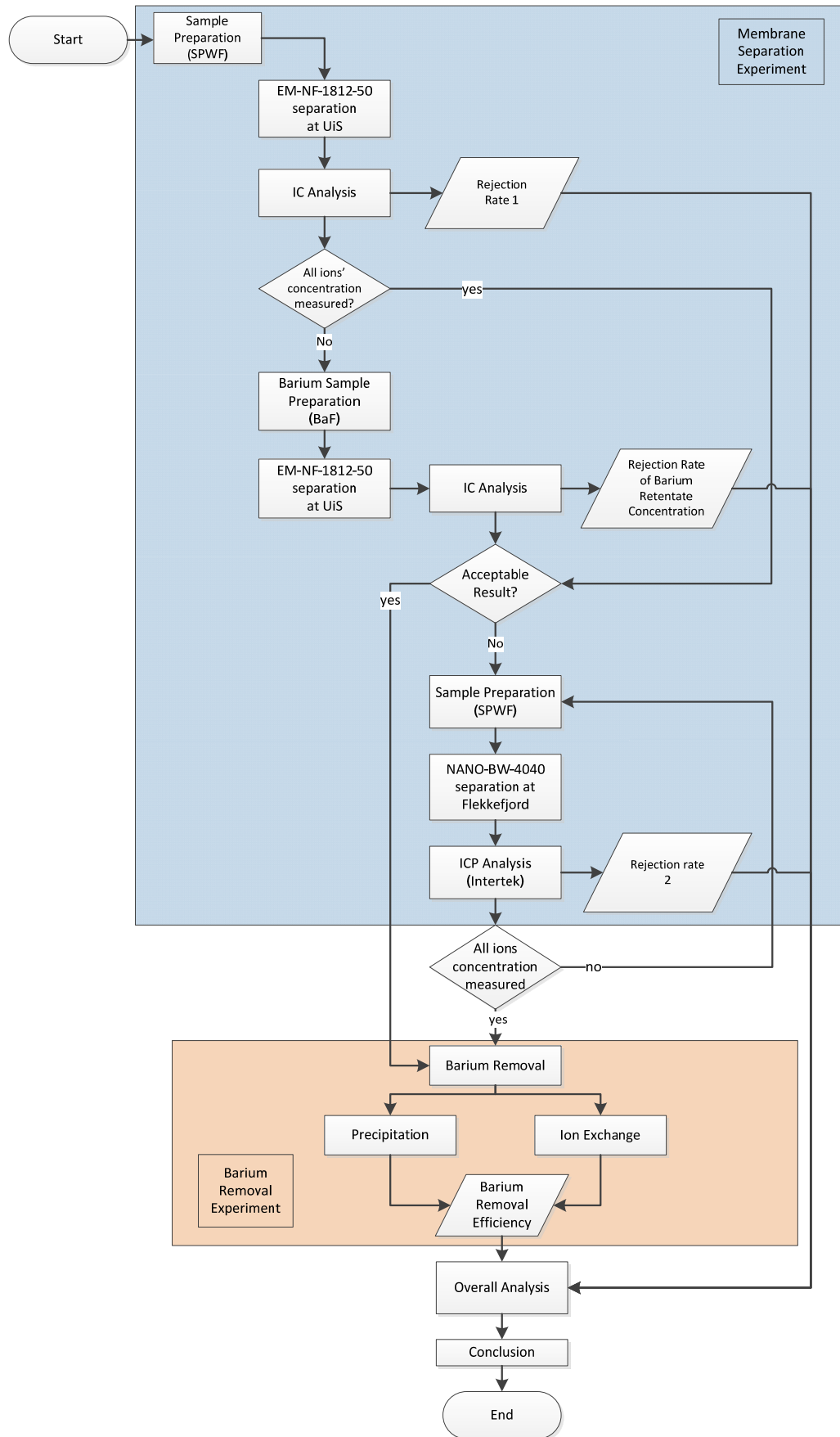


Figure 5-1 Methodology of the Project

Table 5-1 Composition of Tor Field Synthetic Produced Water Compared to Normal Seawater
(Punternvold & Austad, 2007)

Number	Ion	Concentration (mg/l)	
		Tor Field SPW	NSW
1	HCO ₃ ⁻	122	-
2	Cl ⁻	55522	19400
3	SO ₄ ²⁻	0	910
4	Mg ²⁺	1560	1292
5	Ca ²⁺	1560	400
6	Na ⁺	30820	10800
7	K ⁺	624	400
8	Ba ²⁺	4.943	0
9	Sr ²⁺	48.72	0

SPW was prepared with the approximate molar composition. For each NF membrane separation, feed solution was prepared for 50 liters of volume. The mass composition and salt used for the solution of SPW listed in Table A1 Appendix A. Mass of salt required was calculated very precisely using equations below.

$$\text{Molarity (mole/l)} = \frac{\text{mole}}{\text{volume (L)}} \quad (5)$$

$$\text{mole} = \frac{\text{mass (gram)}}{\text{Molecularweight (gram/mole)}} \quad (6)$$

From (5) and (6) mass was calculated as:

$$\text{mass (gram)} = \text{Molarity} \times \text{MW} \times \text{volume} \quad (7)$$

Figure 5-2 showed the equipment required to mix SPW. During mixing the SPW, salts, which contain chloride (Cl⁻), were diluted first using deionized water in the beaker glass using magnetic stirrer. Carbonate was mixed in a separate glass and poured into the salt solution afterwards, to prevent precipitation.



Figure 5-2 Equipment for Synthetic Produced Water Preparation

All of the solution were mixed thoroughly then put into the container to be added with the remaining volume of water until it reached the desired volume (50 l). **Prepared sample were labeled as SPWF** meaning synthetic produced water for feed.

5.1.2. Barium Solution

Barium solution was feed solution prepared separately for both NF membrane separation and ion exchange experiments. The solution itself only contained barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) salt mixed with deionized water. The low concentration of Ba^{2+} in SPWF made it immeasurable in ionic chromatography (IC) analysis after high dilution (IC analysis is explained in section 5.4) hence, another feed solution was prepared. Barium solution for NF membrane separation named as BaF. With the use of BaF, rejection rate for Ba^{2+} in EM-NF-1812-50 membrane was expected to be observable through ionic analysis from output flow using IC instrument.

Unavailability of barium selective resin (explained in section 5.3.2) made Ba solution was prepared to simulate the removal rate of Ba^{2+} only instead of all cations in the feed water for ion exchange experiment. Concentration of Ba^{2+} was made in accordance to SPWC. Another reason in making barium solution for ion exchange was also the limitation of dilution rate in IC machine for output water analysis. By using Ba solution, ionic analysis was expected to be done with measurable barium concentration with low dilution rate.

5.2. NF Membrane Separation

These experiments were conducted in two different places using two different NF membranes: **EM-NF-1812-50 at University of Stavanger** and **NANO-BW-4040 at Membran Teknikk AS in Flekkefjord**. Both membranes performances will be compared after the experiments were done.

5.2.1. Experiments Using EM-NF-1812-50 Membrane

Experiment using EM-NF-1812-50 (Figure 5-3) membrane was the first experiment. It is a single instrument. SPWF used as the feed for the separation process and membrane was operated in fixed optimum pressure of 6.8 bars¹³.



Figure 5-3 EM-NF-1812-50 Membrane Configuration (up) and Element (down)

Feed pump (fp) gave pressure to the feed to make it passed through the membrane. After that, output flow would be SPWP in permeate and SPWC in the concentrate. Each output flow was recirculated to the feed tank. With this way, feed concentration was kept stable. Operation diagram was illustrated in Figure 5-4.

¹³Pressure was measured in bar gauge (barg)

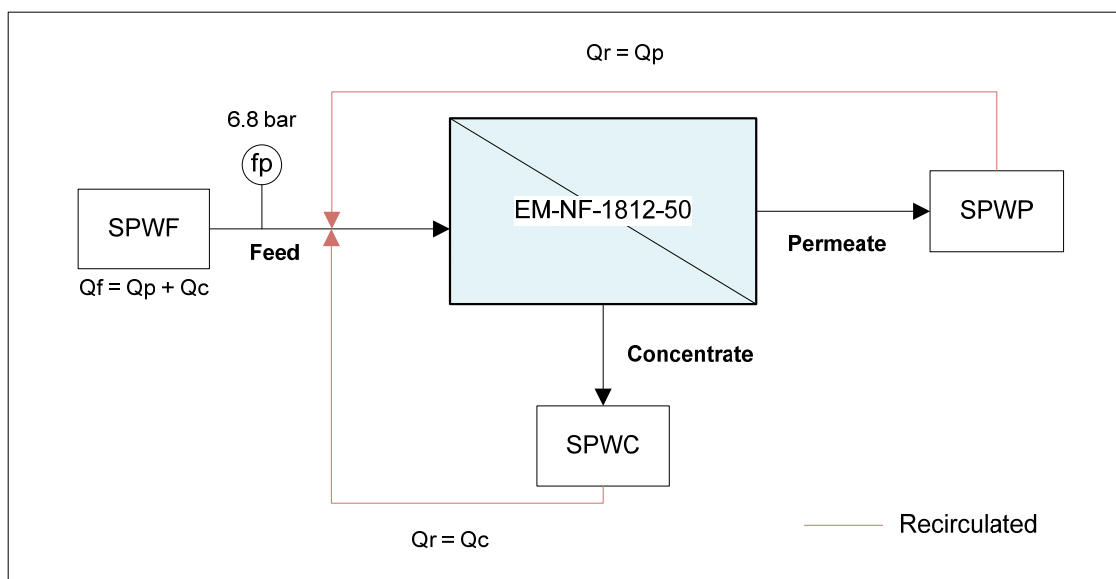


Figure 5-4 EM-NF-1812-50 Membrane Operation Schematic

Separation process was done in room temperature (19 – 20 °C). No cooling instrument to make the temperature stable.

Samples from EM-NF-1812-50 separation were diluted for IC analysis as explained in the following section. Due to high dilution, low concentration of Ba^{2+} was not measurable. In this case, prepared Ba^{2+} solution (BaF) was used as feed for second membrane separation. Configuration and all technical aspect were the same, except the feed was BaF. Operation was done similar to the SPWF steps. The output of this experiment were noted as BaP in the permeate and BaC in the concentrate.

5.2.2. Experiments Using NANO-BW-4040 Membrane

NANO-BW-4040 membrane experiment was done to see the effect in varying a parameter towards the effectiveness of NF membrane separation, in this case: **pressure variation**. Limited ability in EM-NF-1812-50 membrane made this experiment important. NANO-BW-4040 instrument (Figure 5-5) was provided by Membran Teknikk AS in Flekkefjord.

NANO-BW-4040 was equipped with cooling instrument and heat exchanger to make the temperature during operation stable. Recirculated pump was also installed to operate feed and bleed system for the experiment as illustrated in Figure 5-6. Because the aim of the experiment was to increase the concentration in the retentate³, this instrument was able to increase the concentration factor (C_f) by varying the permeate flow rate (Q_p).



Figure 5-5 NANO-BW-4040 Membrane Installation

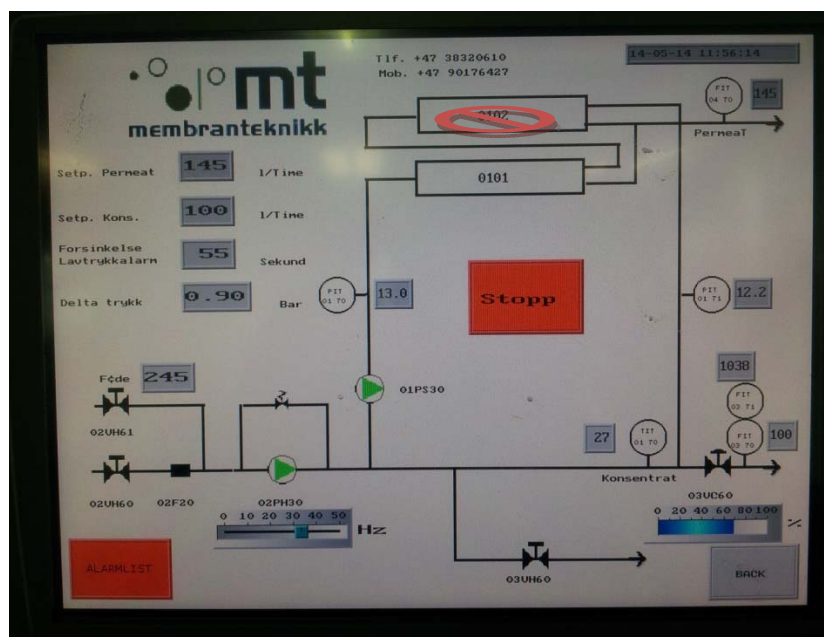


Figure 5-6 NANO-BW-4040 Membrane Operation in Feed and Bleed System
(Membran Teknikk AS, 2014)

Experiment was done with 19 °C feed water with constant flow rate of concentrate (Q_c). Q_c was set as 100 l/hr with 5 variations of Q_p : 80 l/hr, 100 l/hr, 115 l/hr, 130 l/hr and 145 l/hr. C_f was expected to vary between 1,5 – 2,45. For more representative results of all ions rejection rate, samples from permeate and concentrate was analyzed using another ionic analysis (Inductively Coupled Plasma) in Intertek West Lab (explained further in section 5.4). Feed sample was SPW and Ba solution was not necessary. Effect of pressure towards several

parameters would be analyzed. The samples which have highest rejection rate were the one which was interested for further experiment.

5.3. Barium Removal

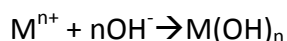
The concentration of Ba^{2+} was originally small (0,003 m Molar or 4,94 mg/l) in accordance to reference SPW. In oil and gas operation, even in very low concentration of barium in big volume of PW can caused $BaSO_4$ scaling when it has contact with SO_4^{2-} . NF membrane was designed to remove divalent ions by retaining them in the concentrate producing permeate water with reduced concentration of divalent ions. In removing divalent ions, NF membrane was widely used. The efficiency was shown in rejection rate of the membrane unit. Unfortunately, **NF membrane separation could not retain selective ions and the rejection rate was varied**. Negatively charged NF membrane would repel all divalent ions with certain different percentage and kept them in the concentrate.

In this project, utilized water would be the concentrate which would contain Ba^{2+} by theory. That is why further treatment of barium removal was necessary and two methods were tested: precipitation and ion exchange. After the experiment, efficiency of each method would be compared. Efficiency of NF membrane in removing barium can also be observed and compared with the chosen barium removal methods.

