



University of  
Stavanger

**Faculty of Science and Technology**

**MASTER'S THESIS**

Study program/ Specialization: <b>Environmental Technology, Offshore Environmental Engineering</b>	Spring semester, 2014  Not-Restricted access
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Thesis title: <b>Smart Water for EOR by Membranes</b>	
Credits (ECTS): 30	
Key words: <b>EOR Nanofiltration Reverse Osmosis Seawater Smart Water</b>	Pages: .....132.....  + Enclosure: .....  Stavanger, 25/06/2014

# **SMART WATER FOR EOR BY MEMBRANES**

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**June 2014**



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University of  
Stavanger

i

## Acknowledgement

I would like to express my gratitude to my supervisor, Professor Torleiv Bilstad for his valuable supervision and giving me this opportunity to work under his guidance. I highly appreciate him as an inspiring and friendly supervisor who always keeps the door open.

I would like to thank Evgenia Protasova, for her guidance and in helping me on every stage of my experiments and suggesting corrections to my report.

I am grateful to Odd Henning Sirnes and Tom Sirnes, Membraneteknikk AS, Flekkefjord, for giving me the opportunity to work with them. My sincere appreciations to Odd Henning Sirnes, for his advice and valuable inputs to my thesis.

I would like to thank Professor Tor Austad, Dr. Skule Strand, and Dr. Tina Pundervold, from the Department of Petroleum Engineering for their support, guidance and valuable inputs through timely meetings for discussion about the project. My sincere thanks to the Ph.D. students in Department of Petroleum Engineering, who helped me with my experiments.

Special thanks to Liv Margaret Aksland for the help and guidance with the experiments in the laboratory and all staffs at the University of Stavanger for their great assistance during the Master Program.

I am also thankful to Kjerstin J. Saltveit, who did her bachelor thesis parallel to my experiment and to my friends for their great support during the course of this thesis.

Finally, I am grateful to my loving parents, my husband and kids for their understanding and great support during the course of my study.

## Abstract

*Design of smart water for carbonate reservoir, using membrane process is the focus of the thesis. The desirable characteristics of smart water is low salinity or low NaCl concentrations while retaining divalent ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  for improving the wettability. Experimental setup of the project consists of a Nanofiltration (NF) and a Reverse Osmosis (RO) membrane system for ion separation.*

*The retentate from NF is selected as the main constituent of the smart water due to the property of NF to retain the divalent ions. The results of the selected NF membrane show retention of 99 % of  $\text{SO}_4^{2-}$ , 61 % of  $\text{Mg}^{2+}$ , 31 % of  $\text{Ca}^{2+}$ , 9 % of  $\text{Na}^+$  and 7 % of  $\text{Cl}^-$  at a feed flow rate of 145 L/h.*

*A sensitivity test by spiking  $\text{Na}_2\text{SO}_4$  in the feed seawater has shown interesting results of decrease in retention of  $\text{Cl}^-$  with an increase of sulphate concentration. The results also show a reduction in permeate flux as the concentration of  $\text{Na}_2\text{SO}_4$  increases.*

*The RO experiments have produced permeate with TDS level as low as 1620 ppm from the filtered seawater having a TDS level of 30200 ppm. The comparison of NF and RO experiments has confirmed the selectivity of NF to retain divalent ions at a low operating pressure for NF.*

*The challenge in producing the smart water requirements is the high TDS left in the retentate by NF. In order to overcome this, three options to dilute the retentate is evaluated in the thesis. The options under consideration are combinations of NF with RO, MSFD (Multi-stage flash distillation) and fresh water. The dilution ratio depends on the tolerable limit of total TDS for smart water and at the same time, retaining the divalent ions in the retentate.*

*Mixing of NF retentate with fresh water ( $0.43 \text{ kWh/m}^3$ ) emerges as the optimal option in terms of minimum energy consumption for smart water production. However, due to the constraints on availability of fresh water and its socio-environmental impact, the combination process of NF and RO ( $3.84 \text{ kW h/m}^3$ ) is proposed as the viable process for producing smart water. This option has the benefit of less environmental impact by reduced energy consumption and no chemical addition.*

**Keywords:** EOR, Nanofiltration, Reverse Osmosis, Seawater, Smart water

## Table of Contents

Acknowledgement.....	ii
Abstract .....	iii
List of Figures .....	iv
List of Tables.....	vi
Abbreviations .....	viii
Nomenclature .....	ix
Chapter 1: Introduction .....	1
1.1    Types of Oil Recovery from Reservoirs.....	2
1.2    EOR Methods .....	4
1.3    Smart Water.....	5
1.3.1    Principle of Smart Water Functionality.....	7
1.3.2    Advantages of Smart Water.....	7
1.4    Objective .....	8
Chapter 2: Theoretical Background.....	9
2.1    Carbonate Reservoirs.....	10
2.1.1    Wettability .....	11
2.1.2    Factors Affecting Wettability .....	12
2.2    Seawater .....	13
2.2.1    Salinity.....	13
2.2.2    Temperature.....	15
2.2.3    Density.....	15
2.2.4    pH .....	15
2.2.5    Conductivity .....	15
2.3    Smart Water Constituents.....	16
2.3.1    Desirable Ionic Composition .....	17
2.3.2    Suggested Mechanism for Wettability Alteration .....	18
2.4    Membrane Separation.....	19
2.4.1    Molecular Weight Cut off (MWCO) .....	21
2.4.2    Membrane Structure .....	22
2.4.3    Membrane Materials.....	23
2.4.4    Membrane Configuration .....	26

2.4.5	Advantages of Membranes over Other Conventional Methods .....	28
2.4.6	Disadvantages of membranes .....	28
2.5	Nanofiltration (NF) Membrane .....	28
2.5.1	Applications of NF Membranes .....	29
2.5.2	Separation Mechanism of NF Membranes .....	30
2.5.3	Membrane Performance .....	33
2.5.4	Parameters Affecting the Performance of NF Membranes.....	34
2.5.5	Advantages of NF Membranes over RO .....	35
2.5.6	Industrial Application of NF Membranes.....	36
2.6	Reverse Osmosis (RO) Membrane .....	36
Chapter 3: Materials and Methods .....		37
3.1	Determination of Total Suspended Solids (TSS) .....	38
3.2	Turbidity.....	38
3.3	Membranes for Separation .....	40
3.3.1	Nanofiltration Membrane (NANO - BW -4040).....	41
3.3.2	Reverse Osmosis Membrane (FILMTEC SW 30- 2540) .....	45
3.4	Calculation of Parameters.....	48
3.5	Analytical Methods for Seawater Characterization.....	48
3.5.1	pH.....	48
3.5.2	Total Salinity and Conductivity Measurement.....	48
3.5.3	Ion Chromatography for Ion Determination.....	49
3.6	Chemicals Used for Sample Preparation .....	50
3.6.1	Synthetic seawater .....	50
3.6.2	Addition of Na <sub>2</sub> SO <sub>4</sub> .....	51
Chapter 4: Results and Discussion .....		52
4.1	Feed Properties .....	53
4.2	Feed Properties of Na <sub>2</sub> SO <sub>4</sub> Sensitivity Experiments .....	53
4.3	Nanofiltration Experiments .....	54
4.3.1	Performance Parameters with Normal Seawater as Feed .....	54
4.3.2	Effect of Feed Ion Concentration on Membrane Properties.....	65
4.3.3	Summary of NF Experiment Analysis.....	77
4.4	Reverse Osmosis (RO) Membrane Experiments.....	77
4.4.1	Experiment Results.....	77
4.5	Comparison between NF and RO.....	83

4.5.1	Effect on Flux .....	84
4.5.2	Effect on TDS.....	85
4.5.3	Membrane Ion Rejection Comparison.....	85
4.6	Smart Water Formulation .....	87
Chapter 5: Economic Analysis of Smart Water Production Options .....		89
5.1	Smart Water Option 1: NF Retentate + RO Permeate.....	90
5.2	Smart Water Option 2: NF Retentate+ Fresh Water.....	92
5.3	Smart Water Option 3: NF + MSFD (Multi Stage Flash Distillation) .....	93
5.4	Energy Consumption .....	94
Chapter 6: Conclusions and Recommendations .....		98
References .....		101
Appendices .....		105
Appendix 1: Analysis of Total suspended solids (TSS) .....		105
Appendix 2 : Membrane Specification for Nano-BW-4040.....		106
Appendix 3: Mass balance for characterisation of samples from Nano- BW-4040 ..		107
Appendix 4: Mass balance for each ion from chromatographic results.....		108
Appendix 5: Mass balance for characterisation of 2* SO <sub>4</sub> <sup>2-</sup> samples .....		111
Appendix 6: Mass balance for characterisation of 3*SO <sub>4</sub> <sup>2-</sup> .....		112
Appendix 7: Chromatography results .....		113
Appendix 8: Mass balance for RO experiments .....		<b>118</b>
Appendix 9: Dilution Machine .....		119

## List of Figures

Figure 1: Types of oil recovery.....	4
Figure 2: Oil recovery mechanism .....	5
Figure 3: Low salinity effect in carbonate reservoir.....	6
Figure 4: Ocean surface salinity .....	14
Figure 5: Effect of low salinity water on oil – wet reservoir.....	18
Figure 6: Model of wettability alteration induced by SW in carbonate reservoirs.....	19
Figure 7: Schematic of a membrane process .....	20
Figure 8: Membrane processes performance.....	21
Figure 9: Comparison of the performance of CA and polyamide membrane.....	25
Figure 10: Spiral wound membrane.....	27
Figure 11: Nanofiltration technology .....	29
Figure 12: Molecular sieving and solution diffusion occurring in a membrane.....	31
Figure 13: HACH 2100N Turbidimeter.....	39
Figure 14: Turbidimeter using the scattered light method.....	40
Figure 15: Stages in membrane analysis.....	40
Figure 16: Experimental setup at Membraneteknikk AS, Flekkefjord.....	42
Figure 17: Process flow sheet of Nano- BW- 4040 .....	43
Figure 18: Filmtec SW- 30-2540 membrane .....	46
Figure 19: Experimental setup for Filmtec 30 - 2540.....	47
Figure 20: Schematic of experimental setup for Filmtec SW 30-2540 .....	47
Figure 21: Ion chromatography machine.....	49
Figure 22: Pressure vs Flux for Nano – BW- 4040 .....	58
Figure 23: Flow rate vs Pressure for SW with no spiking of sulphate .....	59
Figure 24: TDS vs Permeate flow rate and Recovery.....	60
Figure 25: Pressure and recovery vs Rejection of Nano- BW- 4040.....	62
Figure 26: Permeate flow rate vs Rejection for 2* SO <sub>4</sub> <sup>2-</sup> .....	72
Figure 27: Permeate flow rate vs Rejection for 3* SO <sub>4</sub> <sup>2-</sup> .....	72
Figure 28: Rejection of Cl <sup>-</sup> ions in normal, 2 *SO <sub>4</sub> <sup>2-</sup> , 3* SO <sub>4</sub> <sup>2-</sup> seawater .....	73
Figure 29: Rejection of Na <sup>+</sup> ions in normal, 2*SO <sub>4</sub> <sup>2-</sup> , 3* SO <sub>4</sub> <sup>2-</sup> Seawater .....	74
Figure 30: Pressure vs Permeate flow rate for 3 cases.....	75
Figure 31: Flux change vs SO <sub>4</sub> <sup>2-</sup> concentration change .....	75
Figure 32: Permeate flow rate vs TDS of three samples .....	76