5.3.1. Precipitation

Barium has many insoluble compounds. In order to remove barium in the water, Ba^{2+} has to be settled in the form of precipitation. The principle of this experiment was mixing an equal amount of chemical to the barium solution, which gave physical change, usually in the change of color due to the precipitation of barium insoluble compounds. There are two common reactions for barium precipitation: hydroxide and sulfate precipitation. Sulfate precipitation would easily lead Ba^{2+} to produce hard precipitate resulting in scaling formation. That is why hydroxide precipitation was chosen for barium removal procedure.

Hydroxide precipitation usually follows the reaction below:



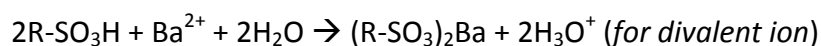
The solubility of the metal during hydroxides precipitation reaches a minimum at a specific pH, 10 for Barium. NaOH and Ca(OH)₂ could be options. Addition of Ca(OH)₂ was chosen since it has the advantages of coagulant during settling process whereas NaOH does not. Easy set-up of beaker glass and magnetic stirrer were prepared. Sample for barium removal came from SPWC and concentrate from Ba solution separation. White precipitation was expected to be observable after several minutes of mixing.

5.3.2. Ion Exchange

Ion exchange was done by draining the feed water through ion exchange resins. The resins are insoluble granular substances, which have acidic or basic substances that can be exchanged in their molecular structure. Barium in multiple mixture solution could be removed using specific resins, which were selective. SST60 and PPC100 could be a choice (Puro-lite, 2013).

The limited availability of selective resin made regular resin of cationic exchanger was used. **Regular ion exchange resins involve changing all the cations** in the sample with H₃O⁺ ions. Thus, to simulate only barium removal, and made the sample could be analyzed using IC, Ba solution was prepared. Ba solution can showed the effectiveness of barium removal using barium selective resins.

The cationic exchanger, Zeolite 325, was shaped like small brown spheres and not soluble in water. It came in the form of R-SO₃H molecules. It was the H⁺ ions present in these molecules that change the place of cations from the solution that surrounds the ionic exchanger. It had to be interfered in water and hydrochloric acid (HCl) during used. When sample-containing barium was drained through an ionic exchanger, the reaction occurred is as shown below:



The result from the draining was expected to have very low concentration of barium. Set up of this experiment was shown in Figure 5-7.

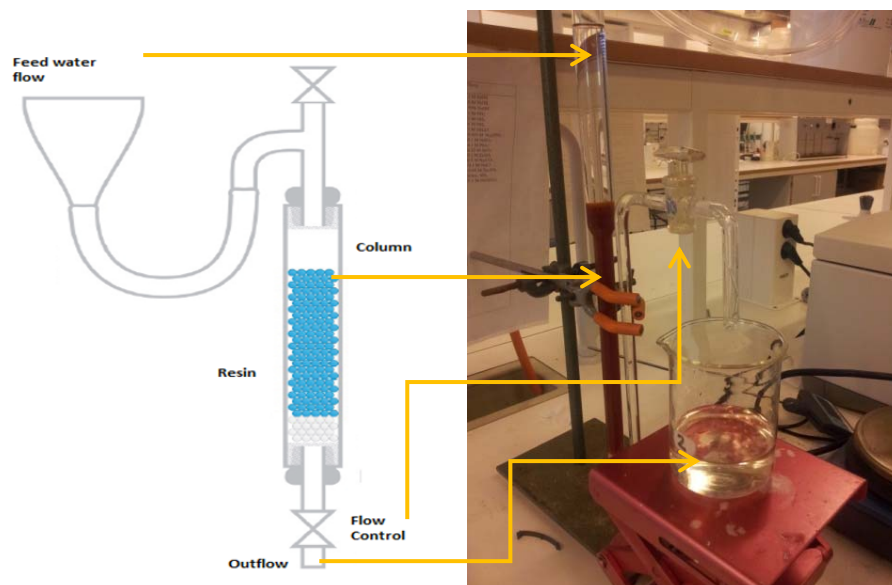


Figure 5-7 Laboratory Scale Set Up for Ion Exchange Experiment

Before starting, HCl 3M was drained through the exchanger. The equilibrium of equations of divalent ions changes and the reaction go to the left. The H^+ is bounded to the ionic exchanger again. After that, before the experiment start, the excess acid has to be washed out of the exchanger by adding 20 ml of distilled water. Open the tap and when the level of the liquid is just above the exchanger mass, add 20 ml distilled water again. The ionic exchanger must not be in contact with air. Air bubbles will prevent the water to be in contact with the active positions, which can reduce the capacity.

Erlenmeyer flask was placed under the ionic exchanger. 25 ml sample was added to the ionic exchanger. Open the tap when the level of the sample was just above the mass, add 10 ml of distilled water and let it sink into the same level again. However, further test using multiple mixture salt solution and appropriate resin to get result that is more representative.

5.4. Ionic Analysis

Ionic Chromatography (IC) Analysis

Ionic chromatography (IC) determines each ion's (anion and cation) concentration in the solution. All samples from the experiment at the University of Stavanger were analyzed using this method. The samples are: SPWF, SPWP and SPWC from SPW EM-NF-1812-50 membrane separation; BaF, BaP and BaC from barium solution membrane separation using EM-NF-1812-50; and barium removal experiments' samples.

Analysis were done using Dionex ICS – 3000 machine (Figure 5-8) for chromatography analysis. The instrument was built for pure water analysis, which means for samples with low TDS value (in the range of millimolar). High dilution rate (500 times) was used for SPW samples for analysis using automatic dilution program (Figure 5-8).



Figure 5-8 Dionex ICS – 3000 Instrument (left) and Dilution Machine (right)

To present the chromatography data quantitatively, instrument is linked to Thermo Scientific™ Dionex™ Chromeleon™ 7.2 program. Chromeleon 7.2., released by Dionex, is a chromatography data system (CDS) software that combines ionic chromatography and mass spectrometry. It controls, process and manage data from chromatography instrument. It identifies the chromatography and visualizes it into peaks. Examples for peak visualization can be seen in Appendix B.

Inductively Coupled Plasma (ICP) Analysis

Due to break up of the IC machine, some of the samples were sent to Intertek West Lab for proper ionic analysis. Using ICP method, small amount of barium concentration in very high TDS solution still can be measured. With this reason, all SPW samples from experiments in Flekkefjord were analyzed here and no separate barium solution needed. The analysis was fully done by Intertek West Lab Technicians.

Chapter 6 - Results and Discussion

This chapter presents and summarizes all the result from the conducted experiments of membrane separation and barium removal. Results are presented in tables; detailed data is available in

6.1. NF Membrane Separation

The performances of each membrane in the separation of divalent ions, as well as effect of permeate flow rate variations, are given in the sections below.

6.1.1. EM-NF-1812-50 Membrane Experiment

Permeate flux

Flow rates of permeate and concentrate were measured at fixed optimum operating pressure of 6.8 bars¹³. Table 6-1 summarized the measurement result (details provided in Table A2 Appendix A).

Table 6-1 Flow Rate Measurements of EM-NF-1812-50 Membrane

Flow	Flow Rate (l/hr)
Feed (Qf) ¹⁴	1,36
Permeate (Qp)	0,04
Concentrate (Qc)	1,32

From the measurement of permeate flow rate, with the membrane area of 0,41 m² (Appendix D), permeate flux for EM-NF-1812-50 membrane was 0,0976 l/m²hr. It was lower than the flux information provided in the specification sheet (see Appendix D) which was 0,19 m³/day (23 l/hr) or 56,54 l/m²hr. Normal flux for NF with spiral wound element typically in the range of 17-34 l/m²hr (Eriksson et al., 2005). Increasing salt concentration resulted in a decrease in permeate flux (Koyuncu et al., 2004). Thus, higher concentration on feed gave lower permeates flux, in this case for EM-NF-1812-50 module during this experiment.

¹⁴Qf = Qp + Qc

Normal flux of EM-NF-1812-50 membrane was tested on 250 ppm¹⁵ NaCl/250 ppm MgSO₄ whereas on this project, TDS on feed was 60832 mg/l nearly two times higher than NSW concentration¹⁶.

Other factors, which can affect the permeate flux, are cross-flow velocity and pressure. Koyuncu et al. (2004) reported that cross-flow velocity was more influential in low NaCl concentration, which makes it not important in having variation of cross-flow velocity for this experiment. Varying pressure was not possible using EM-NF-1812-50 membrane instrument due to small pressure range for this membrane model. To see the effect on pressure variation other membrane model was chosen and the results are discussed in NANO-BW-4040 section.

The flux of EM-NF-1812-50 membrane might be decreasing compared to initial designated flux because the membrane has been stand for a long time. That is why washing prior using was needed. Prewashing the membrane before starting an operation was meant to make the membrane free of the unintended solutes. After washing, the flux of the membrane should be normal, but not as good as a new membrane. This can affect the overall flux during operation.

Rejection rate

Another factor of membrane process efficiency is rejection rate (Cheryan, 1998). Rejection rate of EM-NF-1812-50 membrane on monovalent and divalent ions is depicted in Figure 6-1 – Figure 6-3. Detailed results of ionic composition obtained from IC analysis can be seen in Table A3 Appendix A. Before the experiment started, membrane was washed with RO water for 30 minutes to ensure that the membrane was clean and there were no traces elements left from previous use. To make sure all the area in the membrane was filled only with feed water (SPW) and the sample was not diluted, permeate and concentrate flow were not directly recirculated into the feed tank until 5 minutes of operation.

According to Figure 6-1, EM-NF-1812-50 membrane did not reject the monovalent ions. It can be concluded from permeate and retentate³ concentration of sodium, as well as chloride, after the separation process, which is not showing much difference. Permeate

¹⁵1 ppm = 0.998859 mg/l. In this case, it is assumed that 1 ppm ≈ 1 mg/l

¹⁶NSW typical concentration is 34483 mg/l ≈ 35000 mg/l (www.lenntech.com/composition-seawater.htm)

concentration after separation process was 30067 mg/l for sodium and 55437 mg/l for chloride. In accordance to the result, EM-NF-1812-50 had low rejection on monovalent ions, which were 2,44 % for sodium and 2,55 % on chloride. It was also observed that after the separation process, concentration of sodium and chloride was slightly increasing in the retentate.

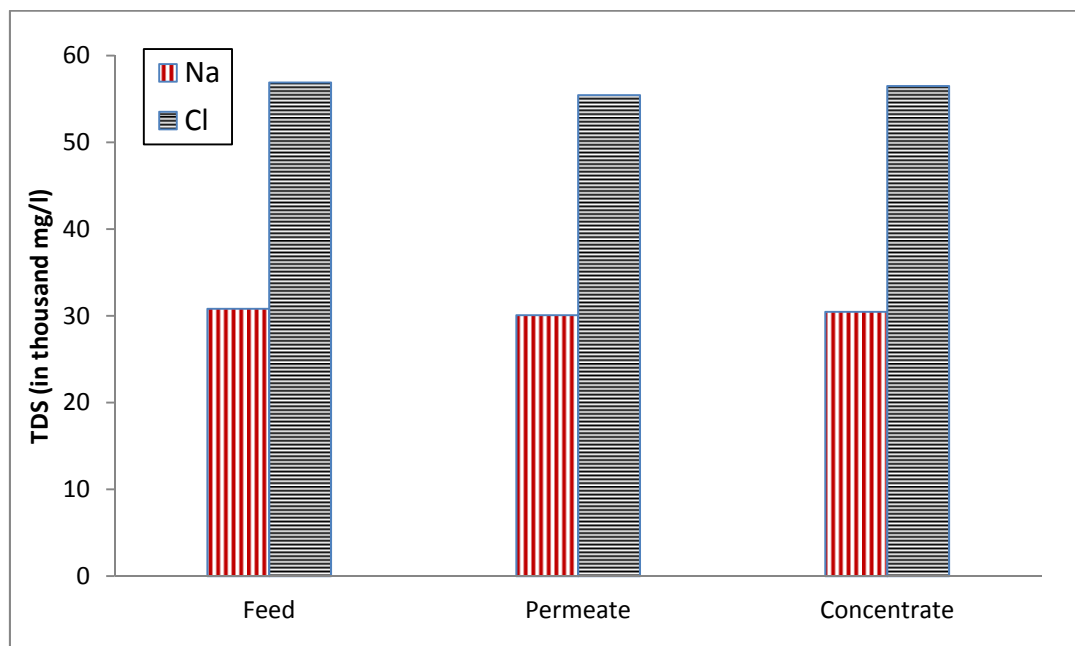


Figure 6-1 Rejection of Monovalent Ions in EM-NF-1812-50 Membrane

Different phenomenon was noticed on the separation of calcium and magnesium. Feed concentration on calcium and magnesium were both noted as 1560 mg/l. During the separation, EM-NF-1812-50 rejected 45,38 % of calcium and 87,69 % of magnesium resulting higher concentration of both ions in the retentate (3163 mg/l calcium and 2097 mg/l magnesium). Concentration in permeate was measured as 852 mg/l of calcium and 192 mg/l of magnesium. Figure 6-2 summed up the separation effectiveness of this membrane on separating divalent ions.

Due to high dilution requirement for IC analysis, separate barium solution was prepared to see the rejection rate of relatively low concentration of barium on EM-NF-1812-50. Feedwater for barium rejection, represented in Figure 6-3, was pure barium chloride solution. Feed and permeate concentration of the solution was marked as 4,94 mg/l and 4,935 mg/l, which made the rejection rate for barium as low as 0,13 %. On retentate side, the concentration of barium was increasing up to 5,09 mg/l.