Figure 33: Pressure vs Flux for Filmtec SW 30 - 2540 .....	79
Figure 34: Pressure vs TDS from Filmtec SW 30 - 2540 .....	80
Figure 35: Pressure vs Membrane rejection for Filmtec SW- 30- 2540 .....	82
Figure 36: Flux vs Pressure for NF and RO .....	84
Figure 37: TDS vs permeate flow rate .....	85
Figure 38: Membrane ion rejection comparison .....	86
Figure 39: Combination of TDS of NF retentate and RO permeate .....	86
Figure 40: Different methods to reduce TDS .....	88
Figure 41: Proposed combination of NF and RO membrane .....	91
Figure 42: Power consumed by different combinations with NF .....	96
Figure 43: Specifications of NANO- BW- 4040 membrane .....	106
Figure 44: Anions (Cl-) present in feed seawater .....	113
Figure 45: Anions present in feed seawater ( $\text{SO}_4^{2-}$ ).....	114
Figure 46 : Cations present in feed seawater .....	114
Figure 47: Anions at 145L/hr for feed, $2*\text{SO}_4^{2-}$ and $3*\text{SO}_4^{2-}$ .....	116
Figure 48: Cations at 145L/ hr for feed, $2*\text{SO}_4^{2-}$ and $3*\text{SO}_4^{2-}$ .....	117
Figure 49: Dilution machine .....	119

## List of Tables

Table 1: Proportion of ions in seawater .....	13
Table 2: Stokes radius and hydration energy of ions .....	32
Table 3: NTU values for water turbidity.....	39
Table 4: Nano- BW- 4040 specifications.....	41
Table 5: Filmtec SW 30 2540 specifications .....	45
Table 6: Synthetic seawater composition .....	51
Table 7: Feed Characteristics.....	53
Table 8: Seawater spiked with Na <sub>2</sub> SO <sub>4</sub> .....	54
Table 9: Performance parameters from NF experiments .....	55
Table 10: Concentration of individual ions calculated using ion chromatography ....	57
Table 11: Pressure vs Membrane rejection for Nano- BW- 4040 .....	61
Table 12: Parameters affecting sulphate and chloride retention .....	63
Table 13: Performance parameters of addition of 2 *SO <sub>4</sub> <sup>2-</sup> on normal seawater.....	66
Table 14: Ion chromatography results with addition of 2*SO <sub>4</sub> <sup>2-</sup> in the feed.....	68
Table 15: Permeate flow vs Ion rejection for SW spiked with 2 *SO <sub>4</sub> <sup>2-</sup> .....	69
Table 16: Performance parameters with addition of 3*SO <sub>4</sub> <sup>2-</sup> in feed seawater .....	70
Table 17: Ion chromatography results with addition of 3*SO <sub>4</sub> <sup>2-</sup> in feed .....	71
Table 18: Rejection with addition of 3 times sulphate on seawater .....	71
Table 19: Performance data of Feed, Retentate and Permeate at varying pressure ....	78
Table 20: Composition of ions when SW 30- 2540 membrane is used.....	81
Table 21: Pressure Vs Membrane rejection for SW 30- 2540 .....	82
Table 22: Recovery of SW 30- 2540 .....	83
Table 23: TDS Balance for NF +RO .....	92
Table 24: Calculation of amount of fresh water required .....	93
Table 25: Calculation of amount of water from distillation .....	93
Table 26: Power consumption .....	95
Table 27: Analysis of Total suspended solids (TSS) .....	105
Table 28: Mass balance (TDS) of experiments with Nano- BW- 4040.....	107
Table 29: Mass balance for chloride .....	108
Table 30: Mass balance for sulphate.....	108
Table 31: Mass balance for sodium .....	109
Table 32: Mass balance for magnesium.....	109

Table 33: Mass balance for calcium .....	110
Table 34: Mass balance performed for 2*SO <sub>4</sub> <sup>2-</sup> spiked seawater .....	111
Table 35: Mass balance for 3 * SO <sub>4</sub> <sup>2-</sup> spiked seawater .....	112
Table 36: Mass balance for pressure change from RO experiments .....	118

## Abbreviations

BW	Brackish Water
CA	Cellulose acetate
CBR	Crude oil, Brine and the Rock
COBS	Crude Oil/Brine/Solid
EOR	Enhanced Oil Recovery
FILMTEC SW-30 2540	Filmtec's RO Module
FW	Fresh Water
GF	Glass microfiber Filter
IOR	Improved Oil Recovery
MF	Microfiltration
MSFD	Multi-Stage Flash Distillation
MW	Molecular Weight
MWCO	Molecular Weight Cut Off
NANO BW -4040	Hydranautics NF Module
NF	Nanofiltration
NTU	Nephelometric Turbidity Units
OOIP	Original Oil In Place
PA	Polyamide
RO	Reverse Osmosis
SW	Sea Water
TDS	Total Dissolved Solids
TEOR	Thermally Enhanced Oil Recovery
TFC	Thin Film Composite
TSS	Total Suspended Solids
UF	Ultra filtration

## Nomenclature

J	Membrane Flux, L/m <sup>2</sup> hr
Q <sub>f</sub>	Feed flow rate, L/hr
Q <sub>p</sub>	Permeate flow rate, L/hr
Q <sub>r</sub>	Retentate flow rate, L/hr
R <sub>obs</sub>	Membrane Rejection, %
T	Temperature, °C
η	Efficiency, %
D <sub>∞</sub>	Diffusion coefficient

# Chapter 1: Introduction

Reservoir rocks are mainly sedimentary. They are divided into sandstone, and carbonate reservoirs. The carbonate reservoirs, which are further divided into limestone, chalk and dolomite, are the most complex reservoirs to characterize and model. Economic significance of these reservoirs is enormous. More than 50 % of the world's remaining oil exists in carbonate reservoirs (Punternold, 2008).

The average oil recovery from carbonate reservoirs is generally lower than that of sandstone reservoirs since the carbonate rock is preferentially oil-wet and often highly fractured (Strand,et.al.2008).Therefore, the enhanced oil recovery potential of these reservoirs is high but is considered a great challenge.

The reservoir carries a multiphase mixture of crude oil, gas and formation water. The oil and gas part is made of mixture of various hydrocarbons and a chemical equilibrium between the *crude oil, brine and the rock (CBR)* have been established in the oil reservoir over millions of years. The distribution of oil and water in the porous system is linked to the wetting properties of the CBR-system; the contact between the rock surface and the fluids, oil and brine.

The terms *water wet, oil wet, and neutral wetting condition* are been used to represent the wetting characteristics. Oil recovery is much easier when the CBR-system is water wet. In many cases, the wetting condition for oil displacement is not ideal with the available source of injection water. The wetting condition can be improved by modifying the ionic composition of the injected fluid. The water flood or secondary recovery then becomes a tertiary oil recovery method.

## 1.1 Types of Oil Recovery from Reservoirs

Oil recovery refers to the process by which oil is extracted from the reservoir. Oil recovery is categorised as primary, secondary and tertiary recovery.

### i. Primary Recovery

Primary recovery uses the natural pressure of the reservoir to transport the oil to the surface. Many offshore reservoirs show significant drop-offs in production within a few years due to pressure reduction. Typical recovery factor for primary recovery is around 5-15 %.

ii. Secondary Recovery

With passage of time, the pressure will decrease resulting in diminished oil production. Secondary recovery methods are applied to maintain the reservoir pressure and displace hydrocarbons to the wellbore. The most common technique involves gas injection and water flooding.

Water flooding of the mature field is most common due to the following features:

- a) Water is easily available and inexpensive
- b) Relatively easy to inject and efficiently displaces oil
- c) Low operating cost

Secondary recovery is continued until the injected fluid is produced in considerable amount from the production wells and the oil production is no longer economical. The primary and secondary recovery in the reservoir produces about 15 - 40 % of the original oil in place (OOIP).

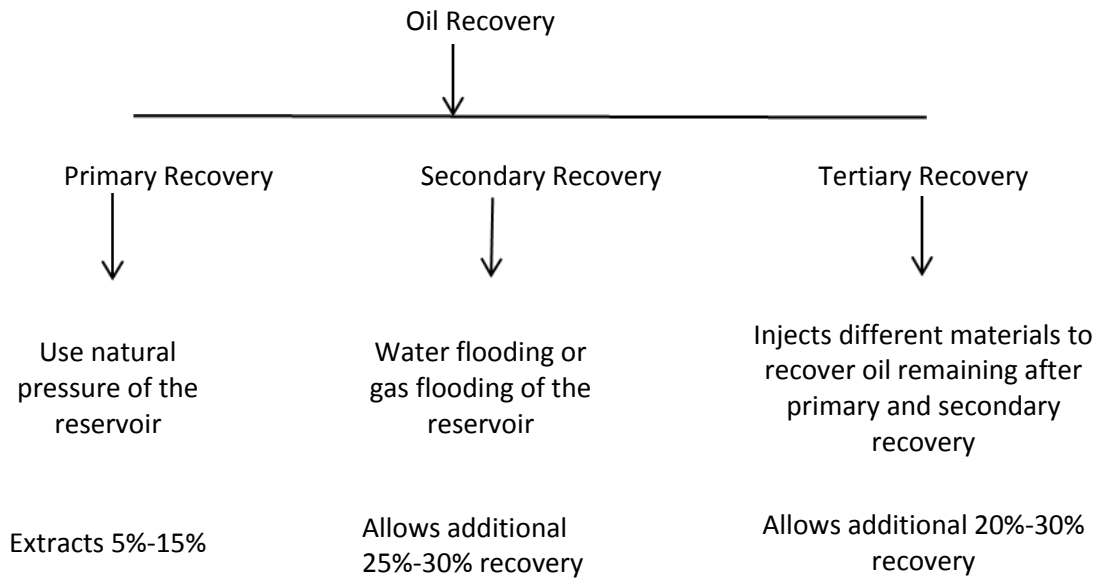
iii. Tertiary Recovery or Enhanced Oil Recovery

EOR technologies are introduced in oil production in order to mitigate the demand-supply balance. Primary and secondary recovery or conventional recovery targets mobile oil in the reservoir and tertiary recovery or EOR targets immobile oil, the oil that cannot be recovered due to capillary and viscous forces.

The implementation of EOR is closely related to the price of oil, general economics and government requirements. EOR is capital and supply intensive and is expensive mainly due to high injection costs. The timing of EOR is also an important factor. In some cases, advanced secondary recovery (improved oil recovery or IOR) technologies are better option than full-field deployment of EOR. In the case of smart water, it is preferred to inject from the beginning of a water flooding process.

The main difference of the different types of oil recovery is shown in **Figure 1**.