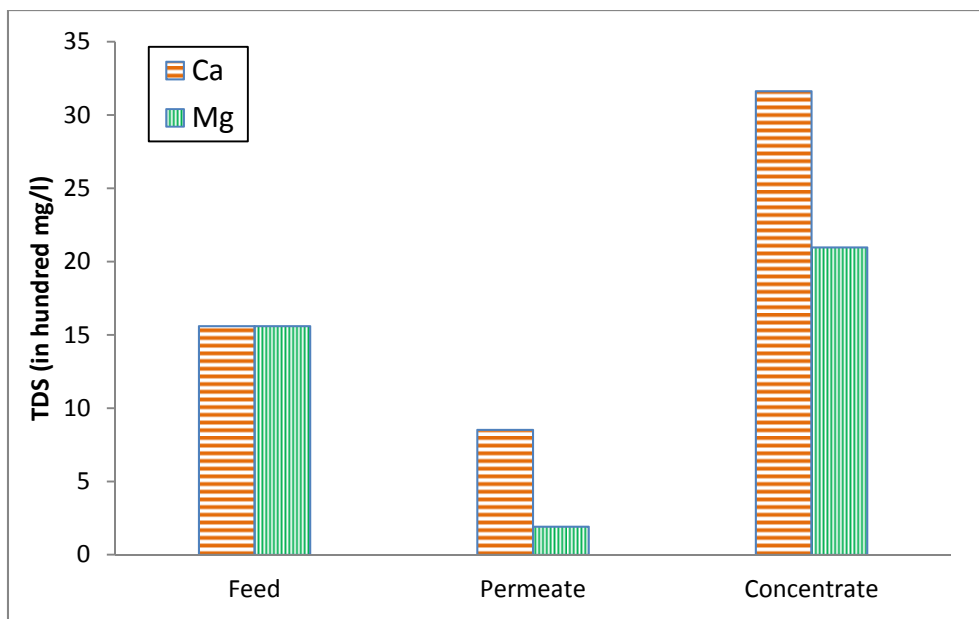


Figure 6-2 Rejection of Divalent Ions in EM-NF-1812-50 Membrane

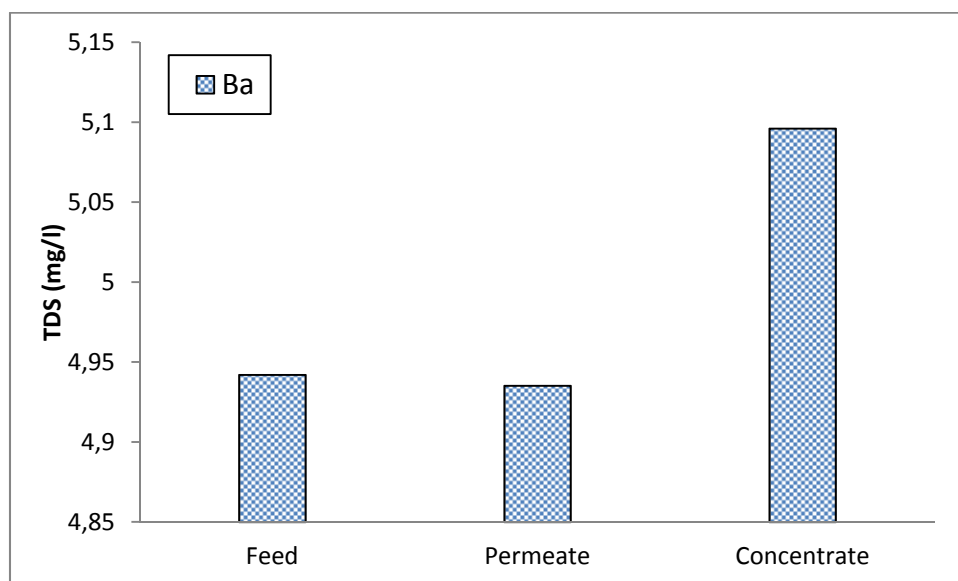


Figure 6-3 Rejection of Ba²⁺ in EM-NF-1812-50 Membrane

Based on these results, the rejection rate of EM-NF-1812-50 is summarized in Table 6-2. EM-NF-1812-50 has highest rejection of magnesium and lowest rejection on barium on pure barium solution. Low rejection rate of monovalent ions tells that there was not any separation process and the ions were going to where the water flows.

Table 6-2 Rejection Rate of EM-NF-1812-50 Membrane of SPW

Ion	% Rejection
Na	2,44
Ca	45,38
Mg	87,69
Cl	2,55
Ba	0,13

Bilstad (1992) reported that NF membrane has poor separation efficiency on rejecting monovalent ions. The idea is emphasized by the rejection rate of monovalent ions in this experiment. NF membrane is characterized as having MWCO in the range of 100 – 1000 so it retains all solutes except monovalent charged ions. According to the result showed in Figure 6-1 concentration of retentate was higher than feed.

Steric partitioning in NF membrane separation takes an account of sieve effect caused by the intrinsic porosity of the membrane. In terms of ionic radius size, Mg^{2+} has lowest ionic radius compared to other ions in the similar group (IIA). The ionic radius nonetheless did not determine the rejection rate of NF membrane. After experiment, Mg^{2+} has higher rejection than Ca^{2+} , which has higher ionic radius. This shows that separation in NF membrane is not based on size. In this case, hydration energy of ions has a role in separation. Stronger hydration energy will reduced the permeability of ions (Krieg et al., 2005). Hydration energy of Mg^{2+} (1926 kJ/mol) is higher than Ca^{2+} (1579 kJ/mol). As the result of that, more Mg^{2+} were retained.

However, some amounts of the monovalent ions were also being retained. The transport of solutes in NF membrane is not as simple as solely based on the size of solutes, but also the electro neutrality condition inside the membrane as explained by Vezzani and Bandini (2002). Negatively charged NF membrane is designed to reject similar divalent anions (e.g. SO_4^{2-}). Its effectiveness in rejecting sulfate was beyond doubt and has been reported in several cases (Bilstad, 1992; Eriksson et al., 2005; Krieg et al., 2005; Wickramasinghe & Mondal, 2008). Divalent cations were retained as it is one of NF membrane characteristic. As the result from that, counter ions were needed to reach the electroneutrality condition after

separation. The absence of divalent anions makes Cl^- as only anion was rejected. This made the concentration of Cl^- was increasing in concentrate side.

Lack of divalent anions also explained the results shown by the rejection rate of calcium and magnesium ions which was less than the rejection rate of MgSO_4 stated in the specification sheet. NF membrane is negatively charged, so anion repulsion really determined the rejection rate of the solutes.

For pure barium chloride solution, very low rejection happened due to low concentration of salt in feed. Krieg et al. (2005) mentioned that during low salinity concentration, flux has larger influence on rejection since flux is linear to pressure difference but salt permeability is not linear to the concentration. Nevertheless, concentration of Ba^{2+} was slightly increasing in the concentrate. Rejection rate between Mg^{2+} & Ca^{2+} and Ba^{2+} as divalent ion in EM-NF-1812-50 membrane experiment was not comparable.

6.1.2. NANO-BW-4040 Membrane Experiment

Permeate Flux Variation

Experiment with NANO-BW-4040 membrane showed that modification of permeate flow rate (Q_p), affected the pressure, permeate flux, as well as rejection rate of several ions. Q_p alterations were done to increase concentration factor (C_f) in order to see the possibility of concentrate more ions in the retentate. Figure 6-4 presents the effect of Q_p -alteration towards flux. It was observed that increasing Q_p led to increase of permeate flux. This condition was obtained with constant concentrate flow rate (Q_c) of 100 l/hr. Lowest flux of 11.45 l/m²hr was noted on lowest Q_p (80 l/hr), while the highest one was noted when the Q_p was set to 145 l/hr. Highest flux was 24 l/m²hr.

Figure 6-4 shows direct correlation of flux and Q_p . From that, further effects on other parameters caused by flux variations were observed. The first one was the effect of flux to pressure. Effect of flux variation towards pressure in feed and concentrate side is explained by Figure 6-5. Increasing flux (which was caused by increasing Q_p) gave increase in feed and concentrate pressure (P_f and P_c). Table A6 in Appendix A summarized the field measurement being taken from each flow rate variation. Lowest pressure applied were 8 bars¹³ on the feed and 9 bars on the concentrate side, while the highest ones were 12.1 bars on the feed and

13 bars on the concentrate side. Pressure difference on feed and concentrate was kept between 0,9 – 1 bar. Highest pressure occurred when the Q_p was set up to 145 l/hr.

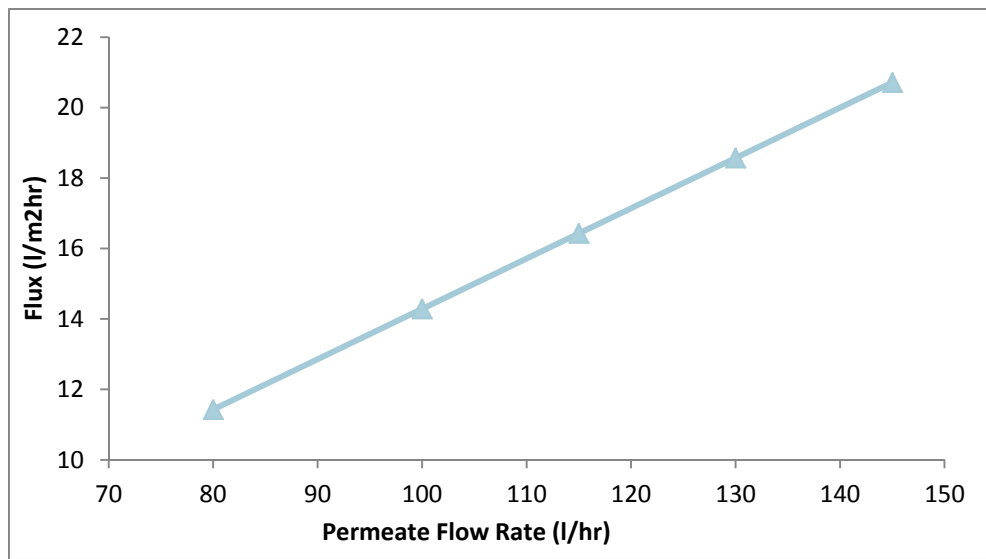


Figure 6-4 Effect of Permeate Flow Rate on Flux in NANO-BW-4040 Membrane

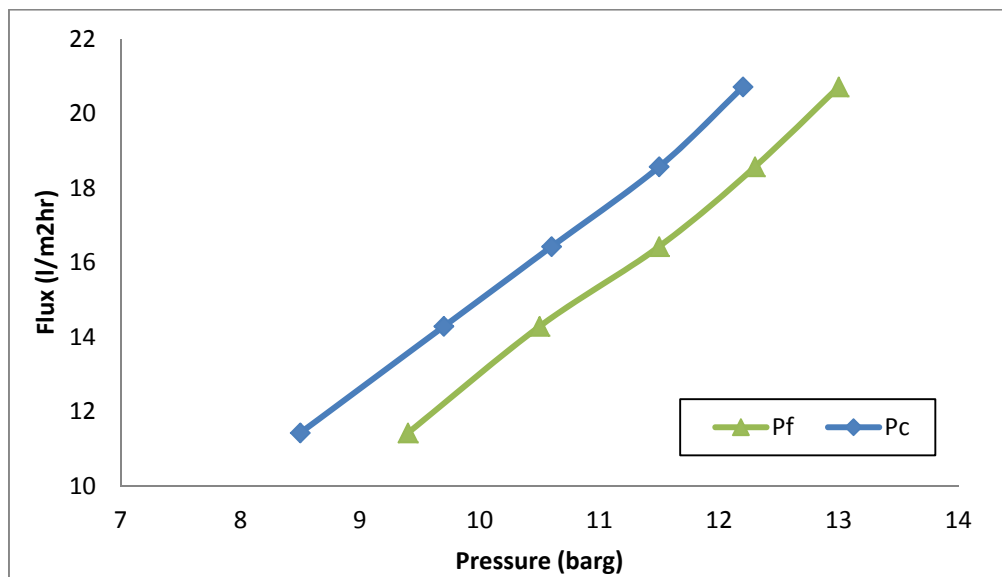


Figure 6-5 Effect of Permeate Flux on Pressure in NANO-BW-4040 Membrane

According to Equation 3, with constant Q_f , increasing Q_p gives increasing C_f . Calculation on C_f was done and tabulated in Table 6-3 Concentration Factor Calculation on NANO-BW-4040. The accuracy of the calculation was tested on the separation process to see whether the actual condition was going in accordance to the calculation.

Table 6-3 Concentration Factor Calculation on NANO-BW-4040

Permeate Flow Rate (Q_p)	Feed Flow Rate (Q_f)	Concentration Factor (C_f)
80	180	1,8
100	200	2
115	215	2,15
130	230	2,3
145	245	2,45

Figure 6-6 confirmed that the actual condition during the experiment was in line with the calculation. It was noticeable that the value of TDS in the retentate was increasing and reached its highest concentration on the highest Q_p . In permeate side TDS concentration was slightly decreasing when Q_p was increasing. Increasing retentate concentration showed that more ions were being retained which affirmed the increasing C_f value as calculated beforehand. It is seen that with higher Q_p NANO-BW-4040 rejected more ions.

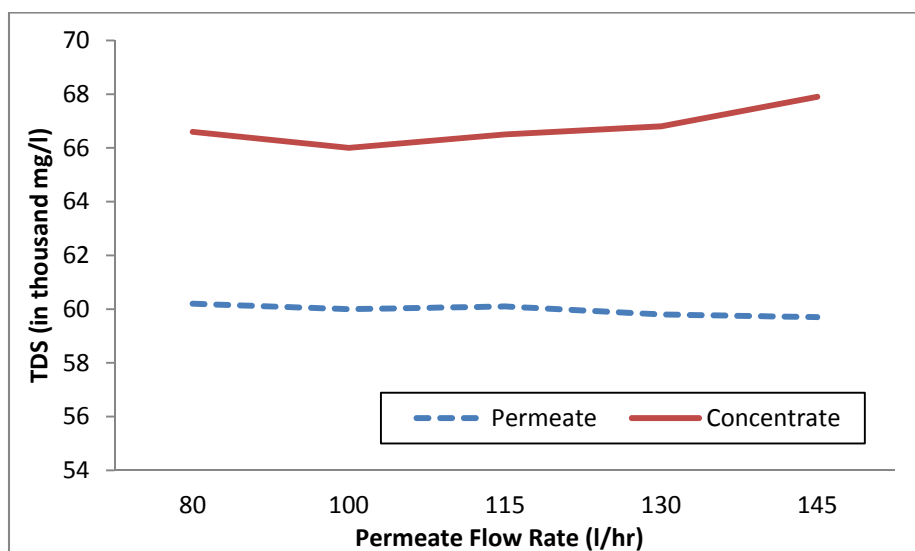


Figure 6-6 Q_p versus TDS in NANO-BW-4040 Membrane

Rejection Rates

To know the details of ion rejections, analysis was divided into several parts: for monovalent ions, divalent ions and barium ion. Figure 6-7 - Figure 6-11 shows the effect of pressure

variation towards rejection rate. Feed concentration of each ion type was measured lower than feed concentration on the earlier experiment using EM-NF-1812-50 membrane. Slightly different feed concentration happened due to the prewashed operation of membrane with clean tap water. When operation started after cleaning, the instrument was filled with clean tap water, by directly operated the feed and bleed system the tap water was recirculated to feed solution. That made a slight change on the feed concentration.

NANO-BW-4040 membrane showed no significant separation on monovalent ions. Figure 6-7 and Figure 6-8 showed separation performances towards monovalent ions. Almost similar concentrations of Na^+ and Cl^- were observed in permeate and feed. Even so, NANO-BW-4040 rejected more Cl^- compared to Na^+ . It was calculated that average rejection rate of Na^+ and Cl^- was 1,86 % and 7,09 % respectively. Na^+ and Cl^- rejection rate were increasing when flux was increased to 18,57 l/m²hr and C_f was 2,3.

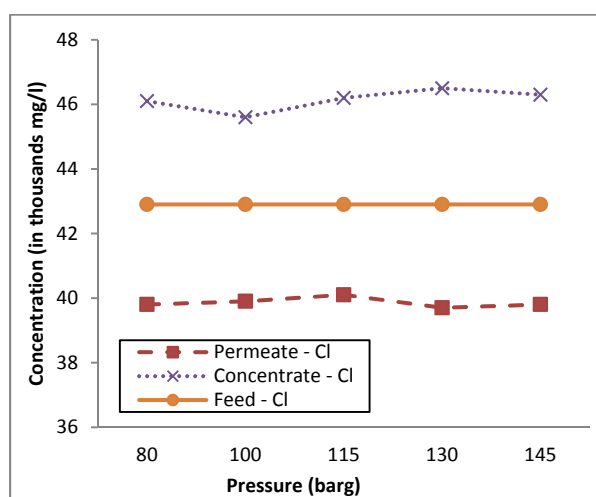


Figure 6-7 Effect of Pressure in Cl^- Rejection in NANO-BW-4040 Membrane

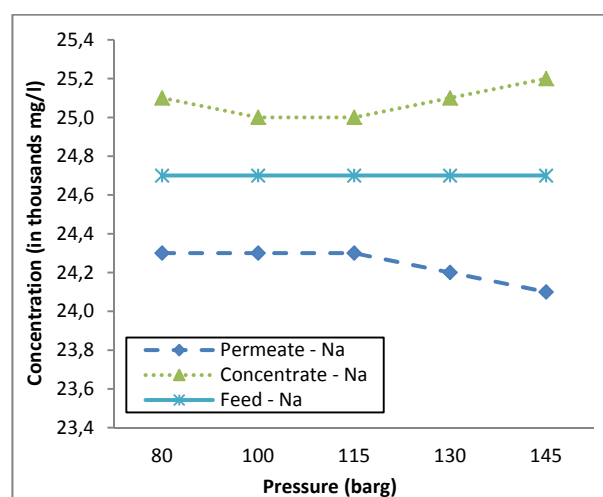


Figure 6-8 Effect of Pressure in Na^+ Rejection in NANO-BW-4040 Membrane

Change of pressure gave different effect on divalent ion rejection compared to monovalent ion, as explained by Figure 6-9 - Figure 6-11. Increasing pressure gave increasing rejection rates on calcium, magnesium and barium. Mg^{2+} had highest rejection rate of average 62,19 % while for Ca^{2+} the rejection rate was 24,56 %. Higher rejection rate resulted in higher concentration of those ions in the retentate.

Compared to feed concentration of 1080 mg/l for Mg^{2+} and 1180 mg/l for Ca^{2+} , retentate had significantly higher concentration (1840 – 1930 mg/l for Mg^{2+} and 1450 – 1510 mg/l for Ca^{2+}). This is in line with the aim of this project.

Another divalent ion, Ba^{2+} , has the average of 38,53 % of rejection rate. Initial feed concentration of barium was 4,5 mg/l; after separation the concentration in the retentate was noted between 6,28 – 6,51 mg/l. Permeate has average Ba^{2+} concentration of 2,76 mg/l.

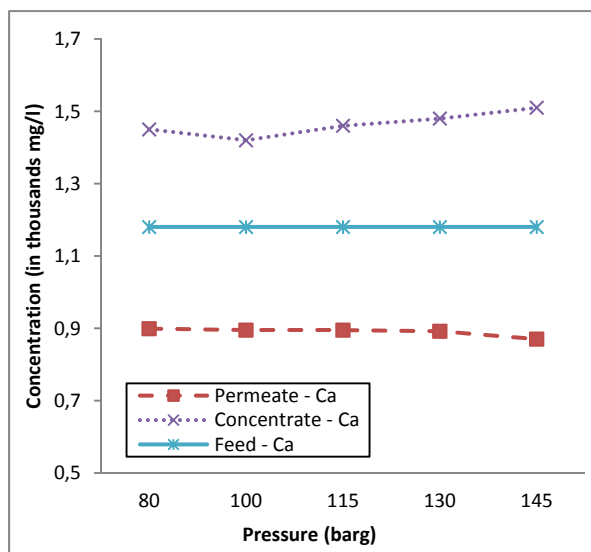


Figure 6-9 Effect of Pressure in Ca^{2+}

Rejection in NANO-BW-4040 Membrane

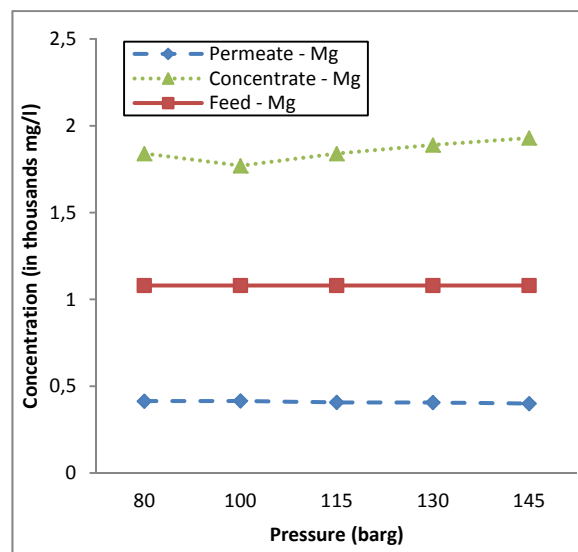


Figure 6-10 Effect of Pressure in Mg^{2+}

Rejection in NANO-BW-4040 Membrane

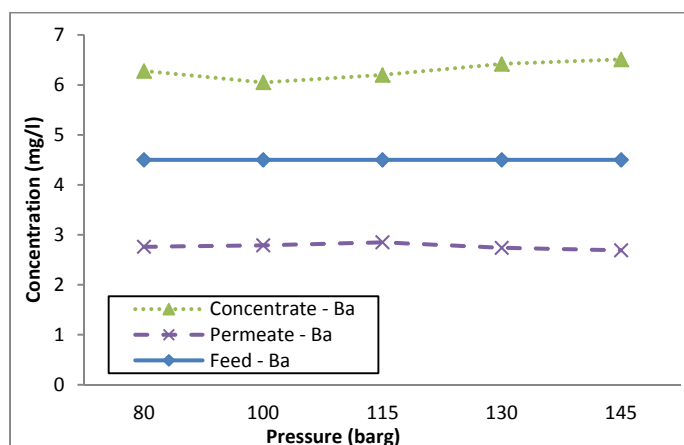


Figure 6-11 Effect of Pressure in Ba^{2+} Rejection in NANO-BW-4040 Membrane

To compare the rejection rate of different ions of our interest on NANO-BW-4040 membrane, Figure 6-12 summed up overall rejection rates for monovalent and divalent ions within 5 types of flux measured.

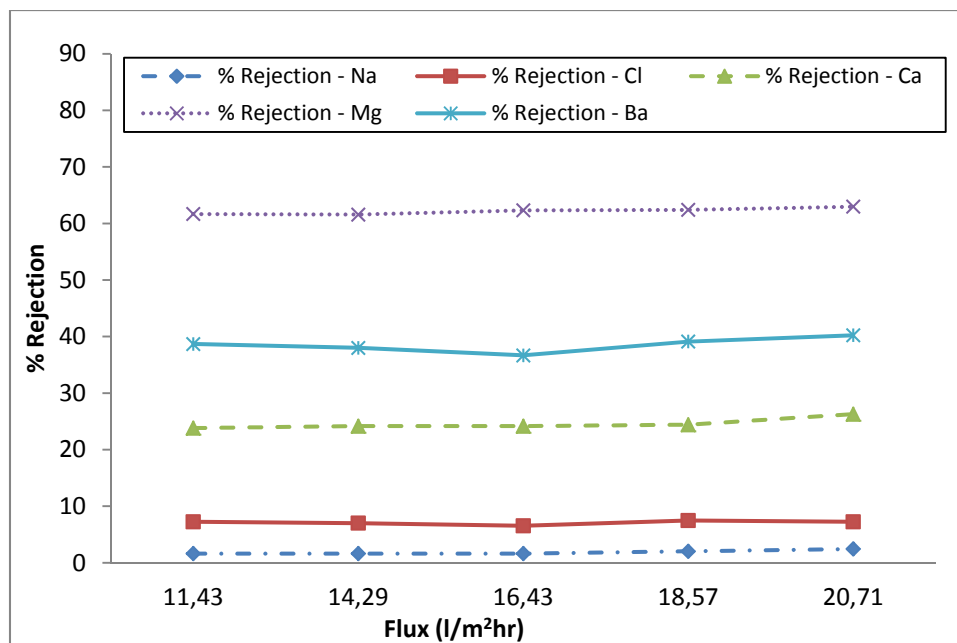


Figure 6-12 % Rejection Rates on NANO-BW-4040 Membrane

In monovalent separation, higher rejection on Cl^- can be explained with the relation of hydration energy and anion rejection as explained in the previous section of EM-NF-1812-50 membrane. Higher hydration energy made divalent cations rejected by NF membrane instead of monovalent anions (Hydration energy of $\text{Na}^+ = 406 \text{ kJ/mol}$). Anion, as the result, has to balance the separation in order to maintain the electroneutrality. For that reason, Cl^- was rejected more than Na^+ . In this case, hydration energy of Cl^- and Na^+ did not determine the rejection rate.

Mg^{2+} , as cations with highest hydration energy, showed the largest value on rejection rate followed by Ba^{2+} and then Ca^{2+} . Increasing flux give increasing value of rejection rate, as is typical characteristic of NF membrane. Theoretically, higher hydration energy of ions will give less permeability of ions through membrane. It means the rejection rate of Ba^{2+} has to be less than Ca^{2+} . This behavior did not fully understandable. That could be happening because the very low concentration of Ba^{2+} in the solution and the combination of hydration energy in multiple salt mixtures in the absence of divalent anions. Permeability and behavior of NF membrane separation was complex in the presence of multiple ions. Further research has to be done to see other possibility affecting the permeability of divalent ions.

6.1.3. Comparison between EM-NF-1812-50 and NANO-BW-4040 Membrane

Both membranes showed the typical behavior of NF membrane where the membrane rejects divalent ions and passing through monovalent ions. NANO-BW-4040 membrane also shows that increase in pressure gave higher flux. However, rejection rate of EM-NF-1812-50 membrane was higher than NANO-BW-4040 membrane. This showed that EM-NF-1812-50 has tighter pore compared to NANO-BW-4040 thus it can concentrate more divalent ions. With this result, EM-NF-1812-50 type of membrane gives better performance. For checking the barium rejection rate on similar membrane, it is recommended to run another test with SPW feed water and more precise ionic analysis.

Pressure was a problem in EM-NF-1820-50 membrane since it was built for fixed pressure. With fixed pressure, flux was hard to be controlled. According to this comparison, NANO-BW-4040 was more desirable for further experiment since high concentration of salt will really affect the flux. With the ability of changing the pressure, wider area of research can be done. Another advantage is the installation of NANO-BW-4040 has the ability to keep the temperature stable during experiment.

Though in general the rejection of monovalent ions and divalent ions showed favorable results, Ba^{2+} rejection behavior was not fully understandable. Lowest hydration energy of Ba^{2+} show higher rejection rate compared to Ca^{2+} which have higher hydration energy. Rejection rate for Ba^{2+} in two different membranes was not comparable since the feed source was not the same. Further research has to be done to check other parameters affecting divalent cations rejection in high salinity solution with the absence of divalent anions.

6.2. Barium Removal

Two methods for barium removal were compared: precipitation and ion exchange. The effectiveness of both methods is presented and discussed in this section. Complete analysis of the ionic composition was tabulated in Table A8 in Appendix A. Other ions, showed up in the table (such as Na, Cl, S, K, P), presented due to impurities of the salt used.

6.2.1. Precipitation

This experiment was aimed to get the barium settled in a form of white precipitation of barium hydroxide ($\text{Ba}(\text{OH})_2$). No precipitation was observed for each experiment as seen in Figure 6-13.

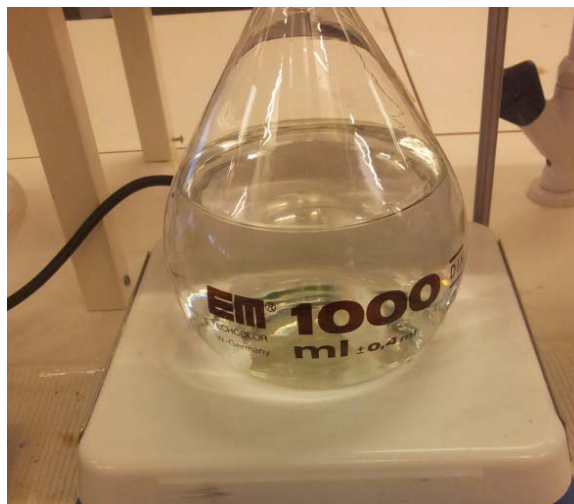


Figure 6-13 Barium Solution without Precipitation

$\text{Ba}(\text{OH})_2$ has K_{sp} value of 5×10^{-3} ($\text{Ba}(\text{OH})_2$ concentration was 0,107 M) in pure water at temperature 25°C . The K_{sp} of $\text{Ba}(\text{OH})_2$ after pH was changed up to 10 was decreasing up to 5×10^{-13} (calculation in Appendix A). $\text{Ba}(\text{OH})_2$ concentration was calculated as 5×10^{-5} M which is lower than 0,107 M. The K_{sp} value did not exceeded the initial K_{sp} so precipitation was not formed. Not only that, the absence of precipitation can be explained by inappropriate temperature regime during the experiment.

K_{sp} value for $\text{Ba}(\text{OH})_2$ is in the temperature of 25°C , while during the experiment the temperature could not be kept constant. At given conditions, it can be concluded that precipitation of barium in a low concentration for removal is not efficient. To test the method again, the experiment needs to be modified by using variation of temperature to change the K_{sp} as well as to get the optimum temperature to precipitate barium as $\text{Ba}(\text{OH})_2$ or by choosing different precipitation method (sulfate or carbonate).