**Figure 1: Types of oil recovery**

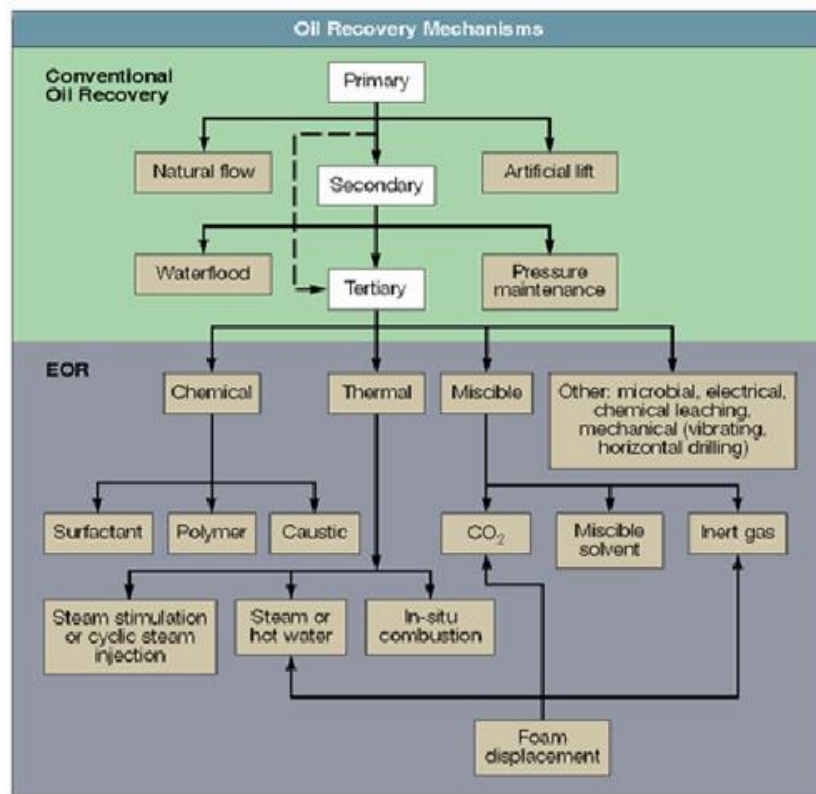
## 1.2 EOR Methods

EOR methods are classified by the main mechanism of oil displacement. The basic mechanisms for recovering oil from rock other than by water alone are:

- i. A reduction of oil viscosity
- ii. The extraction of the oil with a solvent
- iii. The modification of capillary and viscous forces between the oil, injected fluid and the rock surface

EOR methods are classified into following methods and are shown in **Figure 2:**

- Thermally enhanced oil recovery methods (TEOR)
- Miscible solvents injection methods
- CO<sub>2</sub> flooding
- Polymer flooding
- Microbial Injection
- Smart water



**Figure 2: Oil recovery mechanism**

(Petrosas, 2011)

### 1.3 Smart Water

*Smart water* injection for EOR is of considerable importance. Smart water is produced by adjusting the ionic composition of the injected seawater in such a way that the change in the equilibrium of the initial CBR-system modifies the initial wetting conditions. Therefore, the oil is easily displaced from the porous network (Austad, 2012). Ekofisk chalk reservoir in the Norwegian sector of the North Sea is a good example to show the effectiveness of smart water on EOR and a general outline about the reservoir is discussed below.

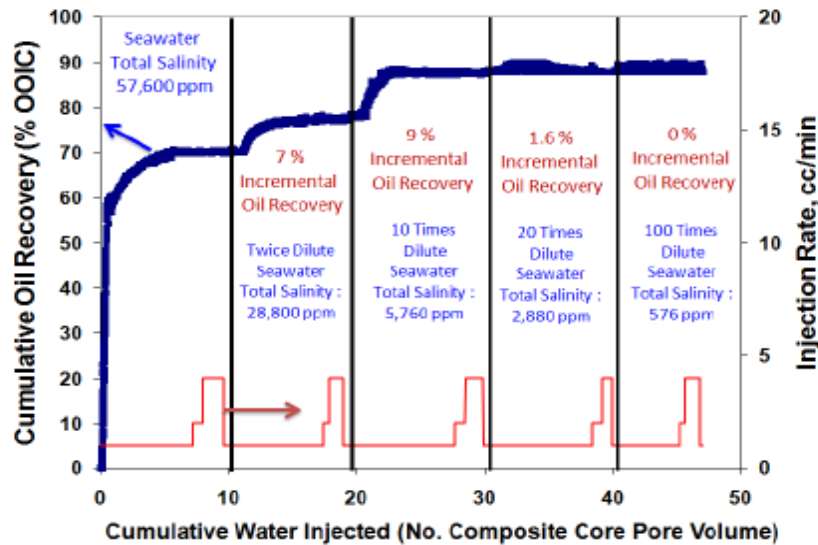
**Ekofisk carbonate reservoir:** The chalk reservoir in Ekofisk has been flooded with seawater for about 25 years with remarkable success (Austad, 2012). The Ekofisk reservoir is a preferentially oil-wet reservoir.

The main parameters, which influenced the tremendous success of smart water in Ekofisk, are:

- The high reservoir temperature of **130 °C** which is excellent for SW to act as a wettability modifier

- Highly fractured reservoir, which allows the injected SW to imbibe from the fractures into the matrix blocks
- Both oil and initial formation water will be displaced into the fractures and is transported well through the fracture system to the producers.
- Low matrix permeability of 1-2 milliDarcy (mD).

The low salinity EOR effects in a carbonate reservoir can be observed from **Figure 3**.



**Figure 3: Low salinity effect in carbonate reservoir**

(SPE 137634 Ali A.Yousef et al. Saudi Aramco, 2013)

In this thesis, the possibility of smart water or chemically modified seawater production using NF or a combination of NF and RO membranes is studied.

For the last three decades, membrane filtration has emerged as a separation technology for treatment of water, which is competitive in many ways with conventional separation techniques, such as distillation. Membrane demineralization of seawater using reverse osmosis (RO) dates from the 1960s. The high pressure used in RO resulting in considerable energy cost is the main disadvantage of this process. Thus, low-pressure NF membranes with lower rejections of dissolved components, but with higher water permeability (compared with RO), is a great improvement for separation technology. The technique that is often used for the evaluation of

membranes is the water flux and rejection behaviour of uncharged and charged solutes.

### 1.3.1 Principle of Smart Water Functionality

The physical principle for enhanced oil recovery by smart water is by altering the wetting properties of the CBR-system, which has a positive effect on the capillary pressure and relative permeability of oil and water regarding oil recovery.

- The physical and chemical mechanism for the *wettability modification process*-taking place at the rock surface determines the efficiency of recovery. For both carbonates and sandstone reservoirs, the oil recovery by injecting original formation water was different from the recovery obtained when injecting water with different composition from formation water, which is already in equilibrium with the CBR-system (Austad, 2012)
- In addition to wettability alteration, the *compaction/compression of the rock* caused by seawater is also an important drive mechanism for oil recovery.

By using smart water, oil recovery can be increased considerably from both carbonate and sandstone reservoir.

### 1.3.2 Advantages of Smart Water

Smart water flooding has several advantages compared to other EOR methods (Kokal and Al-Kaabi, 2010).

- Smart water flooding can achieve higher ultimate oil recovery with minimal investment in current operations, assuming that a water-flooding infrastructure is already in place.
- It can be injected during the early life cycle of the reservoir.
- The payback is faster, even with small incremental oil recovery
- The technique is cheap, environmentally friendly and no expensive chemicals are used.

From a cost-effective point of view, the smartest water should be injected from the start of the water flooding process (Austad, 2012).

## 1.4 Objective

The **objective** of the thesis is *to determine the technical and economic limits, in which NF and RO separation could be used advantageously for the production of smart water from seawater for EOR in carbonate reservoir.*

Softening membranes or NF membranes act as a selective barrier between monovalent and divalent ions in seawater and helps to attain the required ionic composition and low salinity for smart water.

This method can provide a simple, environment friendly and inexpensive technique to produce smart water.

## **Chapter 2: Theoretical Background**

CBR-interactions can lead to large deviations in the displacement efficiency of water floods. The distribution of oil and formation water in the porous system is related to the wetting properties of the CBR system. A number of studies were done in the past, which confirm that injecting different salinity brines increases the oil recovery in carbonate reservoirs, although the exact mechanism is not completely understood.

The composition of injected seawater is manipulated so that it should not be the same as the formation water. According to the laboratory studies by different research groups on the wetting properties of the CBR- systems, it was established that the injected water, which is different in composition when compared to the formation water, can alter the established chemical equilibrium of the CBR- system (Austad, 2012).

To understand the process of smart water, literature survey is done for different topics.

## 2.1 Carbonate Reservoirs

Massive hydrocarbon reserves are estimated to be in carbonate reservoirs. Carbonate rocks are a class of sedimentary rocks, which are formed out of tiny particles of matter. These tiny particles tend to settle together since they are easily transported by wind or water, either on land or at the bottom of water. With time, these accumulated sediments are transformed into a solid material. The physical, chemical, and biological processes that result in the formation of sedimentary rocks take place at the surface of the earth through millions of years.

The primary components included in carbonate rocks are carbonate minerals. These minerals include *calcium carbonate (limestone)* and *calcium magnesium carbonate (dolomite)*.

Carbonate reservoirs exhibit highly varying properties in case of permeability, porosity and flow mechanisms. These reservoirs have very complex pore distribution and flow paths in a small area, which makes the oil recovery very difficult.

### 2.1.1 Wettability

Several studies have shown that performance by water flooding is dependent on the composition of injected brine solution. Researchers have suggested that the *wettability alteration* towards more water wetting conditions to be the reason for improvement in oil recovery.

Wettability controls the flow, location and distribution of fluids in the reservoir (Anderson, 1986).

*Wettability is the tendency of a fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids* (Punternold, 2008). In a CBR system, it is a measure of the preference that the rock has for either the oil or water.

- If the rock is water-wet, there is a tendency for water to occupy the small pores and to contact the majority of the rock surface.
- If the rock is oil-wet, the rock is preferentially in contact with the oil and oil will occupy the small pores and contact the majority of the rock surface.

Wettability refers to the wetting preference of the rock and does not refer to the fluid that is in contact with the rock.

The wettability of a rock surface is determined by the thickness of the water film between the rock surface and the crude oil. The main properties related to wettability are:

- The system is stable and remains water-wet for a very thick film.
- The film will break if it is unstable, resulting in the adsorption of polar components onto the rock surface.
- The stability of the water film depends on the extent of the disjoining pressure, which results from the intermolecular or inter-ionic forces.
- The main interactions between crude oil/brine/solid (COBS) are identified as polar interactions, surface precipitation, acid/base interactions and ion-binding or specific interactions between charged sites and higher valence ions (Fathi, Austad and Strand, 2011).
- For the ion-bonding mechanism, di- and multivalent ions can bind at both oil and solid-water interfaces and/or bridge between them (Fathi, Austad and Strand, 2011).



## 2.1.2 Factors Affecting Wettability

The main factors affecting the wettability of a reservoir is discussed below:

- Crude oil composition - The water-wetness of most reservoir minerals can be altered by the adsorption of polar compounds or by the deposition of organic matter originally present in the crude oil.

Surface-active agents present in the oil contain both a polar and a hydrocarbon end. The polar end adsorbs on the rock surface, exposing the hydrocarbon end and makes the surface more oil-wet.

- The degree to which the wettability is altered by the original surfactants present in the oil is also determined by:
  - Pressure
  - Temperature
  - pH - The brine pH affects the wettability and other interfacial properties of the CBR system. For example, in alkaline flooding, alkaline chemicals can react with some crude oil to produce surfactants that alter wettability.
  - Mineral surface – Sandstone reservoirs are found to be more water - wet while carbonate reservoirs are found to be more oil-wet. The surfaces will preferentially adsorb compounds of the opposite polarity or acidity by an acid/base reaction. For example, silica normally has a negatively charged, weakly acidic surface in water near neutral pH, while the *carbonates have positively charged weakly basic surface*. Wettability of silica is strongly affected by the organic bases, while the carbonates will be more strongly affected by the organic acids (Anderson, 1986).
  - Ionic composition
  - Brine chemistry - Multivalent cations enhance the adsorption of surfactants on the mineral surface (Austad, 2012).

## 2.2 Seawater

Normal seawater composition includes dissolved solids, dissolved gases, nutrients and materials released from organisms. The most important components, which influence the characterisation of seawater, are presented below.

### 2.2.1 Salinity

Salinity is defined as the total amount of dissolved solids (grams) in 1000 grams of water, and is represented as parts per thousand. It is also written as [0/00]. These dissolved solids carry a charge thus salinity is usually determined by measuring the seawater's conductivity.

The most abundant ion in seawater is chloride, followed by sodium, sulphate, magnesium, potassium and calcium. These components make up to 99.27 % of the oceans salinity. The dissolved salts are always making up the same salts in the same proportion as shown in **Table 1**.