6.2.2. Ion Exchange

Ion exchange experiment was done using two types of concentration as the feed: barium concentration before membrane separation (e.g. feed water type) and after membrane separation (e.g. retentate water type). After both of the experiments, pH of the solution decreased from 7.2 to 3. The concentration of barium after ion exchange is presented in Table 6-4.

Table 6-4 Barium Concentration after Ion Exchange

Experiment	Barium Concentration (mg/l)	
	Feed	Final
Before separation	4,5	0.008
After separation	6,51	<0.004

According to Table 6-4 **Barium Concentration after Ion Exchange** both results on ion exchange show efficient removal of barium - as high as 99 %. Lower concentration of barium was found in water samples after separation. This has occurred because the resin was regenerated with HCl before the process was done. Regeneration process optimized the exchange mechanism of the resin.

Based on the results above, ion exchange is an effective method in removing barium at low concentration. Effect of ion exchange on other ions was not observed because the barium-selective resin was not available, so pure barium solution was used to simulate. For further experiment, barium-selective resin has to be presented in order to really see the removal rate of barium and the effect on other ions, whether the resin made change on other cations.

Concentration of barium before and after the separation process was low. The result after ion exchange showed that despite the concentration difference, removal efficiency is significantly high. From these results it can be summarized that ion exchange removes barium as much as 99 % of the initial feed concentration independently on where membrane separation takes place.

If ion exchange is done prior to NF membrane separation, it acts as pretreatment. Feed produced water with lower barium concentration becomes the source for ion exchange feed water. On the other hand, if ion exchange is located after membrane separation, feed water for ion exchange will become more concentrated after NF membrane separation, providing higher barium concentration as feed for ion exchange. But by arranging ion exchange as post-treatment after NF membrane separation, it will ensure that barium concentration will not increase or retain because of separation process. With this option, barium concentration will be 99 % lower than in the feed water.

6.2.3. Comparison on Barium Removal Techniques

Based on previous experiment, precipitation method was not effective to remove barium. Further, ion exchange gave excellent performance in removing barium. After the ion exchange process, barium was removed 99 %. This made ion exchange as more desirable combination to remove barium from the SPW. Placement of ion exchange after membrane separation was chosen instead of as pretreatment to make sure that after ion exchange, barium will not be concentrated in the retentate. That will give a risk of increasing barium concentration.

6.3. Combination of Membrane Separation and Barium Removal Technique in Produced Water Treatment as Smart Water Source

After membrane separation and ion exchange as treatment, concentrate water would have higher concentration of divalent ions (around 3000 mg/l) and high concentration of monovalent ion (60000 mg/l). The aim of the experiment was to see if NF membrane separation and barium removal could be a potential treatment of produced water to increase its quality as smart water (e.g. by increasing the determining ion Mg^{2+} and Ca^{2+}).

With higher flux and higher concentration factor (thus, higher pressure), divalent ion was retained in the concentrate which made their concentration higher. Ion exchange was also proved efficient in removing barium, which can cause $BaSO_4$ scaling if PW is meant to be mixed with SW. The main problem is very high TDS of the final water. TDS has to be decreased up to 5000 mg/l.

According to the experiment, high rate of dilution (means large volume of fresh water) is needed to make this treatment appropriate to make PW as a better source of smart water. But by removing Ba^{2+} in PW and increasing Ca^{2+} and Mg^{2+} , some volume fraction of PW can be added to SW as smart water source without inducing the precipitation of BaSO_4 .

Chapter 7 - Conclusions and Recommendations

Conclusions

- Both EM-NF-1812-50 and NANO-BW-4040 membranes showed significant behavior of NF membrane on divalent ions rejection and passing through the monovalent ion. That is why both membranes are appropriate instrument to concentrate divalent ions in the retentate.
- Pressure was observed directly related to flux and TDS in the concentrate. Increasing pressure increases flux thus increases TDS in the concentrate. It means with higher flux rejection rate will also be increasing.
- NF membrane separation is a complex process. It is not solely depending on size of the ions, but also broadens aspect like hydration energy and electroneutrality of the membrane.
- With the absence of divalent anions as counter ions, NF separation can retain 62 % of Mg^{2+} and 24 % of Ca^{2+} . That causes the increase the rejection rate of Cl^- as much as 7 % as the result of cation's low permeability to keep the electroneutrality balance.
- Ion exchange is an effective way to remove barium, while membrane have 30 % rejection rate, but not selective to barium. That made ion exchange is more beneficial in removing selective barium when using barium selective resin.
- End product of this experiment (retentate) still has high TDS (60000 ppm), so high dilution rate is needed to lower the TDS up to 5000 ppm. If barium was removed and retentate has higher concentration of Ca^{2+} and Mg^{2+} , some volume of it can be mixed with SW as smart water source
- According to overall experiments, combination of NF membrane separation and ion exchange for barium removal gave satisfying result. It has the potential for PW treatment to increase the performance of smart water by increasing the concentration of divalent determining ions as well as remove the barium. More research for lowering TDS needs to be done.

Recommendations

In order to provide more detailed information for barium removal from produced water, several recommendations are suggested:

- Using real pretreated produced water as feed water for membrane separation and ion exchange.
- Similar source of feed water need to be used for all experiments. Using pure solution (e.g. barium solution) is not recommended.
- In testing the efficiency of barium removal, real selective resin has to be utilized for maximum result. Feed water for ion exchange has to be the same water from the concentrate of NF membrane separation
- Other method of precipitation can be done with variation of temperature
- More advance ionic analysis like ICP is recommended to get better accuracy of the results, which not required high dilution.

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Appendices

Appendix A

Table A1 - Composition of Constructed SPW for 50 L Sample

Chemical Salt	Mass (gram)	Mr (gr/mol)	mol (gram/mr)	Concentration (mol/L)
NaHCO ₃	8,4007	84,007	0,1	0,002
NaCl	3909,636	58,44	66,9	1,338
CaCl ₂ *2H ₂ O	286,6773	147,014	1,95	0,039
KCl	59,64104	74,5513	0,8	0,016
MgCl ₂ *6H ₂ O	660,7575	203,31	3,25	0,065
SrCl ₂ *6H ₂ O	7,46536	266,62	0,028	0,00056
LiCl	6047,5041	42,394	142,65	2,853
BaCl ₂ *2H ₂ O	0,439668	244,26	0,0018	0,000036

Table A2 – Flow Rate Measurement in EM-NF-1812-50 Membrane

	Volume (ml)	Time (minutes)	Flow Rate		
			ml/min	ml/hr	l/hr
Permeate	35	45	0,777778	46,6666667	0,046667
Concentrate	110	5	22	1320	1,32
Feed	145		22,77778	1366,66667	1,366667

Table A3 - Result from IC Analysis of EM-NF-1812-50 Membrane

Number	Sample Name	Ionic Concentration (mg/l)				
		Na	Ca	Mg	Cl	Ba
1	Feed	30820	1560	1560	56888	4,942
2	Permeate	30067	852	192	55437	4,935174
3	Concentrate	30465	3163	2097	56486	5,096012
Rejection Rate (%)		2,44	45,38	87,69	2,55	0,14

Table A4 - Mass balance for Chloride in NANO-BW-4040 Membrane

Ion	TDS Feed (mg/l)	Qf (l/hr)	Mass F (mg/hr)	TDS Permeate (mg/l)	Qp (l/hr)	Mass P (mg/hr)	TDS Concentrate (mg/l)	Qc (l/hr)	Mass C (mg/hr)	Mass (P+C)	Balance	balance error w.r .t feed%
Na	30820	1,366667	42120,67	30067	0,046667	1403,127	30465	1,32	40213,8	41616,93	503,74	1,195944983
Cl	56888	1,366667	77746,93	55437	0,046667	2587,06	56486	1,32	74561,52	77148,58	598,3533	0,769616637

Table A5 – Recapitulation of the Result from Intertek

Number	Sample Number	Ionic Concentration (mg/L)								
		Na	Ca	Mg	Ba	Fe	Sr	K	S	Cl
1	SPWF	24700	1180	1080	4,5	0,1	36,6	486	1,4	42900
2	SPWP1	24300	899	414	2,76	0,1	21,8	478	<1	39800
3	SPWP2	24300	895	415	2,79	0,1	21,6	477	<1	39900
4	SPWP3	24300	895	407	2,85	0,1	21,3	472	<1	40100
5	SPWP4	24200	892	406	2,69	0,1	21,1	477	<1	39700
6	SPWP5	24100	870	400	2,74	<0.1	20,8	476	<1	39800
7	SPWC1	25100	1450	1840	6,28	<0.1	51	501	2,1	46100
8	SPWC2	25000	1420	1770	6,05	0,1	50,7	495	2,1	45600
9	SPWC3	25000	1460	1840	6,2	0,1	50,8	494	2	46200
10	SPWC4	25100	1480	1890	6,51	0,1	54	498	2,1	46500
11	SPWC5	25200	1510	1930	6,42	0,1	52,5	507	2,1	46300

Table A6 – Field measurement (using TDS meter) on SPW for NANO-BW-4040 Membrane

Flow rate (Q, l/hr)			pH			Temperature (T, °C)			Conductivity (mS/cm)			Salinity			TDS (ppm)		
F	P	C	F	P	C	F	P	C	F	P	C	F	P	C	F	P	C
180	80	100	7,3	7,07	6,73	25,1	26	25,8	99,8	94,1	104,1	off limit	off limit	31,6	63900	60200	66600
200	100	100	7,3	7,18	6,71	25,1	23,4	23,5	99,8	93,8	103,3		68	31,7		60000	66000
215	115	100	7,3	7,03	6,93	25,1	23,5	24	99,8	93,9	104		67,9	31,8		60100	66500
230	130	100	7,3	7	7,03	25,1	24,6	24,7	99,8	93,5	104,4		68,5	32,4		59800	66800
245	145	100	7,3	7,17	7,07	25,1	25,4	24,9	99,8	93,3	106,2		67,9	33,2		59700	67900

Table A7 - Field Measurement using TDS meter for Ba Solution for NANO-BW-4040 Membrane

Flow rate (Q, l/hr)			pH			Temperature (T, °C)			Conductivity (mS/cm)			Salinity			TDS (ppm)		
F	P	C	F	P	C	F	P	C	F	P	C	F	P	C	F	P	C
180	80	100	6,96	7,22	7,22	21	20	21	47,2	44,3	49	30,6	28,6	31,6	30200	28300	31300
200	100	100		7,39	7,31		20	19		43,4	48,18		27,7	31,7		27800	30800
215	115	100		7,34	7,41		20	20		42,9	49,2		27,5	31,8		27400	31500
230	130	100		7,25	7,24		19	19		42,5	50,1		27,1	32,4		27200	32100
245	145	100		7,21	7,25		20	19		42,8	51		27,2	33,2		27400	32600

Table A8– Recapitulation for Ba Solution Ionic Composition

Number	Sample Number	Ionic Concentration (mg/L)								
		Na	Ca	Mg	Ba	Fe	Sr	K	S	Cl
1	BaF	81	9,9	9,4	3,9	<0.02	0,28	2,1	0,96	180
2	BaP1	87	8,9	7,7	2,4	<0.02	0,22	2,3	0,071	180
3	BaP5	78	7,4	6,3	2,2	<0.02	0,21	2,1	0,085	160
4	BaC1	110	14	16	4,7	<0.02	0,44	3	2,1	250
5	BaC5	110	15	16	5,2	<0.02	0,45	3,2	2,2	250
6	BaIE2	0,99	1,4	0,14	0,008	<0.02	0,008	<0.3	0,52	88
7	BaIE1	2,8	0,97	0,098	<0.004	0,062	0,005	<0.3	4,9	380
8	BaPrec	0,58	36	0,17	150	<0.02	0,043	<0.3	<0.07	80

Calculation for Ba(OH)₂K_{sp}

In 25 °C:



$$K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = [s] [2s]^2 = 5 \times 10^{-3}$$

$$4s^3 = 5 \times 10^{-3}$$

$$s = 0,107 \text{ M}$$

When Ba(OH)₂ is in solution with pH = 10, pK_w = 14



$$\text{pH} = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$[\text{H}^+] = 1 \times 10^{-10} \text{ M}$$

$$\text{pOH} = 4$$

$$[\text{OH}^-] = 10^{-4} \text{ M}; [\text{Ba}^{2+}] = 5 \times 10^{-4} \text{ M}$$

$$K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = [0,5 \times 10^{-4}] [10^{-4}]^2$$

$$K_{sp} = 5 \times 10^{-13}$$

Appendix B

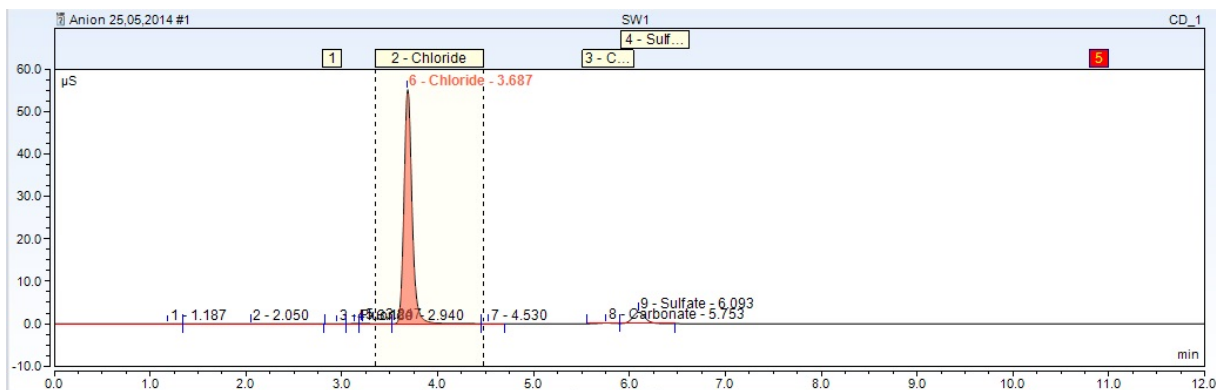


Figure B1 – Example for Chloride Peak in IC Analysis

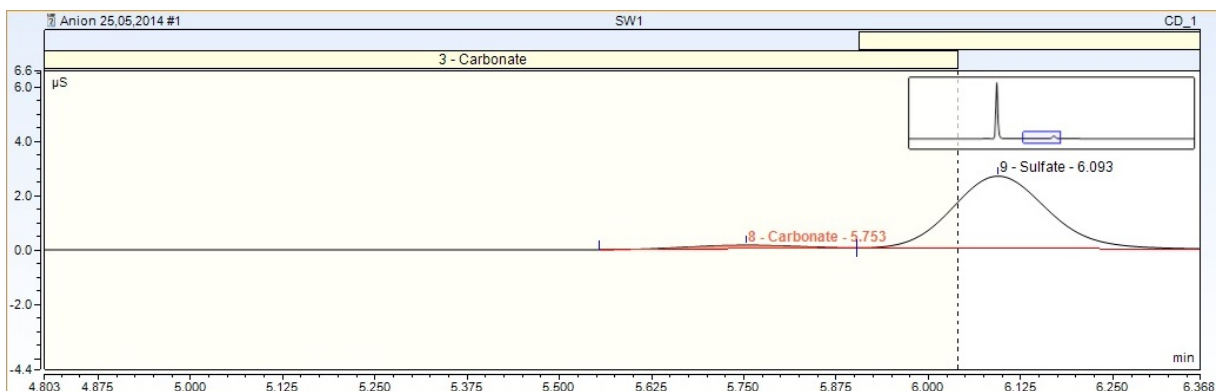


Figure B2 – Example for Carbonate Peak in IC Analysis

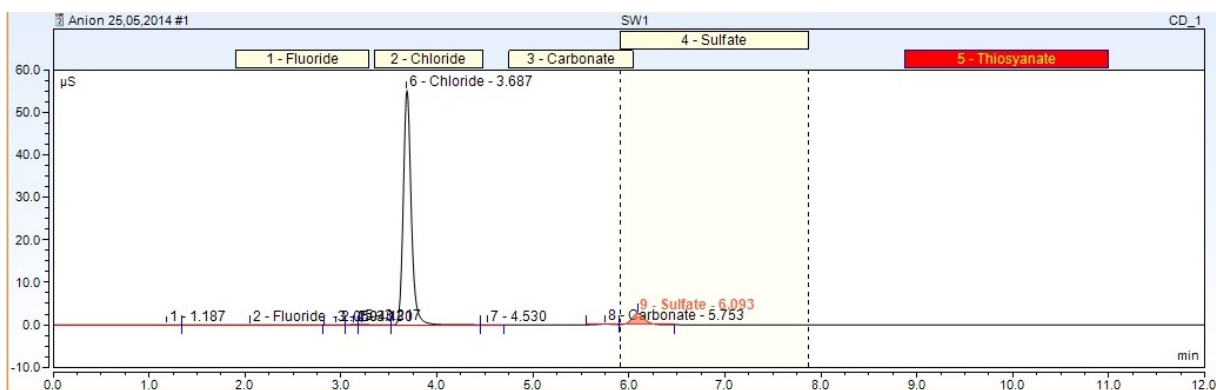


Figure B3 – Example for Sulfate Peak in IC Analysis

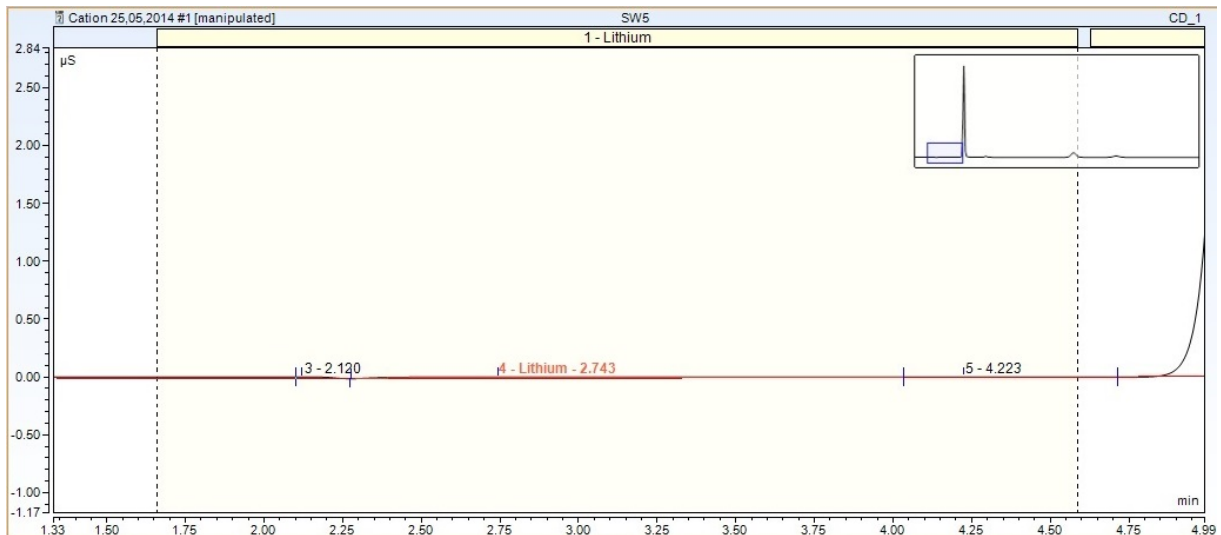


Figure B4 – Example for Lithium Peak in IC Analysis

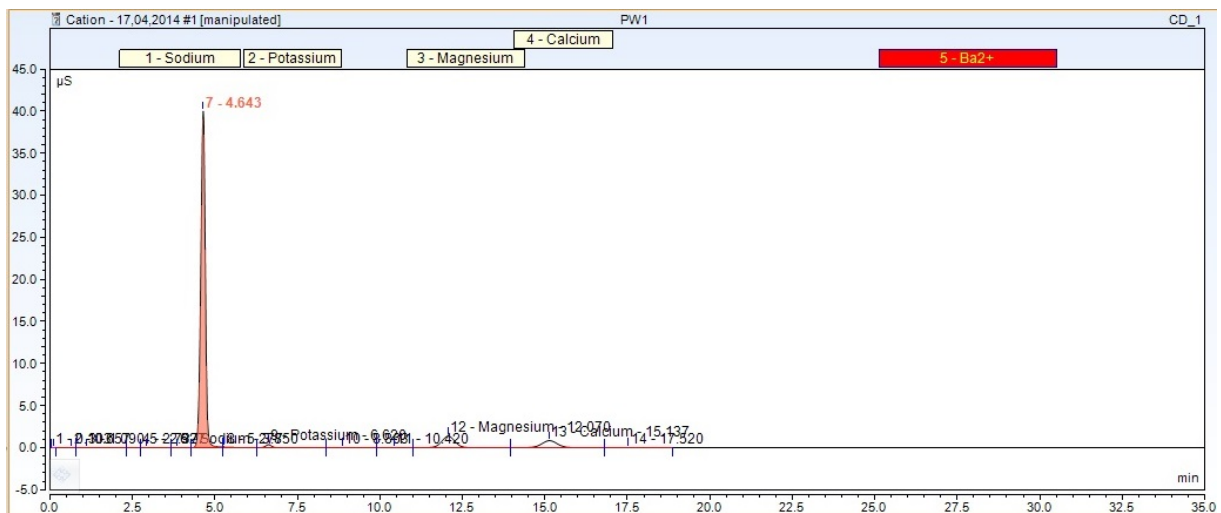


Figure B5 – Example for Sodium Peak in IC Analysis

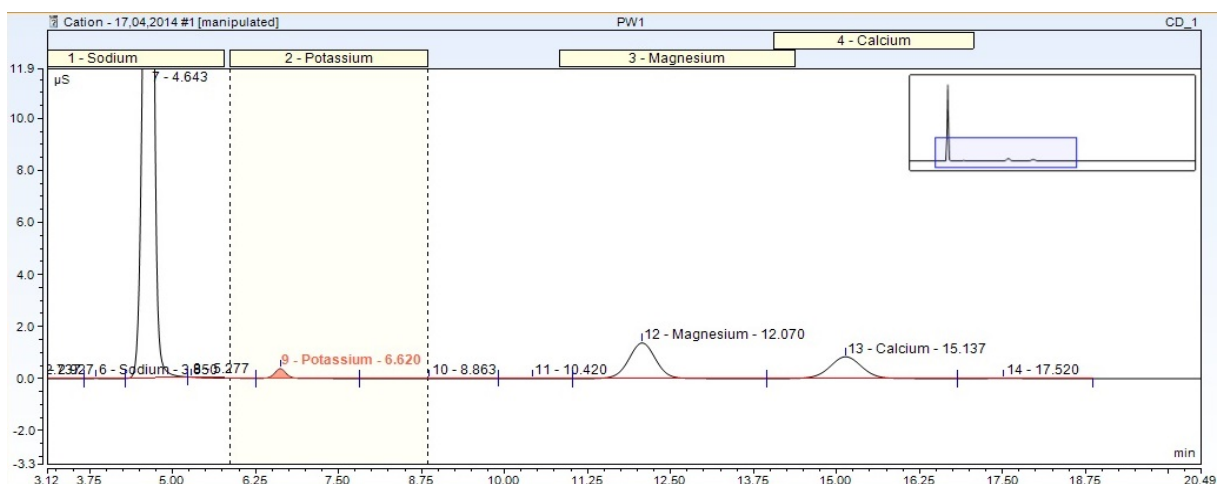


Figure B6 – Example for Potassium Peak in IC Analysis

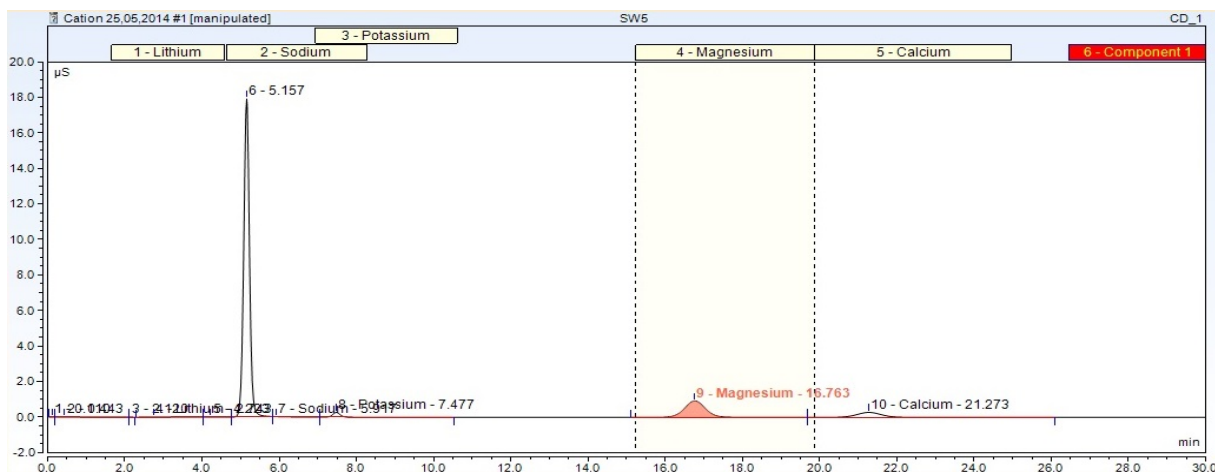


Figure B7 – Example for Magnesium Peak in IC Analysis

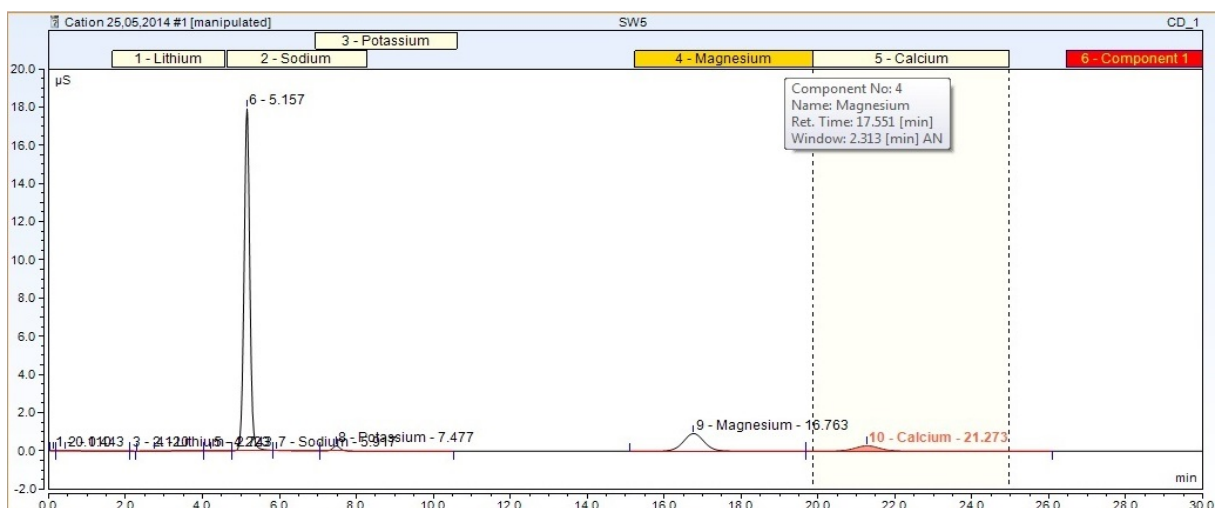


Figure B8 – Example for Calcium Peak in IC Analysis

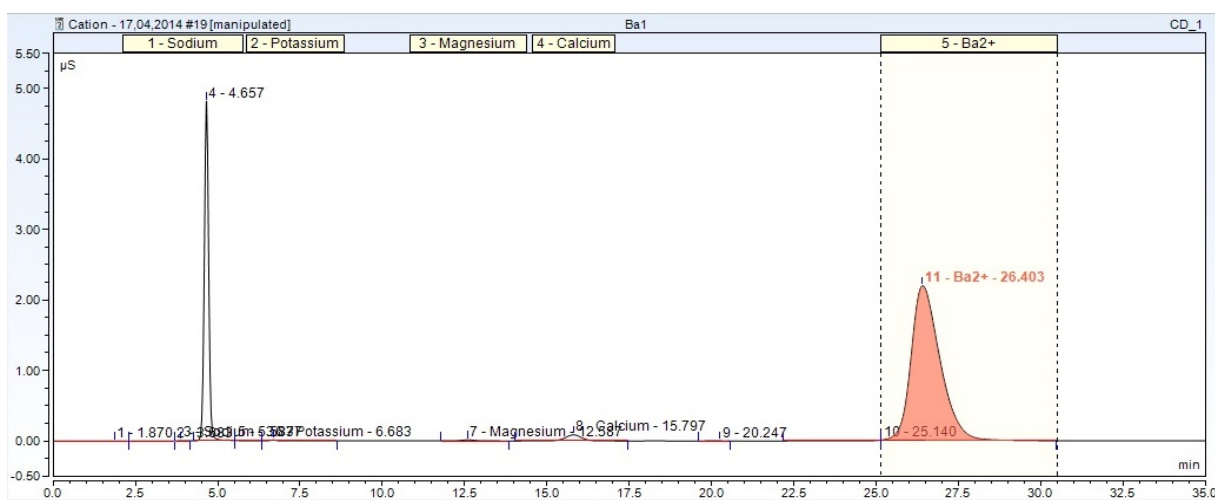


Figure B9 – Example for Barium Peak in IC Analysis

Appendix C

Laboratory result from Intertek West Lab



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Our ref: 2014-04846

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Page: 1 of 20

Your ref: Torleiv Bilstad

Laboratory Report

Objective: lone analysis
Sampling location: n/a
Sampled by: Universitetet i Stavanger
Received date: 20.jun.2014
Tested: June 2014

If you should have any questions to the report, please do not hesitate to contact us.