**Table 1: Proportion of ions in seawater**

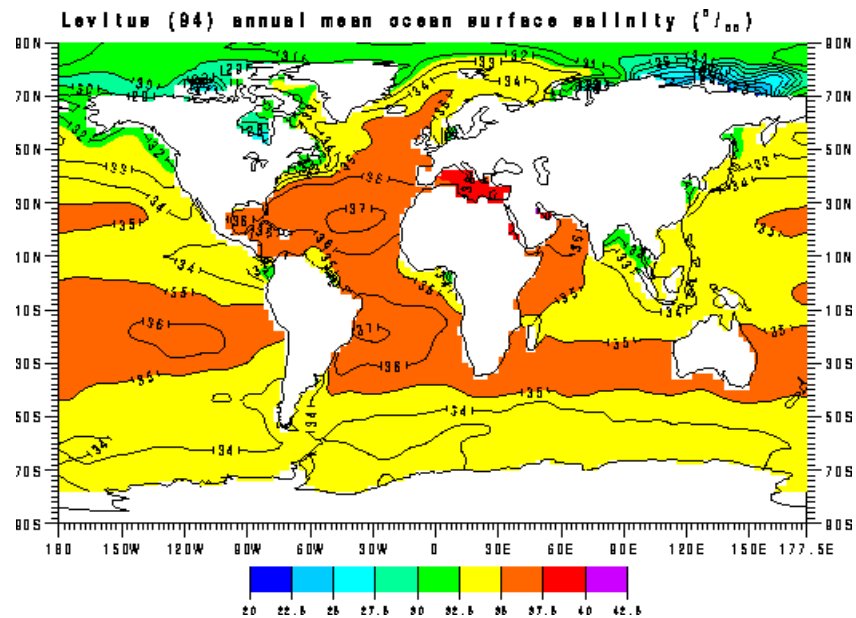
(Pinet, 2013)

Salt Ion	Ions in Seawater (‰)	Ions by weight (%)
Chloride (Cl <sup>-</sup> )	18.980	55.04
Sodium (Na <sup>+</sup> )	10.56	85.65
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	2.649	93.33
Magnesium (Mg <sup>2+</sup> )	1.272	97.02
Calcium (Ca <sup>2+</sup> )	0.400	98.18
Potassium (K <sup>+</sup> )	0.380	99.28
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	0.140	99.69
Bromide (Br <sup>-</sup> )	0.065	99.88
Boric Acid (H <sub>3</sub> BO <sub>3</sub> )	0.026	99.95
Strontium (Sr <sup>2+</sup> )	0.013	99.99
Fluoride (F <sup>-</sup> )	0.001	99.99
Total	34.482	99.99

Ocean salinity can vary due to several factors such as:

- The relative amount of evaporation or precipitation in an area affects the salinity. If there is more evaporation than precipitation, then the salinity increases since salt does not vaporize into the atmosphere. In case of more precipitation than evaporation then the salinity decreases.
- The freezing and thawing of ice also affects ocean salinity. The thawing of large icebergs, which is made of frozen fresh water and lacks any salt, will decrease the salinity while the actual freezing of seawater will increase the salinity temporarily. This temporary increase happens in the initial stages of freezing of seawater when small ice crystals form at about minus 2°C. These ice crystals are made of frozen freshwater and the salts are not part of them so the liquid between these crystals becomes increasingly salty. Finally, as seawater freezes, the ice crystals trap areas with brine and the completely large piece of frozen seawater is salty.

Ocean surface salinity at different areas is shown in **Figure 4**.



**Figure 4: Ocean surface salinity**

(National Aeronautics & Space Administration, 2014)

### 2.2.2 Temperature

The temperature of seawater differs with the amount of sun that hits its surface. This depends on the length of time and the angle of the sun's rays. The temperature is higher if there is longer time and direct rays falling on the surface.

Consequently, tropical areas that get more year-round and direct sun have warmer surface waters. In polar areas, there may be no sun for several months every year together with very steep angles of the sun's rays. These results in tropical ocean surface water have high temperature and polar regions have lower temperature.

### 2.2.3 Density

Density of seawater depends on temperature, pressure and salinity.

- Water becomes less dense when temperature increases.
- Water becomes denser when pressure increases.
- Water becomes denser when salinity increases.

Seawater is very dense when it is cold, highly saline and deep whereas a warm, less saline, surface water mass is less dense.

### 2.2.4 pH

pH is a measure of the acidity or alkalinity of a substance. Ocean water has an excellent buffering system and generally has a pH between 7.5 and 8.5 (Pinet, 2013). pH is measured using a pH meter.

### 2.2.5 Conductivity

The concentration of ions present has been determined by measuring the conductivity.

**Conductivity** is the ability of a solution, or all materials to pass an electric current. The current is carried by cations and anions in solutions, whereas in metals electrons carry it.

Conductivity measurement is an extremely widespread and useful method for measuring total ions in a solution. The high reliability, sensitivity and relatively low

cost of conductivity instrumentation make it a potential primary parameter of any good monitoring program. Some applications use resistivity for measurement, which is the inverse of conductivity.

**Total dissolved solids (TDS)** can also be calculated, which is related to conductivity by a factor dependent upon the level and type of ions present. The amount of salt in water is generally described by the concentration of total dissolved solids (TDS) in the water. TDS refers to the sum of all cations, anions, minerals and metals dissolved in water. TDS is expressed in mg/L.

Conductivity is one way to measure the inorganic materials such as calcium, bicarbonate, phosphorus, nitrogen, iron, sulphur and other ions dissolved in water. The conductivity of a solution is proportional to its ionic concentration since the charge of the ions in solution facilitates the conductance of electrical current.

Conductivity of a solution to pass electricity depends on a number of factors:

- Concentration
- Mobility of ions
- Valence of ions
- Temperature

The conductivity meter applies an alternating current (I) at an optimal frequency to two active electrodes and measures the potential (V).

Both the current and the potential are used to calculate the conductance (I/V). The conductivity meter then uses the conductance and cell constant to display the conductivity.

$$\text{Conductivity} = \text{cell constant} \times \text{conductance}$$

The measurement unit is micro Siemens per centimetre units ( $\mu\text{S}/\text{cm}$ ).

## 2.3 Smart Water Constituents

Seawater contains reactive ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  towards the chalk surface, which can change the surface charge of  $\text{CaCO}_3$ .

### Effect of $\text{SO}_4^{2-}$ :

As the concentration of  $\text{SO}_4^{2-}$  in the imbibing seawater varied from 0 to 4 times the concentration of ordinary seawater, the oil recovery increased from 10 % to 50 % of OOIP (Austad, 2012).

Observed that the sulphate present in seawater adsorbs onto the positively charged water-wet sites on the surface of chalk and lower the positive surface charge (Fathi, Austad and Strand, 2012).

### **Effect of Ca<sup>2+</sup>:**

When the concentration of Ca<sup>2+</sup> in seawater was changed from 0 to 4 times the original concentration in seawater, the oil recovery increased from 28 % to 60 % after 30 days of imbibition. In this case, the sulphate concentration remained constant and similar to the seawater concentration (Austad, 2012).

Excess of Ca<sup>2+</sup> will localize close to the chalk surface, due to less electro- static repulsion (Fathi, Austad and Strand, 2012).

### **Effect of Mg<sup>2+</sup>:**

At high temperatures, Mg<sup>2+</sup> can substitute Ca<sup>2+</sup> and substitute Ca<sup>2+</sup> linked to carboxylic groups on the chalk surface (Fathi, Austad and Strand, 2012).

### **Effect of Na<sup>+</sup> and Cl<sup>-</sup> :**

If the double layer consists plenty of ions, which are not active in the wettability alteration process such as Na<sup>+</sup> and Cl<sup>-</sup>, the access of active ions, Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> to the carbonate surface is partly prevented (Fathi, Austad and Strand, 2012).

## **2.3.1 Desirable Ionic Composition**

The desirable ionic composition is determined by the effect of ions on improving oil recovery. The objective is to increase the wettability of water in the formation rock and displace the oil. Low to moderate salinity diluted seawater (*2-10 times dilution/6000 ppm-28000 ppm*) or modified seawater depleted in monovalent ions but augmented with sulphate (*4 times*) and divalent ions (*1 times calcium and magnesium*) are most suitable for smart water flooding in a carbonate reservoir (Ayirala and Yousef, 2014).

The net effects of ionic composition are:

**Low Salinity SW:** The concentration of NaCl in seawater is much larger than the concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>. An increase in NaCl concentration of seawater decreases the oil recovery. Thus, seawater depleted in NaCl should be

smarter water than ordinary seawater as seen in **Figure 5** and oil recovery by smart water increased from 37 to 47 % of OOIP compared to ordinary seawater (Austad, 2012).

**Low Salinity with  $\text{SO}_4^{2-}$ :** At temperatures below  $100^\circ\text{C}$ , seawater depleted in NaCl, but spiked with sulphate seemed to be the smartest water regarding oil recovery. The oil recovery increased dramatically from 37 to 62 % of OOIP by spiking the NaCl depleted seawater with 4 times the sulphate concentration in ordinary SW (Fathi et al., 2010a).

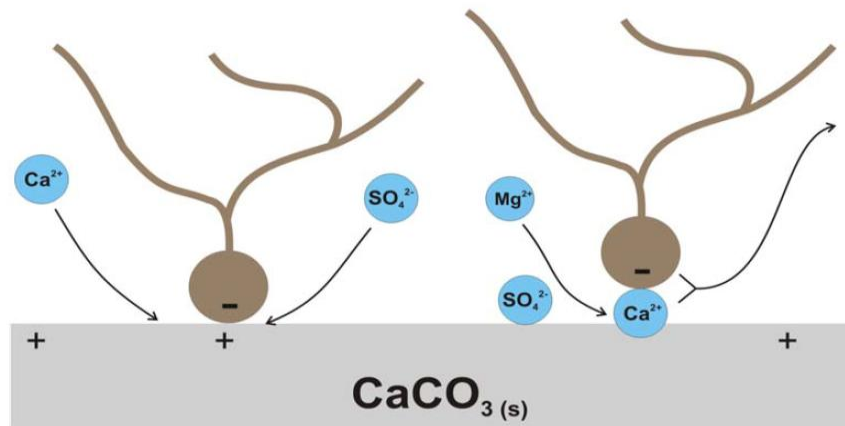


**Figure 5: Effect of low salinity water on oil – wet reservoir**

(Water Standard, 2010)

### 2.3.2 Suggested Mechanism for Wettability Alteration

A number of experiments were carried out on seawater flooding on carbonate reservoirs. Based on these experiments, wettability alteration was proposed to be a key reason for the improvement of the oil recovery. A schematic model of the chemical mechanism for wettability modification was suggested in **Figure 6** (Austad, 2012).



**Figure 6: Model of wettability alteration induced by SW in carbonate reservoirs**

(Austad, 2012)

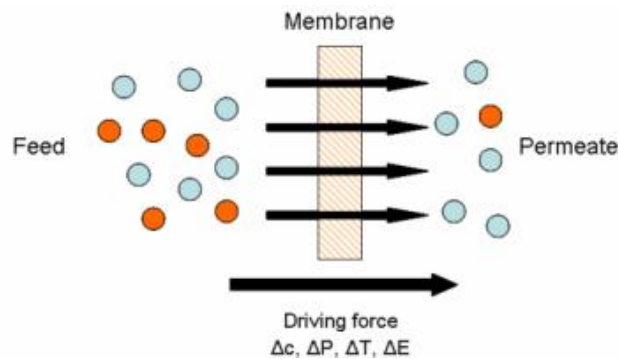
- It is found out that injection brines with high sulphate content, coupled with high temperature results in high recovery by spontaneous imbibition (Ayirala and Yousef, 2014).
- As seawater is injected into the fractured carbonate reservoir, the sulphate ions will adsorb onto the positively charged surface and lower the positive charge.
- Due to less electrostatic repulsion, the concentration of  $\text{Ca}^{2+}$  close to the rock surface is increased and  $\text{Ca}^{2+}$  can bind to the negatively charged carboxylic group and release it from the surface.
- Both the concentration of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  at the carbonate surface increases as the temperature is increased. This also depends on the reservoir temperature.
- At high temperature,  $\text{Mg}^{2+}$  is even able to displace  $\text{Ca}^{2+}$  from the carbonate rock. This shows that  $\text{Mg}^{2+}$  should also be able to displace the  $\text{Ca}^{2+}$  - carboxylate complex from the surface (Austad, 2012).