Regards
Intertek West Lab AS

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Laboratory Report

Sample marking 1
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-001

Parameter	Results	Unit	PQL		Method/standard	Uncertainty	
			Lower	Upper		Rel	Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K							
Sodium, Na	24700	mg/l	100	50000	I-1-29/ICP-OES	10%	±25
Calcium, Ca	1180	mg/l	5	35000	I-1-29/ICP-OES	10%	±5
Magnesium, Mg	1000	mg/l	0,1	3000	I-1-29/ICP-OES	10%	±0,1
Barium, Ba	4,50	mg/l	0,05	1500	I-1-29/ICP-OES	10%	±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15%	±0,2
Strontium, Sr	36,8	mg/l	0,05	1600	I-1-29/ICP-OES	10%	±0,1
Potassium, K	486	mg/l	10	26000	I-1-29/ICP-OES	15%	±10
Sulphur, S	1,4	mg/l	1	1100	I-1-29/ICP-OES	10%	±1
Chloride in water, titration							
Chloride, Cl-	42900	mg/l	1000	300000	Mod. NS 4758	10%	-

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 2
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-002

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	24300	mg/l	100	58000	I-1-29/ICP-OES	10% ±25
Calcium, Ca	899	mg/l	5	35000	I-1-29/ICP-OES	10% ±5
Magnesium, Mg	414	mg/l	0,1	3000	I-1-29/ICP-OES	10% ±0,1
Barium, Ba	2,76	mg/l	0,05	1500	I-1-29/ICP-OES	10% ±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15% ±0,2
Strontium, Sr	21,8	mg/l	0,05	1600	I-1-29/ICP-OES	10% ±0,1
Potassium, K	478	mg/l	10	28000	I-1-29/ICP-OES	15% ±10
Sulphur, S	<1	mg/l	1	1100	I-1-29/ICP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl-	39800	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 3
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-003

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	24100	mg/l	100	58000	I-1-29/ICP-OES	10% ±25
Calcium, Ca	870	mg/l	5	35000	I-1-29/ICP-OES	10% ±5
Magnesium, Mg	400	mg/l	0,1	3000	I-1-29/ICP-OES	10% ±0,1
Barium, Ba	2,74	mg/l	0,05	1500	I-1-29/ICP-OES	10% ±0,05
Iron, Fe	<0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15% ±0,2
Strontium, Sr	20,8	mg/l	0,05	1800	I-1-29/ICP-OES	10% ±0,1
Potassium, K	476	mg/l	10	28000	I-1-29/ICP-OES	15% ±10
Sulphur, S	<1	mg/l	1	1100	I-1-29/ICP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl-	39800	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 4
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-004

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	25100	mg/l	100	58000	I-1-29/ICP-OES	10% ±25
Calcium, Ca	1450	mg/l	5	35000	I-1-29/ICP-OES	10% ±5
Magnesium, Mg	1840	mg/l	0,1	3000	I-1-29/ICP-OES	10% ±0,1
Barium, Ba	6,28	mg/l	0,05	1500	I-1-29/ICP-OES	10% ±0,05
Iron, Fe	<0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15% ±0,2
Strontium, Sr	51,0	mg/l	0,05	1600	I-1-29/ICP-OES	10% ±0,1
Potassium, K	501	mg/l	10	26000	I-1-29/ICP-OES	15% ±10
Sulphur, S	2,1	mg/l	1	1100	I-1-29/ICP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl-	46100	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 5
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-005

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	25200	mg/l	100	58000	I-1-29//CP-OES	10% ±25
Calcium, Ca	1510	mg/l	5	35000	I-1-29//CP-OES	10% ±5
Magnesium, Mg	1930	mg/l	0,1	3000	I-1-29//CP-OES	10% ±0,1
Barium, Ba	6,42	mg/l	0,05	1500	I-1-29//CP-OES	10% ±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29//CP-OES	15% ±0,2
Strontium, Sr	52,5	mg/l	0,05	1600	I-1-29//CP-OES	10% ±0,1
Potassium, K	507	mg/l	10	28000	I-1-29//CP-OES	15% ±10
Sulphur, S	2,1	mg/l	1	1100	I-1-29//CP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl-	46300	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 6
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-006

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Barium, Ba	3,9	mg/l	0,002	10000	I-1-32	15% ±0,002
Calcium, Ca	9,9	mg/l	0,25	10000	I-1-32	15% ±0,2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20% ±0,01
Potassium, K	2,1	mg/l	0,15	200000	I-1-32	15% ±0,15
Magnesium, Mg	9,4	mg/l	0,01	5000	I-1-32	15% ±0,01
Sodium, Na	81	mg/l	0,2	200000	I-1-32	15% ±0,2
Sulphur, S	0,96	mg/l	0,035	20000	I-1-32	15% ±0,03
Strontium, Sr	0,28	mg/l	0,002	20000	I-1-32	20% ±0,002
Chloride in water, IC						
Chloride, Cl-	180	mg/l	1		ISO 10304-1	15% ±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 7
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-007

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Barium, Ba	2,4	mg/l	0,002	10000	I-1-32	15% ±0,002
Calcium, Ca	8,9	mg/l	0,25	10000	I-1-32	15% ±0,2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20% ±0,01
Potassium, K	2,3	mg/l	0,15	200000	I-1-32	15% ±0,15
Magnesium, Mg	7,7	mg/l	0,01	5000	I-1-32	15% ±0,01
Sodium, Na	87	mg/l	0,2	200000	I-1-32	15% ±0,2
Sulphur, S	0,0710	mg/l	0,035	20000	I-1-32	15% ±0,03
Strontium, Sr	0,22	mg/l	0,002	20000	I-1-32	20% ±0,002
Chloride in water, IC						
Chloride, Cl-	180	mg/l	1		ISO 10304-1	15% ±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 8
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-008

Parameter	Results	Unit	PQL		Method/standard	Uncertainty	
			Lower	Upper		Rel	Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K							
Barium, Ba	2,2	mg/l	0,002	10000	I-1-32	15%	±0,002
Calcium, Ca	7,4	mg/l	0,25	10000	I-1-32	15%	±0,2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20%	±0,01
Potassium, K	2,1	mg/l	0,15	200000	I-1-32	15%	±0,15
Magnesium, Mg	6,3	mg/l	0,01	5000	I-1-32	15%	±0,01
Sodium, Na	78	mg/l	0,2	200000	I-1-32	15%	±0,2
Sulphur, S	0,0850	mg/l	0,035	20000	I-1-32	15%	±0,03
Strontium, Sr	0,21	mg/l	0,002	20000	I-1-32	20%	±0,002
Chloride in water, IC							
Chloride, Cl-	160	mg/l	1		ISO 10304-1	15%	±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 9
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-009

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Barium, Ba	4,7	mg/l	0,002	10000	I-1-32	15% ±0,002
Calcium, Ca	14	mg/l	0,25	10000	I-1-32	15% ±0,2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20% ±0,01
Potassium, K	3,0	mg/l	0,15	200000	I-1-32	15% ±0,15
Magnesium, Mg	16	mg/l	0,01	5000	I-1-32	15% ±0,01
Sodium, Na	110	mg/l	0,2	200000	I-1-32	15% ±0,2
Sulphur, S	2,1	mg/l	0,035	20000	I-1-32	15% ±0,03
Strontium, Sr	0,44	mg/l	0,002	20000	I-1-32	20% ±0,002
Chloride in water, IC						
Chloride, Cl-	250	mg/l	1		ISO 10304-1	15% ±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 10
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-010

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Barium, Ba	5,2	mg/l	0,002	10000	I-1-32	15% ±0,002
Calcium, Ca	15	mg/l	0,25	10000	I-1-32	15% ±0,2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20% ±0,01
Potassium, K	3,2	mg/l	0,15	200000	I-1-32	15% ±0,15
Magnesium, Mg	16	mg/l	0,01	5000	I-1-32	15% ±0,01
Sodium, Na	110	mg/l	0,2	200000	I-1-32	15% ±0,2
Sulphur, S	2,2	mg/l	0,035	20000	I-1-32	15% ±0,03
Strontium, Sr	0,45	mg/l	0,002	20000	I-1-32	20% ±0,002
Chloride in water, IC						
Chloride, Cl-	250	mg/l	1		ISO 10304-1	15% ±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 11
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-011

Parameter	Results	Unit	PQL		Method/standard	Uncertainty	
			Lower	Upper		Rel	Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K							
Barium, Ba	0,008	mg/l	0,002	10000	I-1-32	15%	±0,002
Calcium, Ca	1,4	mg/l	0,25	10000	I-1-32	15%	±0,2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20%	±0,01
Potassium, K	<0,3	mg/l	0,15	200000	I-1-32	15%	±0,15
Magnesium, Mg	0,14	mg/l	0,01	5000	I-1-32	15%	±0,01
Sodium, Na	0,99	mg/l	0,2	200000	I-1-32	15%	±0,2
Sulphur, S	0,52	mg/l	0,035	20000	I-1-32	15%	±0,03
Strontium, Sr	0,008	mg/l	0,002	20000	I-1-32	20%	±0,002
Chloride in water, IC							
Chloride, Cl-	88	mg/l	1		ISO 10304-1	15%	±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 12
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-012

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Barium, Ba	<0,004	mg/l	0,002	10000	I-1-32	15% ±0,002
Calcium, Ca	0,97	mg/l	0,25	10000	I-1-32	15% ±0,2
Iron, Fe	0,0620	mg/l	0,01	100000	I-1-32	20% ±0,01
Potassium, K	<0,3	mg/l	0,15	200000	I-1-32	15% ±0,15
Magnesium, Mg	0,0980	mg/l	0,01	5000	I-1-32	15% ±0,01
Sodium, Na	2,8	mg/l	0,2	200000	I-1-32	15% ±0,2
Sulphur, S	4,9	mg/l	0,035	20000	I-1-32	15% ±0,03
Strontium, Sr	0,005	mg/l	0,002	20000	I-1-32	20% ±0,002
Chloride in water, IC						
Chloride, Cl-	380	mg/l	1		ISO 10304-1	15% ±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking 13
Sampled Date 19.jun.2014
Sample type Process water

Results for sample 2014-04846-013

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Barium, Ba	150	mg/l	0,002	10000	I-1-32	15% ±0.002
Calcium, Ca	38	mg/l	0,25	10000	I-1-32	15% ±0.2
Iron, Fe	<0,02	mg/l	0,01	100000	I-1-32	20% ±0.01
Potassium, K	<0,3	mg/l	0,15	200000	I-1-32	15% ±0.15
Magnesium, Mg	0,17	mg/l	0,01	5000	I-1-32	15% ±0.01
Sodium, Na	0,58	mg/l	0,2	200000	I-1-32	15% ±0.2
Sulphur, S	<0,07	mg/l	0,035	20000	I-1-32	15% ±0.03
Strontium, Sr	0,043	mg/l	0,002	20000	I-1-32	20% ±0.002
Chloride in water, IC						
Chloride, Cl-	80	mg/l	1		ISO 10304-1	15% ±1

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking A
Sampled Date 24.jun.2014
Sample type Process water

Results for sample 2014-04846-014

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	25000	mg/l	100	58000	I-1-29/ICP-OES	10% ±25
Calcium, Ca	1420	mg/l	5	36000	I-1-29/ICP-OES	10% ±5
Magnesium, Mg	1770	mg/l	0,1	3000	I-1-29/ICP-OES	10% ±0,1
Barium, Ba	8,05	mg/l	0,05	1500	I-1-29/ICP-OES	10% ±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15% ±0,2
Strontium, Sr	50,7	mg/l	0,05	1800	I-1-29/ICP-OES	10% ±0,1
Potassium, K	495	mg/l	10	28000	I-1-29/ICP-OES	15% ±10
Sulphur, S	2,1	mg/l	1	1100	I-1-29/ICP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl ⁻	45800	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking B
Sampled Date 24.jun.2014
Sample type Process water

Results for sample 2014-04846-015

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	25000	mg/l	100	50000	I-1-29/ICP-OES	10% ±25
Calcium, Ca	1460	mg/l	5	35000	I-1-29/ICP-OES	10% ±5
Magnesium, Mg	1840	mg/l	0,1	3000	I-1-29/ICP-OES	10% ±0,1
Barium, Ba	6,20	mg/l	0,05	1500	I-1-29/ICP-OES	10% ±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15% ±0,2
Strontium, Sr	50,8	mg/l	0,05	1600	I-1-29/ICP-OES	10% ±0,1
Potassium, K	494	mg/l	10	26000	I-1-29/ICP-OES	15% ±10
Sulphur, S	2,0	mg/l	1	1100	I-1-29/ICP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl-	46200	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking C
Sampled Date 24.jun.2014
Sample type Process water

Results for sample 2014-04846-016

Parameter	Results	Unit	PQL		Method/standard	Uncertainty
			Lower	Upper		Rel Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K						
Sodium, Na	25100	mg/l	100	56000	I-1-29/ICP-OES	10% ±25
Calcium, Ca	1480	mg/l	5	35000	I-1-29/ICP-OES	10% ±5
Magnesium, Mg	1890	mg/l	0,1	3000	I-1-29/ICP-OES	10% ±0,1
Barium, Ba	6,51	mg/l	0,05	1500	I-1-29/ICP-OES	10% ±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15% ±0,2
Strontium, Sr	54,0	mg/l	0,05	1600	I-1-29/ICP-OES	10% ±0,1
Potassium, K	498	mg/l	10	26000	I-1-29/ICP-OES	15% ±10
Sulphur, S	2,1	mg/l	1	1100	I-1-29/ICP-OES	10% ±1
Chloride in water, titration						
Chloride, Cl-	46500	mg/l	1000	300000	Mod. NS 4756	10% -