## 2.4 Membrane Separation

For smart water production using membranes, filtered seawater is generally used. A membrane acts as a selective barrier between two adjacent phases, regulating the transport of solutes between the two compartments. The main advantage of membrane technology when compared with other unit operations is its unique separation principle. The membrane allows transport of one or few components readily than rest of components present in solution. The driving force for this transport can be either a pressure gradient, a concentration gradient, temperature gradient or an electrical



potential gradient. A schematic representation of a membrane process is given in **Figure 7**.



**Figure 7: Schematic of a membrane process**

(Nanoglowa, 2011)

A feed stream is divided into two streams, *the concentrate (or the retentate) stream and the permeate stream*. Either the retentate or the permeate can contain the desired product depending on the application. ***For smart water production, retentate from the membrane is used.***

The appropriate membrane process should be determined by the specific application objective such as particulate or dissolved solids removal, hardness reduction or very pure water production, removal of specific gases or chemicals etc. The following subdivisions explain the different membrane processes and the types of membranes commonly used.

Membrane processes which uses pressure as a driving force include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), which remove small particles or soluble species.

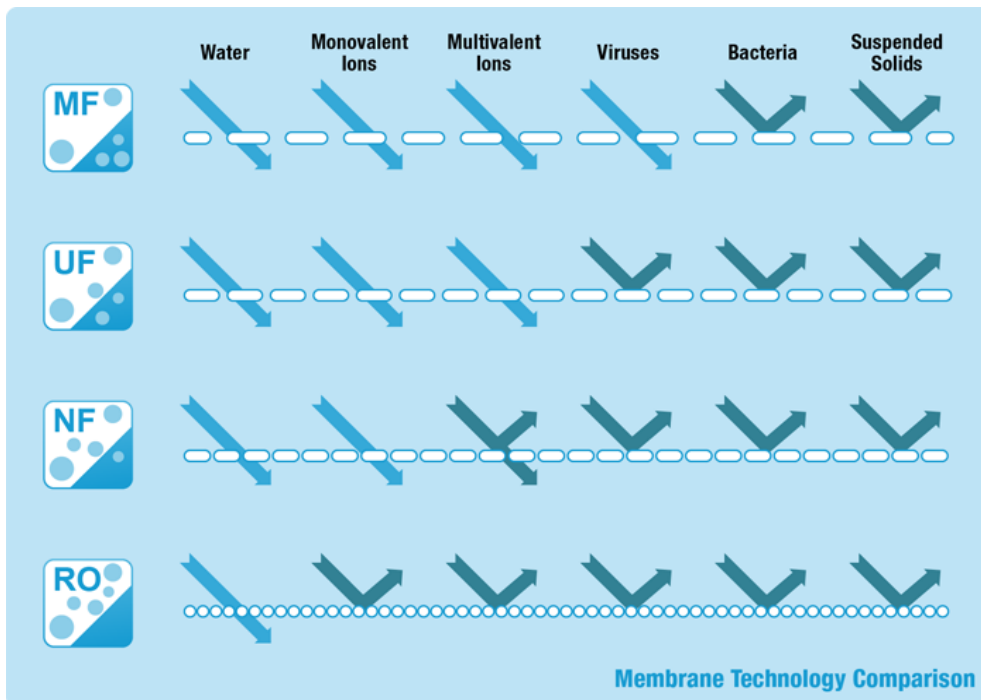
All membranes work on the principle of particle filtration and the unique feature between them is their effective pore size. Pore size affects the minimum size of particle that can be rejected by the membrane.

- Reverse osmosis membrane reject almost all material, excluding water and simple organic species (very short chain alcohols and acids). RO deals with separation of ionic size particles in the range of ***0.001 micron or less*** and molecular weight 200 g/mole or less.
- The NF Membrane lie in-between the RO and UF separation range and is suitable for the separation of particle sizes in the range of ***0.01micron to***

**0.001micron** with a MW of 200 g/mole and above. NF allows only monovalent ions and water being able to pass through.

- Microfiltration allows significantly larger particles to pass through and is able to retain particles above its pore size of **0.1-micron** range.
- Ultrafiltration has a pore size of **0.01micron**, permitting it to reject most proteins, bacteria and suspended solids.

**Figure 8** provides a graphical representation of the process of the four membrane processes where each filtration technologies find its application.



**Figure 8: Membrane processes performance**

(Koch Membrane Systems Inc., 2014)

### 2.4.1 Molecular Weight Cut off (MWCO)

*Molecular weight Cut off* is a term used to describe the potential separating capabilities of a membrane (especially UF membrane) and is defined as the molecular weight of a theoretical solute with a 90 % rejection of that membrane (Cheryan,1998).

## 2.4.2 Membrane Structure

Membrane structures are created through different processing methods. The membranes are classified into symmetric, asymmetric and composite membranes according to the uniformity of the pore structure along the membrane cross section.

### 2.4.2.1 Symmetric Membranes

Symmetric membranes have a homogenous pore diameter or pore cross section across the thickness of the membrane.

### 2.4.2.2 Asymmetric Membranes

An asymmetric membrane consists of a very thin skin layer (0.1-1.0 micron) on a highly porous thick substructure (100-200 microns).

*Thin skin layer* acts as the selective membrane and its separation characteristics depend on the nature of membrane material or the pore size. The mass transport rates are determined mainly by the skin thickness.

*Porous sub-layer* acts as a support for the thin, fragile skin layer and has little effect on the separation characteristics. In a typical asymmetric membrane, the selective barrier layer and the micro porous support always consist of the same polymer.

### 2.4.2.3 Thin Film Composite Membranes (TFC)

Composite membranes consist of at least two layers, with different structure. A thin dense skin layer of 0.01 to 0.1  $\mu\text{m}$  is formed over an approximately 100  $\mu\text{m}$  thick micro porous film.

Composite membranes differ from asymmetric membranes by the mode of fabrication which includes:

- Casting of the micro porous support
- Installation of the barrier layer on the surface of the micro porous support layer

This mode of preparation leads to significant advantages of the composite membrane over asymmetric membranes:

- i. It improves the permeation rate which is inversely proportional to the thickness of the barrier layer

- ii. Increases the rejection rate of the membranes
- iii. Minimizes the pressure drop across the membrane (Cheryan, 1998)

The materials used for the support layer and the skin layer can differ and adjusted for the finest combination of high water flux and low solute permeability (Cheryan,1998).

The thin film composite membrane structures are generally used for RO and NF, which requires high flux and high salt rejection rate.

The materials used for NF membranes are highly cross-linked, which results in long-term stability and membrane life in aggressive environments.

### 2.4.3 Membrane Materials

Membranes can be classified into organic, inorganic and mixtures of organic or inorganic materials.

#### 2.4.3.1 Organic Membranes

Polymeric membranes account for the biggest percentage of installed membranes currently in use. Different polymers are used to acquire, the required MWCO, to achieve the desired resistance to fouling, or to have better performance when contacted with a specific process fluid.

Organic membranes are commonly made of natural or synthetic polymer such as cellulose acetate, polysulfide, aromatic polyamides, polyacrylonitrile etc.

#### *Cellulose acetate (CA)*

The raw material is cellulose, a polymer of  $\beta$ -1,4linked glucose unit. Cellulose and its derivatives are usually linear, rod-like and rather inflexible molecules, which are important characteristics for RO and UF (Cheryan, 1998).

#### *Advantages:*

- Good fouling resistance due to its hydrophilic nature
- Possible to manufacture wide range of pore size from RO to MF, with reasonably high fluxes
- High water permeability
- Inexpensive and easy to manufacture

*Disadvantages:*

- Narrow temperature range, with maximum temperature of 30 °C, resulting in low flux
- CA membranes are susceptible to hydrolysis and can only be used over a limited pH 3- 6.
- CA membranes are vulnerable to microbial attack
- Undergo degradation at temperatures above 35 °C (Cheryan, 1998).
- Poor chlorine resistance
- Undergo creep, under high pressure, over its operating lifetime (Cheryan, 1998).
- CA is highly biodegradable due to its cellulose backbone.

***Aromatic polyamides***

Polyamides (PA) membranes are characterized by having an amide bond (-CONH-) in its structure and PA overcomes some problems associated with CA membranes.

*Advantages:*

- PA have better resistance to hydrolysis and biological attack
- PA can be operated over a pH range of 4 to 11
- Can withstand higher temperature

*Disadvantages:*

- PA membranes have lesser chlorine tolerance and bio fouling tendencies
- Have lower water permeability than CA membranes.

Polyamide forms the contact skin layer in many composite membranes. The supporting porous sub layer of these membranes is usually made of polysulfone (Cheryan, 1998).

***Polysulphone***

Polysulphone membranes are widely used in MF and UF. It is characterized by having diphenylene sulphone repeating units.

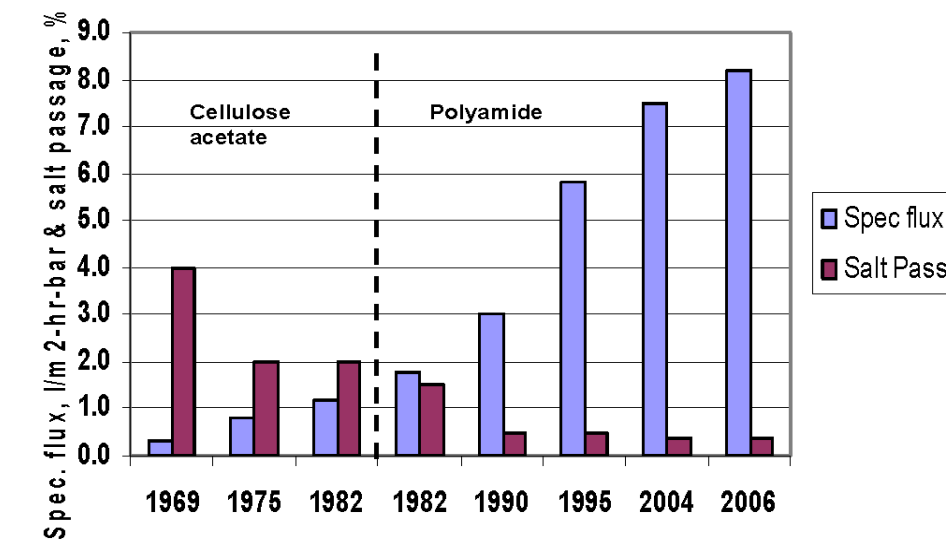
*Advantages:*

- Its structure contributes to high degree of molecular immobility, producing high rigidity, strength, creep resistance, dimensional stability and heat deflection temperature
- Wide pH tolerance and better chlorine resistance

*Disadvantages:*

- Low pressure limits
- Hydrophobic nature which make it susceptible for fouling

A comparison of the specific flux and salt passage for cellulose acetate membrane and polyamide membrane is shown in **Figure 9**.



**Figure 9: Comparison of the performance of CA and polyamide membrane**

(Advanced membrane technologies Stanford University, May 07, 2008)

#### 2.4.3.2 Inorganic Membranes

Membranes are prepared from inorganic materials such as ceramics, glass and metals to compete with organic membranes for specific applications such as:

- Possible to operate at elevated temperatures, with *metallic membranes* stable at temperatures from 500 – 800°C and many *ceramic membranes* stable at over 1000°C
- They are more resistant to chemical attack and have long life cycle (Cheryan, 1998).

Disadvantage of inorganic membrane over organic membrane is with their pore properties, cost and incompetence for surface modification. Brittle nature of ceramic membrane is also a drawback.

#### 2.4.3.3 Hybrid Membranes

Organic-inorganic hybrid constituents offer specific advantages for the preparation of artificial membranes for high selectivity, flux and also good thermal and chemical resistance.

### 2.4.4 Membrane Configuration

For practical applications, membranes are stored in a module. The design of the membrane module depends on the membrane shape. Various membrane shapes and module designs are implemented in different membrane processes and rejection and flux for the same membrane could be different in different module designs.

Membranes are manufactured as *flat sheets*, *hollow fibres*, *tubular* and *spiral modules*. In this thesis, spiral wound module is used.

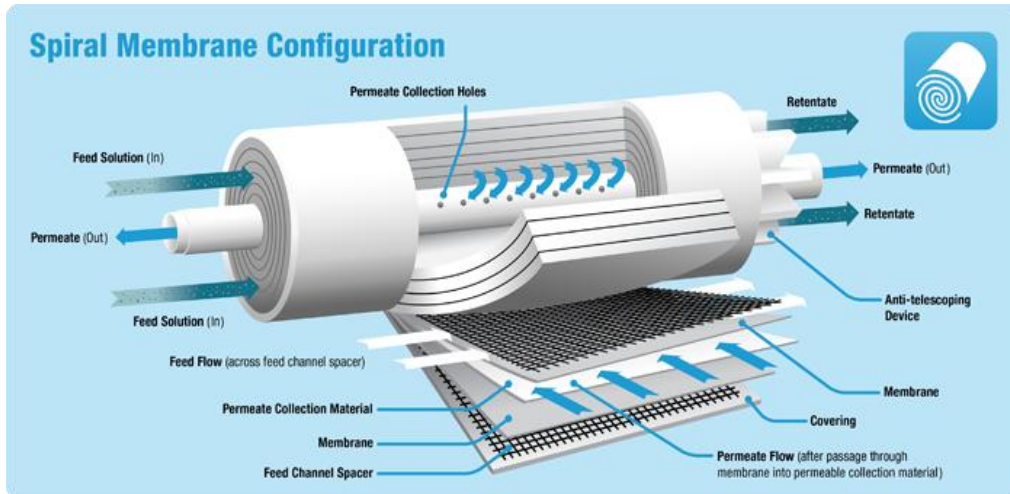
#### **Spiral wound module**

A spiral wound is the most inexpensive and compact designs available today. These membrane elements are designed around flat sheets. A spiral wound module consists of one to more than 30 membranes leafs. Multileaf designs are used to increase the membrane area without excessively increasing the length of the feed channel or permeate flow path (Cheryan, 1998).

Each leaf is made of two membrane sheets glued together end-to-end with a permeate spacer in between them. The glue line seal the permeate (inner) side of the leaf against the feed/concentrate (outer side). The open side of the leaf is connected to and closed against a perforated central tube, which collects the permeate from all leaves. The leaves are turned up with a sheet of feed spacer between each of them, thus providing the channel for feed and concentrate flow.

During the process, the feed water enters the face of the element through the feed spacer channels and exit on the opposite end as the concentrate (Cheryan, 1998).

A schematic construction of a spiral wound membrane element is shown in **Figure10**.



**Figure 10: Spiral wound membrane**

(Koch Membrane Systems Inc., 2014)

*Advantages:*

- Spiral modules operate in turbulent flow resulting in better flux
- Narrow channel height ,so much more membrane area can be packed into a given pressure vessel
- Surface area - to - volume ratio is high with an average about 200-300 ft<sup>2</sup>/ft<sup>3</sup>
- The combination of pressure drop, low flow rates and relatively high turbulence results in lowest energy consumption (Cheryan, 1998)
- Capital cost lowest among all membrane module designs

*Disadvantages:*

- Pressure drop in the feed channel is very high due to the parasitic drag exerted by the spacer. This pressure drop can result in a magnifying effect at high flow rates that can damage the membrane (Cheryan, 1998).
- Mesh spacers in the feed channel creates dead spots directly behind the mesh in the flow path resulting in partial blockage of the feed channel

Spiral wound configuration is the most used configuration for reverse osmosis and nanofiltration membranes.



## 2.4.5 Advantages of Membranes over Other Conventional Methods

The main advantages of membranes over other conventional methods are:

- Separation is achieved without a phase change and therefore it is more energetically efficient than distillation
- Very less or no chemical addition is required
- Membrane processes are usually operated at ambient temperature
- Lower operating cost;
- Selective removal of pollutants with complexing agents or by membrane surface modification
- Zero discharge can be achieved by reusing the permeate water and removed compounds
- Continuous operation is possible
- Modular design without significant size limitation
- Minimal labor requirement

## 2.4.6 Disadvantages of membranes

Main problems encountered in using membranes are:

- Requires pretreatment of feed samples
- Relatively high capital and operating cost
- Low flux
- Fouling of the membrane
- Long construction time for large scale plants

## 2.5 Nanofiltration (NF) Membrane

NF is a membrane separation technique with a pore size of approximately **1nm**. The NF membrane will thus reject particles having size greater than 1nm. NF is also referred to as "*loose*" **RO** due to its large membrane pore structure when compared to the membranes used in RO.

- NF lies between the separation limits of Reverse Osmosis (RO) and Ultrafiltration (UF).
- The separation phenomenon in RO is based on solution diffusion, while in UF is due to sieving effect of the membrane. NF uses both these effects, with an addition effect of charge, which is due to the surface characteristics of NF membrane (Bowen and Welfoot, 2002).
- NF retains multivalent ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  from normal seawater due to pore size

### 2.5.1 Applications of NF Membranes

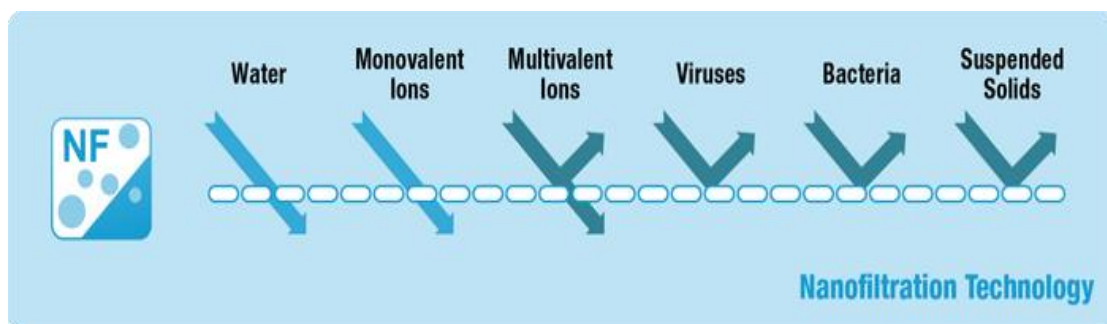
From the beginning, the water treatment has been the major application area for NF. The reason for this is that NF membranes were developed for softening and NF membranes are still denoted as *softening membranes*.

Currently, NF is seen as a combinatory process capable of removing hardness and a wide range of other applications in one-step. (Abhang et.al. 2013)

It is beneficial to use NF membranes when:

- Monovalent salts need not be retained
- Separation of anions with different valency must be achieved
- Separation between a monovalent salt and low molecular weight organic material is required (e.g. separation of dyes from sodium chloride)
- Purification of acids, bases or solvent particularly when the contaminants are in the NF MWCO range

The NF membrane performance technology is shown schematically in **Figure 11**.



**Figure 11: Nanofiltration technology**

(Koch Membrane Systems Inc., 2014)

## 2.5.2 Separation Mechanism of NF Membranes

Depending on the physicochemical characteristics of the membrane and the solute, separation can be achieved by one or several mechanisms. This implies that separation can be due to physical selectivity or chemical selectivity. *The former involves charge repulsion, size exclusion, or steric hindrance and latter involves solvation energy, hydrophobic interaction or hydrogen bonding.*

- NF membranes have a slightly charged surface. Most NF membranes are negatively charged at neutral pH (Abhang, et. al., 2013).
- The surface charge plays a major role in the transportation mechanism and separation properties of nano membrane.
- Monovalent ions are partly rejected by NF membranes and the concentration difference between feed and permeate is smaller than for a complete rejection. This is advantageous for NF as the osmotic pressure are lower compared to RO and lower pressure needs to be applied resulting in lower energy consumption.
- The mechanism of transport and rejection of ions in NF is due to *Sorption-surface capillary flow (Donnan exclusion), Sieving and Solution -diffusion.*
- *Sorption surface-capillary flow or Donnan exclusion:* The ion separation resulting from electrostatic interactions between ions and membrane surface charge is based on the *Donnan exclusion mechanism* (Childress and Elimelech, 2000).

In this mechanism, the co-ions, which have the same charge as that of the membrane, are repulsed by the membrane surface and in order to satisfy the electro neutrality condition, an equivalent number of counter ions is retained resulting in salt retention. The Donnan effect leads to a difference in rejection according to ion charge.

Multivalent ions (eg.  $\text{SO}_4^{2-}$ ) have a higher rejection in NF than monovalent ions because the charge interactions are larger and co-ions are efficiently retained (Childress and Elimelech, 1996).

The Donnan effect is dependent on several factors such as:

- i. Salt concentration
- ii. Valence of the co-ion
- iii. Valence of the counter- ion

## iv. Charge of the membrane

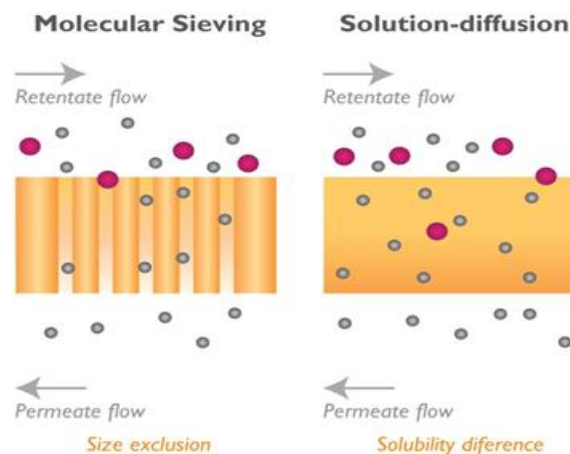
An increase in salt concentration leads to a decrease in rejection. With increase in concentration, the shield effect of the cations on the membrane charged groups increases, resulting in a decrease on the membrane repulsion forces on anions occur (Peeters et al., 1998).

- **Sieving effect (Steric hindrance):** The membrane rejects solutes having larger molecular weight than MWCO of the membrane and ones having a lower molecular weight will permeate easily through the membrane. Thus, solutes having different molecular weights can be separated based on sieving effect.

The transportation of a non-charged solute through an NF membrane is determined by a steric exclusion mechanism. Steric exclusion applies to NF as well as UF and MF membranes. A separation between two non-charged different solutes is by the difference in their size and shape (Abhang, et. al., 2013).

- **Solution-diffusion theory:** This describes the membrane as a porous film into which both water and solutes dissolve. The transport of solute in the membrane is mainly under concentration gradient forces and water transport by the hydraulic pressure gradient. The solute transport through the membrane depends on hindered diffusion and convection.

The mechanism of sieving and solution diffusion is shown in **Figure 12**.



**Figure 12: Molecular sieving and solution diffusion occurring in a membrane**

(CO2CRC, 2011)

Sieving mechanism is applied for the retention of ions, where the hydrated ion radius needs to be considered in water solutions. *Stokes radius (Stoke-Einstein Relationship) and Hydration energy* are expected to influence the retention of ions in a solution.