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking D
Sampled Date 24.jun.2014
Sample type Process water

Results for sample 2014-04846-017

Parameter	Results	Unit	PQL		Method/standard	Uncertainty	
			Lower	Upper		Rel	Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K							
Sodium, Na	24300	mg/l	100	56000	I-1-29/ICP-OES	10%	±25
Calcium, Ca	895	mg/l	5	35000	I-1-29/ICP-OES	10%	±5
Magnesium, Mg	415	mg/l	0,1	3000	I-1-29/ICP-OES	10%	±0,1
Barium, Ba	2,79	mg/l	0,05	1500	I-1-29/ICP-OES	10%	±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15%	±0,2
Strontium, Sr	21,8	mg/l	0,05	1600	I-1-29/ICP-OES	10%	±0,1
Potassium, K	477	mg/l	10	26000	I-1-29/ICP-OES	15%	±10
Sulphur, S	<1	mg/l	1	1100	I-1-29/ICP-OES	10%	±1
Chloride in water, titration							
Chloride, Cl-	39900	mg/l	1000	300000	Mod. NS 4756	10%	-

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking E
Sampled Date 24.jun.2014
Sample type Process water

Results for sample 2014-04846-018

Parameter	Results	Unit	PQL		Method/standard	Uncertainty	
			Lower	Upper		Rel	Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K							
Sodium, Na	24300	mg/l	100	58000	I-1-29/ICP-OES	10%	±25
Calcium, Ca	895	mg/l	5	35000	I-1-29/ICP-OES	10%	±5
Magnesium, Mg	407	mg/l	0,1	3000	I-1-29/ICP-OES	10%	±0,1
Barium, Ba	2,85	mg/l	0,05	1500	I-1-29/ICP-OES	10%	±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15%	±0,2
Strontium, Sr	21,3	mg/l	0,05	1800	I-1-29/ICP-OES	10%	±0,1
Potassium, K	472	mg/l	10	28000	I-1-29/ICP-OES	15%	±10
Sulphur, S	<1	mg/l	1	1100	I-1-29/ICP-OES	10%	±1
Chloride in water, titration							
Chloride, Cl-	40100	mg/l	1000	300000	Mod. NS 4756	10%	-

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.



Laboratory Report

Sample marking F
Sampled Date 24.jun.2014
Sample type Process water

Results for sample 2014-04846-019

Parameter	Results	Unit	PQL		Method/standard	Uncertainty	
			Lower	Upper		Rel	Abs
7-ion, Na,Ca,Mg,Ba,Fe,Sr,K							
Sodium, Na	24200	mg/l	100	56000	I-1-29/ICP-OES	10%	±25
Calcium, Ca	892	mg/l	5	35000	I-1-29/ICP-OES	10%	±5
Magnesium, Mg	406	mg/l	0,1	3000	I-1-29/ICP-OES	10%	±0,1
Barium, Ba	2,69	mg/l	0,05	1500	I-1-29/ICP-OES	10%	±0,05
Iron, Fe	0,1	mg/l	0,1	2000	I-1-29/ICP-OES	15%	±0,2
Strontium, Sr	21,1	mg/l	0,05	1600	I-1-29/ICP-OES	10%	±0,1
Potassium, K	477	mg/l	10	26000	I-1-29/ICP-OES	15%	±10
Sulphur, S	<1	mg/l	1	1100	I-1-29/ICP-OES	10%	±1
Chloride in water, titration							
Chloride, Cl-	39700	mg/l	1000	300000	Mod. NS 4756	10%	-

Explanation: PQL = Practical Quantification limit. # = The analysis is performed by sub contractor.

The uncertainty is expressed at 95% confidence level. If both a relative and an absolute uncertainty argument is stated, it is the argument that represents the highest uncertainty that applies.

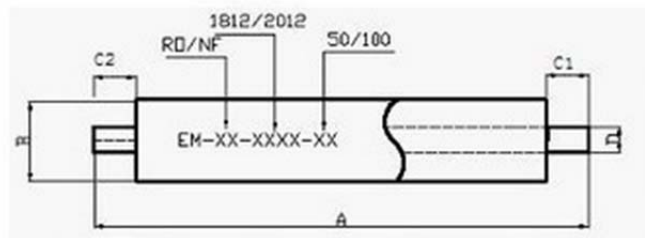
Appendix D

Product Specification of EM-NF-1812-50 and NANO-BW-4040 Membrane

Product Description						
Item specification:						
Brand Name: E-MEM						
Model No: EM-NF-1812-50GPD						
NF membrane						
Good replacement for DOW/CSM residential membrane						
Salt rejection: >=40%						
MgSO ₄ : >=93%						
Produced water: :50GPD						
Application:						
a. Apply to water purifier/NF systems						
b. Suitable for small systems of various household pure water machine, hospital, laboratory pure water device etc.						
Features:						
1. Innovative membrane design						
2. Less fouling						
3. More consistent						
4. Less frequency cleaning						
5. Reduce energy use						
6. Lower consumption of chemical and longer life						
Operation Ratings:						
Max. Working Pressure: 300psi(2.07Mpa)						
Max. Feed water Temperature: 45C						
Max. Feed water SDI: 5						
Free Chlorine Concentration of Feed water: <0.1ppm						
pH Range of Feed water during Continuous Operation: 3~10						
pH Range of Feed water during Chemical Cleaning: 2~12						
Max. Pressure Drop of Single Membrane Element: 10psi(0.07Mpa)						
Membrane size			EM-NF-1812-50	EM-NF-2012-100	EM-RO-1812-50	EM-RO-2012-75
Area	ft ²		4.4	6.0	4.4	5.0
	m ²		0.41	0.56	0.41	0.46
performance (%)	rejection	stable	≥40/93	≥40/93	97.5	97.5
		min	35/90	35/90	95.0	95.0
	flux	m ³ /d	0.19	0.38	0.19	0.28
		GPD	50	100	50	75
testing condition	feed concentration		250ppm NaCl/250ppm MgSO ₄		250ppm NaCl	
	temperature (°C)			25±1		
	feed pH			7.5±0.5		
	recovery (%)			8±1		
	pressure (MPa)		0.21		0.41	
	max pressure (psi/MPa)			300/2.07		
	max temperature (°C)			45		
	max feed SDI ₁₅			5		
extreme operation condition	max feed flow					
	gpm (lpm)			2.0 (7.6)		
	max single membrane pressure drop (psi/MPa)			10/0.07		
	feed chlorine (ppm)			<0.1		
	feed pH range			3~10		
	cleaning pH range			2~12		

is_customized: Yes
Purifying Position: Terminal Purification
Brand Name: E-MEM
Use: Household Pre-Filtration
Power (W): 0
Water treatment machine Type: Water Purifier
Voltage (V): 0
Color: Blue
Material: Nanofiltration
Certification: CE,NSF
Function: Indirect Drink
Model Number: EM-NF-1812-50
Type: RO membrane
Salt rejection(NaCl): >40%
Salt rejection(MgSo4): >93%
Produced water: 50GPD
Membrane area: 4.4ft2
length: 12"
diameter: 1.8"

Size:



E-MEM®	EM-NF-1812-50	EM-NF-2012-100	EM-RO-1812-50	EM-RO-2012-75	EM-RO-2012-100	EM-RO-2812-150	EM-RO-2812-200	EM-RO-3012-300	EM-RO-3012-400
A(±2.0mm)	298	298	298	298	298	298	298	298	298
B(±1.0mm)	44.5	48.0	44.5	48.0	48.0	71.0	71.0	76.0	76.0
C1(±1.0mm)	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
C2(±1.0mm)	22.0	12.0	22.0	12.0	12.0	12.0	12.0	12.0	12.0
D(±0.1mm)	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0

Source: http://www.e-mem.cn/en/pro_detail.asp?id=78

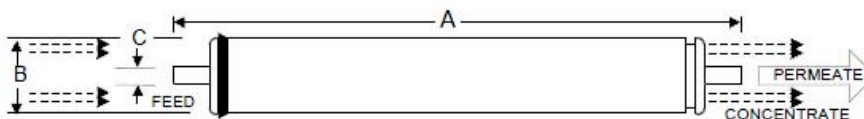


Membrane Element		NANO-BW-4040
Performance:	MgSO₄ Permeate Flow (Nominal): MgSO ₄ Rejection (Nominal):	2000 gpd (7.6 m ³ /d) 99.7% (99.5% minimum)
Type	Configuration: Membrane Polymer: Nominal Membrane Area: Feed/Brine Spacer Thickness:	Spiral Wound Composite Polyamide 75 ft ² (7 m ²) 34 mil (0.87 mm)
Application Data*	Maximum Applied Pressure: Maximum Chlorine Concentration: Maximum Operating Temperature: pH Range, Operation (Cleaning): Maximum Feedwater Turbidity: Maximum Feedwater SDI (15 mins): Maximum Feed Flow: Minimum Ratio of Concentrate to Permeate Flow for any Element: Maximum Pressure Drop for Each Element:	600 psig (4.1 MPa) < 0.1 PPM 113 °F (45 °C) 3.0 - 9.0 (1.0 - 11.5) 1.0 NTU 5.0 16 GPM (3.6 m ³ /h) 5:1 10 psi

** The limitations shown here are for general use. For specific projects, operating at more conservative values may ensure the best performance and longest life of the membranes. See Hydranautics Technical Bulletins for more detail on operation limits, cleaning pH, and cleaning temperatures.

Test Conditions The stated performance is based on the following test conditions:

2000 ppm MgSO₄
130 psi (0.9 MPa) Applied Pressure
77 °F (25 °C) Operating Temperature
15% Permeate Recovery
6.5 - 7.0 Feed pH



A, inches (mm)	B, inches (mm)	C, inches (mm)	Weight, lbs. (kg)
40.00 (1016)	3.95 (100.3)	0.75 (19.1)	8 (3.6)

Notice: Permeate flow for individual elements may vary + or - 20 percent. All membrane elements are supplied with a brine seal, interconnector, and o-rings. All membrane elements are supplied with a brine seal, interconnector, and o-rings. Elements are vacuum sealed in a polyethylene bag containing less and then packaged in a cardboard box.

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12/15/10

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Appendix E

Table E1 – Characteristic of 4 Main Types of Membrane
(AWWA, 2007; Cheryan, 1998; Schafer et al., 2005)

	RO	NF	UF	MF
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical Asymmetrical
Driving force	Pressure	Pressure	Pressure	Pressure
Thin film thickness	150 µm 1 µm	150 µm 1 µm	150 - 250 µm 1 µm	10 - 150 µm
Pore size	<0.002 µm	<0.002 µm	0.2 - 02 µm	4 - 0.02 µm
Concentrate	HMWC, LMWC sodium chloride glucose amino acids	HMWC mono- di- and oligosaccharides polyvalent negatives ions	Macro molecules, proteins, polysaccharides, virus	Suspended articles, clay, bacteria
Permeate	Water	Monovalent ions, undissociated acids, water	Small molecules, water	Dissolved solutes, water
Membrane Material(s)	CA Thin Film	CA Thin film	Ceramic PSO, PVDF, CA, Thin film	Ceramic PP, PSO, PVDF
Membrane Module	Tubular, spiral wound, plate-and-frame	Tubular, spiral wound, plate-and-frame	Tubular, hollow fiber, spiral wound, plate-and-frame	Tubular, hollow fiber
Operating Pressure (bar)	15 - 150	5 - 35	1 - 10	<2
Example of usage	Dyeing effluent, desalination	Antibiotics, softening	Milk, biogas waste	

Table E2 – Characteristics of Different Module (Cheryan, 1998; Schafer et al., 2005; Wagner, 2001)

Characteristics	Plate & Frame	Spiral – Wound	Tubular	Hollow Fibre
Packing density (m ² /m ³)	Moderate (200 - 500)	High (500 - 1000)	Low-Moderate (70 - 400)	High (500 - 5000)
Energy Usage	Low-Moderate (laminar)	Moderate (Spacer-losses)	High (Turbulent)	Low (Laminar)
Fouling tendency	Average	Average	Low	Low – High
Standardization	No	Yes	No	No
Plant investment	High	Low	Low – high	Medium
Replacement	Sheet (or Cartridge)	Element	Tubes (or Element)	Element
Cleaning	Moderate	Can be difficult (solids)	Good - Physical clean possible	Backflush Possible
Ease of Manufacture	Simple	Complex (automated)	Simple	Moderate
Limitations for NF	Pressure Containment	None	None	Burst pressure of fibres

Transport equations

$$j_i = -K_{i,d} D_i \frac{d\bar{c}_i}{dx} - \frac{z_i \bar{c}_i K_{i,d} D_i F}{RT} \frac{d\psi}{dx} + K_{i,c} \bar{c}_i V \quad (1)$$

with

$$K_{i,d} = \frac{6\pi r}{K_{i,z}} \quad (2)$$

$$K_{i,c} = \frac{(2 - \phi_1) K_{i,z}}{2K_{i,z}} \quad (3)$$

$$K_{i,z} = \frac{9}{4} \pi^2 \sqrt{2} (1 - \lambda_1)^{-5/2} \left[1 + \sum_{n=1}^2 a_n (1 - \lambda_1)^n \right] + \sum_{n=0}^4 c_{n+3} \lambda_1^n \quad (4)$$

$$K_{i,z} = \frac{9}{4} \pi^2 \sqrt{2} (1 - \lambda_1)^{-5/2} \left[1 + \sum_{n=1}^2 b_n (1 - \lambda_1)^n \right] + \sum_{n=0}^4 b_{n+3} \lambda_1^n \quad (5)$$

$$\phi_1 = (1 - \lambda_1)^2 \quad (\text{cylindrical pores}) \quad (6)$$

$$\lambda_1 = r_{1,Stokes} / r_p \quad (7)$$

$a_1 = -73/60, a_2 = 77.293/50.400, a_3 = -22.5083, a_4 = -5.6117, a_5 = -0.3363,$
 $a_6 = -1.216, a_7 = 1.647, b_1 = 7/60, b_2 = -2.227/50.400, b_3 = 4.0180, b_4 = -3.9788,$
 $b_5 = -1.9215, b_6 = 4.392, b_7 = 5.006.$

Figure E1 – Detailed equation on extended Nerst-Planck Equation (Szymczyk, 2009)