- *Rejection of solutes increases with increasing stokes radius* (Kreig,et.al.,2004 )
- *The ions that have higher hydration energy are more retained*

### Stokes radius

The radius of a hard sphere that diffuses at the same rate as that solute and which can be influenced by the water molecules that move with the ion (Richards, et.al, 2013).

### Hydration energy

It is the force required to extract the solute from the solvent to put it into the pores. This means that it would require more energy to extract ions with higher hydration energy to push it into the pores than ions with lower hydration energy. Thus, hydration energy can influence the retention (Richards, et.al, 2012).

**Table 2** shows the stokes radius and the hydration energy of different ions.

**Table 2: Stokes radius and hydration energy of ions**

(Hussain, Abashar and Al-Mutaz, 2006)

Ion	Stokes radius (nm)	Hydration energy (KJ.mol <sup>-1</sup> )
Na <sup>+</sup>	0.184	407
Cl <sup>-</sup>	0.121	376
F <sup>-</sup>	0.117	515
NO <sub>3</sub> <sup>-</sup>	0.128	329
SO <sub>4</sub> <sup>2-</sup>	0.231	1138
Ca <sup>2+</sup>	0.310	1584
Mg <sup>2+</sup>	0.341	2018

The mechanism of retention by negatively charged NF membrane is very complex when the solution has multi ions (e.g. Seawater).

*According to the Donnan exclusion, in the case of ion mixtures, electrostatic interactions between co-ions occur resulting in a decrease in monovalent ions rejection, especially when less permeable co-ions are present in the solution.* For example, in a mixed solution with NaCl and Na<sub>2</sub>SO<sub>4</sub>, the concentration of the divalent anion influences the monovalent anion retention. When Na<sub>2</sub>SO<sub>4</sub> is spiked to a solution of constant sodium chloride concentration, the retention of Cl<sup>-</sup> decreases as the concentration of Na<sub>2</sub>SO<sub>4</sub> increases. The Na<sup>+</sup> ions, which readily pass through the membrane, should be accompanied by a negatively charged ion in order to maintain electro neutrality. The negatively charged membrane repels the negatively charged ions. Thus, Cl<sup>-</sup> ions with the lower potential are forced to permeate preferentially compared with the SO<sub>4</sub><sup>2-</sup> ions (Krieg, et al. 2004).

### 2.5.3 Membrane Performance

The performance of a given membrane can be evaluated using the parameters such membrane flux, rejection characteristics and recovery rate.

#### 2.5.3.1 Membrane Flux

*Flux (J) is the amount of fluid passing through the membrane i.e. the volumetric rate of flow of the permeate through the membrane. It is usually represented in terms of volume per unit membrane area per unit time (litres /m<sup>2</sup>/hour) (Cheryan, 1998).*

The flux across a membrane is a function of a number of variables, predominantly the pore size, pressure drop and water viscosity.

The design of membrane systems should be based on a steady long-term flux rate that can be expected from the membrane over a long period of operation.

$$\text{Membrane Flux}(J) \left[ \frac{L}{m^2hr} \right] = \frac{\text{Permeate flow rate (L/hr)}}{\text{Nominal membrane area}(m^2)}$$

#### 2.5.3.2 Rejection Characteristics

Rejection characteristics of a membrane describe the desalting degree. The desalting degree of a membrane shows the percent rejection of salts by the membrane. Membrane rejection (**Robs**) % is calculated from the following equation:

$$\text{Membrane Rejection (Robs)}[\%] = \left(1 - \frac{C_p}{C_o}\right) * 100$$

where,

$C_p$  = Salt concentration in the permeate

$C_o$  = Salt concentration in the feed

The rejection ability of ions depends on the salt diffusion coefficient ( $D_o$ ) and the solute size ( $r_s$ ). The ion diffusivity follows the order  $Cl^- > Na^+ > SO_4^{2-} > Mg^{2+}$  while the solute size follows the sequence  $Mg^{2+} > SO_4^{2-} > Na^+ > Cl^-$  (Ahmad et.al. 2004).

### 2.5.3.3 Membrane Recovery

Recovery is defined as the percentage of feed water that emerges from the membrane as a product or permeate.

Recovery is calculated from the equation,

$$\text{Recovery} = \left[\left(\frac{F_p}{F_f}\right) * 100\right]$$

where,

$F_p$  = Flow rate of permeate

$F_f$  = Flow rate of feed

## 2.5.4 Parameters Affecting the Performance of NF Membranes

Water flux and salt/ion rejection are the main performance indicators in nano filtration process.

Performance of a NF membrane can be affected by:

### **Membrane characteristics:**

- i. *Surface characteristics:* Pore structure, hydrophobicity and chemical structure of membrane affects the retention characteristics and fouling. Fouling affects water flux.
- ii. *Pore charge (electro kinetics) characteristics:* Affect the transport mechanism in nanofiltration. pH of the system affects the charge and resulting zeta potential of the membrane because membrane functional groups protonate and deprotonate over the pH range (Childress and Elimelech, 2000).

***Operating parameters:***

The most important operating parameters affecting the performance of NF process are:

- i. Pressure: The driving force in the NF process is the pressure difference. The effective driving pressure is the difference between the applied hydraulic pressure and the osmotic pressure applied on the membrane by the solutes. Nanomembranes usually provide good separation at net pressures of 10 bars or higher.
- ii. Temperature: With an increase in temperature, the flux increases due to reduction in viscosity
- iii. Cross flow velocity: With an increase in the cross flow velocity, the flux increases due to the removal of fouling layer from the membrane surface.
- iv. pH: The pH is a critical parameter which affects electro kinetics and hence performance of nano membranes by:
  - The nano membrane surface is negatively charged at neutral or higher pH but lose their charge at acidic pH
  - pH can be responsible for changes in the feed solution, affecting the membrane performance. E.g., change in solubility of ions at different pH regimes, causing different rejection rate and change in the dissociation state of ions at different pH ranges (Abhang,et. al., 2013)
  - pH of the system affects the charge and resulting zeta-potential of the membrane because membrane functional groups protonate and deprotonate over the pH range (Childress and Elimelech, 2000).
- v. Salinity: With an increase on the ionic strength of the surrounding liquid, the effective pore radius of the charged pore will also increase. The rejection of monovalent ions will decrease when their concentration in the feed solution increases. The *shield effect* of membrane charge also increases as the ionic strength of feed solution increases (Childress and Elimelech, 2000).

### **2.5.5 Advantages of NF Membranes over RO**

- Low operation pressure
- More open pores leading to higher flux



- Selective retention of monovalent and divalent ions makes it suitable for specific application
- Low investment
- Lower operating and maintenance cost
- Lower energy consumption

### 2.5.6 Industrial Application of NF Membranes

- Water and wastewater treatment
- NF membranes are particularly useful in the fractionation and selective removal of solutes from complex process streams
- Treating pulp-bleaching effluents in the textile industry
- Separation of pharmaceuticals
- Removal of minerals in the dairy industry
- Metal recovery from wastewater
- Virus removal

## 2.6 Reverse Osmosis (RO) Membrane

Osmosis is a natural process of flow through a semi-permeable membrane. When pure water of the same temperature is present on both sides of the membrane and the pressure on both sides is also equal, no water flow can happen through the membrane. When the salt on one side is dissolved into the water, a flow through the membrane from the pure water to the water containing salts will occur and tries to equalize concentration differences.

In **reverse osmosis**, the osmotic pressure is overcome by applying external pressure higher than the osmotic pressure on the feed water. This results in a water flow in the reverse direction to the natural flow across the membrane and leaves the dissolved salts behind with an increase in salt concentration.

- The driving force for reverse osmosis is the difference between applied pressure and the osmotic pressure.
- The energy consumption of RO is directly related to the concentration of salts, since a higher salt concentration results in higher osmotic pressure.

## **Chapter 3: Materials and Methods**

This chapter describes the equipment and materials used for the characterization of feed seawater and the product streams from the different membrane process experiments. Quality of the seawater passing through the membrane is very important as it can affect the performance of the membrane. Filtered seawater collected on 11th February from *Merkjarvik* was used as feed in the experiments. The experiments done are presented below.

### 3.1 Determination of Total Suspended Solids (TSS)

TSS analysis of the seawater was done by drying and weighing, according to the standards **SM 2540 D**.

Glass microfibers filter, 696 with particle *retention capacity of 1.5 $\mu$ m* was used for filtration of seawater.

Well-mixed, seawater samples are filtered through the GF/C filter and evaporated in a weighed dish. The filter paper was then dried to a constant weight, in an oven at 105 °C. The increase in weight over that of the empty dish represents the total suspended solids present in the sample.

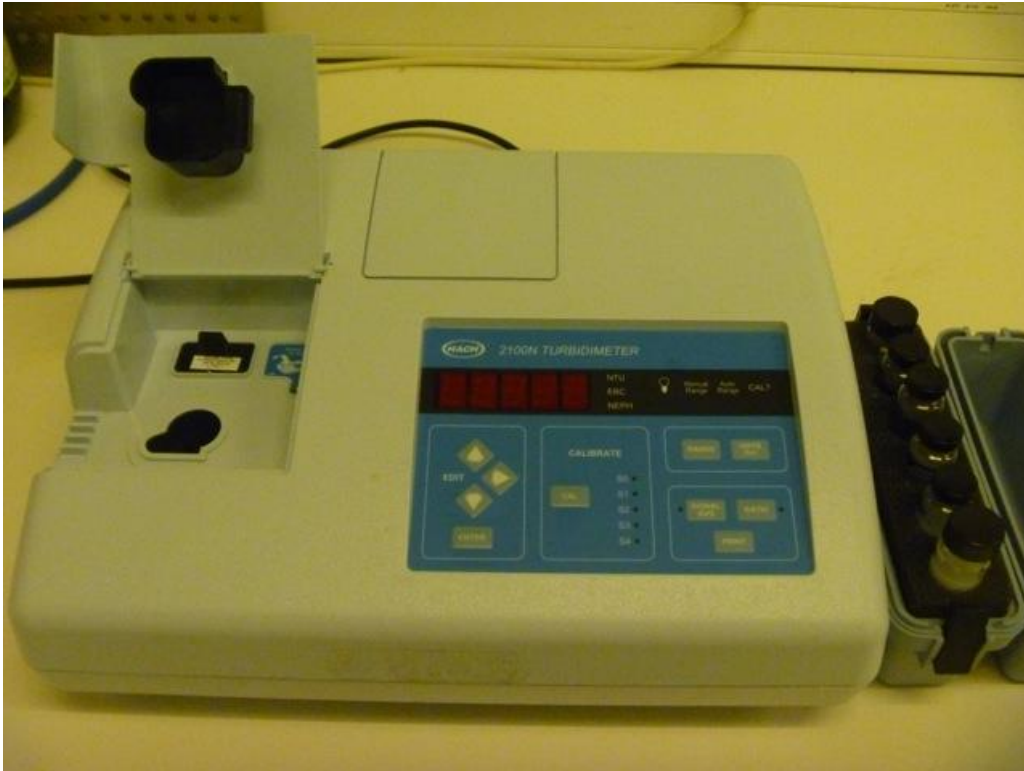
$$\text{mg, total solids /L} = \frac{(\text{Weight of dried residue +dish [mg]} - \text{Weight of the dish}) * 1000}{\text{Sample volume, mL}}$$

*Note: 2540D is the method generally used for total suspended solids dried at 105 °C.*

*Grade 696 is used for observing specific pollutants (e.g., Mercury in water) and in marine chemistry to filter particulate components in seawater.*

### 3.2 Turbidity

Turbidity is a suspension of fine colloidal particles that do not settle readily in a solution and results in a "cloudiness". Turbidity is measured in Nephelometric Turbidity Units (NTU). A turbidimeter (*HACH 2100N Turbidimeter*) was used to determine the relative clarity or the turbidity of the sample and is shown in **Figure 13**.



**Figure 13: HACH 2100N Turbidimeter**

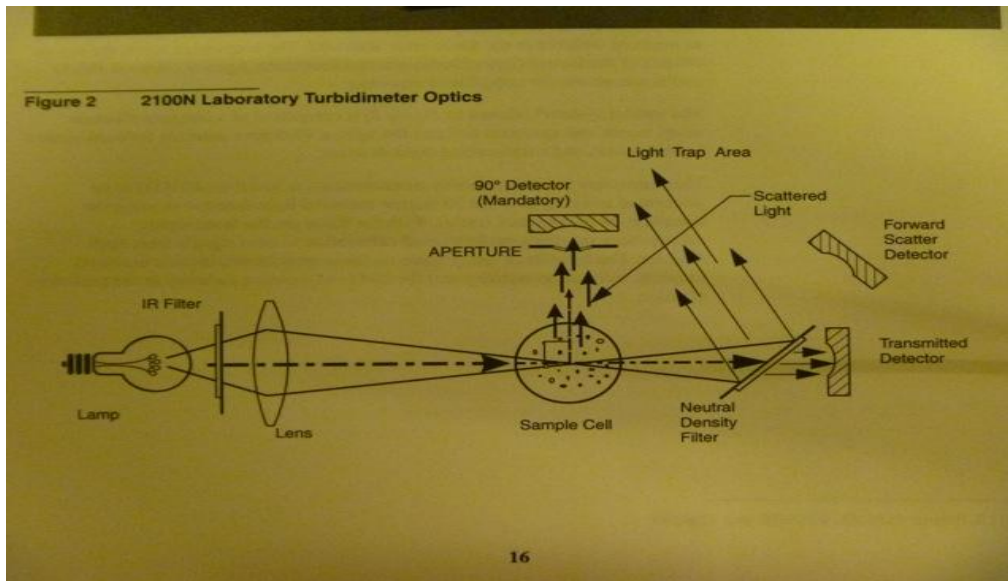
A turbidimeter consists of a *light source*, a *focusing lens* for directing a beam of light through the sample, a *photoelectric detector* positioned at a 90° angle from the beam, to measure the amount of light scattered and a *light trap*, to prevent any light already past the sample from being detected, to avoid faulty readings.

NTU scale for water quality is used to check the quality of water and is shown in **Table 3**.

**Table 3: NTU values for water turbidity**

Quality	NTU
Excellent	$\leq 10$
Fair	$\leq 15-30$
Poor	$> 30$

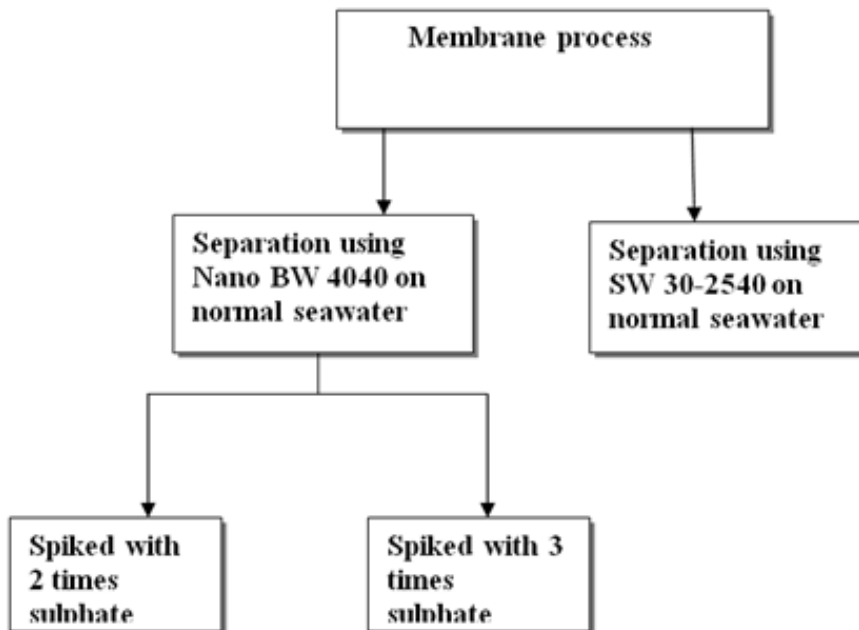
A schematic of the working principle is shown in **Figure 14**.



**Figure 14: Turbidimeter using the scattered light method**  
(2100N Laboratory Turbidimeter Optics Manual)

### 3.3 Membranes for Separation

Two types of membranes have been used for the experiments with seawater. The stages in the experiment are represented as:



**Figure 15: Stages in membrane analysis**

### 3.3.1 Nanofiltration Membrane (NANO - BW -4040)

Main experiments were done at *Membraneteknikk AS, Flekkefjord*.

The NF membrane used was Hydranautics **BW** (Brackish water), have a size of **40\*40** inches. The membrane brochure is given in **Figure 42** in Appendix 3.

The specifications of the membrane according to the manufacturer are shown in **Table 4**.

**Table 4: Nano- BW- 4040 specifications**

Membrane Type	Polyamide thin –film composite
Maximum operating temperature	45° C
Maximum operating pressure	41 Bars
pH range	3-9
Nominal membrane area	7 m <sup>2</sup>
Membrane configuration	Spiral wound

The experimental setup for NANO BW- 4040 the membrane is shown in **Figure 16**.



**Figure 16: Experimental setup at Membraneteknikk AS, Flekkefjord**

The pilot unit consisted of:

- One feed water tank consisting of 300 liters of filtered seawater
- The membrane, pump and instrumentation were connected in the unit as seen in **Figure16**
- A temperature regulating system for the feed water (only for chilling) which consists of a chilled water recirculation loop
- All pressures are measured in gauge (i.e. barg).

The process flow sheet of the membrane Nano BW 4040 is shown in **Figure 17**

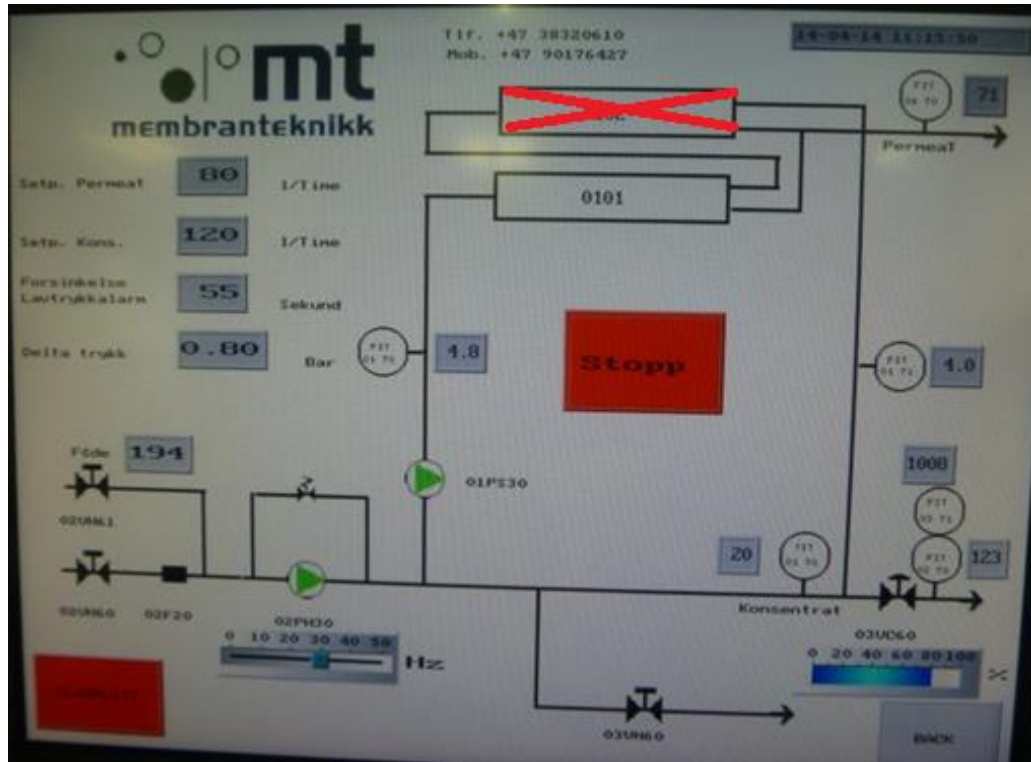


Figure 17: Process flow sheet of Nano BW 4040

- Only one membrane is used for separation, though in the process sheet two membranes are shown.

Experiments were done on:

### 1) Normal seawater

- The operation of the pilot unit is automated to ensure safe operation of the pumps. The unit was operated through a touch – screen panel and adjusting the regulating valves located on the front side of the unit.
- First, filtered seawater were passed through the membrane by varying the flow rate of the permeate.
- Flow rate of the retentate was kept constant .Permeate flow rate was varied from **45 L/h to 145 L/h** and the retentate flow rate, at **120 L/h** throughout the experiment.
- For each flow rate, both retentate and permeate samples were collected for ion chromatography tests.
- The applied pressure was in the range of 3 and 12 bar.



- pH, conductivity, salinity, TDS and temperature was measured for each sample.
- The temperature was maintained by a temperature regulating circulation loop
- *Mass balance for the experiment is done using the principle, mass flow inside = Mass flow outside.*

**2) Sulphate concentration spiked two times in feed seawater**

- Sulphate concentration on the feed was doubled in the second stage, to observe if there is any effect of added chemicals on the behavior of other ions as well as to observe membrane separation and its properties.
- An amount of **3.4 g/L** of Na<sub>2</sub>SO<sub>4</sub> was added to normal seawater in order to change the sulphate concentration. Feed samples for further testing was also collected.
- The two times spiked sulphate feed sea water was passed through the membrane at varying permeate flow rate from **80 L /h to 145 L/h** and constant retentate flow rate of **120 L/h**.
- Both retentate and permeate samples were collected for ion chromatography tests for every flow rates
- pH, conductivity, pressure, salinity, TDS and temperature was measured for each sample

**3) Sulphate concentration spiked three times in feed seawater**

- Sulphate concentration on the feed was tripled on the third stage, to check if an increase in concentration of one sample has any effect on the separation of other constituents in the feed, as well as to observe any effect on membrane separation and its properties.
- An amount of **6.8 g/L** of Na<sub>2</sub>SO<sub>4</sub>, was added to normal seawater in order to change the sulphate concentration. Feed samples for further testing was collected.
- The three times spiked sulphate feed seawater was passed through the membrane at varying permeate flow rate from **80 L /h to 145 L/h** and constant retentate flow rate of **120 L/h**.

- Both retentate and permeate samples were collected for ion chromatography tests for every flow rates
- pH, conductivity, salinity, pressure, TDS and temperature was measured for each sample.

### 3.3.2 Reverse Osmosis Membrane (FILMTEC SW 30- 2540)

The RO experiments were done at **University of Stavanger (UiS)**. The experiments were carried out as one of the option to reduce the TDS level of NF retentate.

The RO membrane used for the separation is *Filmtec SW 30-2540*. The specifications of the membrane according to the manufacturer are given in **Table 5** and the used membrane is shown in **Figure 18**.

**Table 5: Filmtec SW 30 2540 specifications**

Membrane Type	Polyamide thin –film composite
Maximum operating temperature	45° C
Maximum operating pressure	69 Bars
pH range	2-11
Nominal membrane area	2.8 m <sup>2</sup>
Recovery (%) for a NaCl concentration of concentration 32000 ppm	8%



**Figure 18: Filmtec SW- 30-2540 membrane**

For the experiment the steps done are:

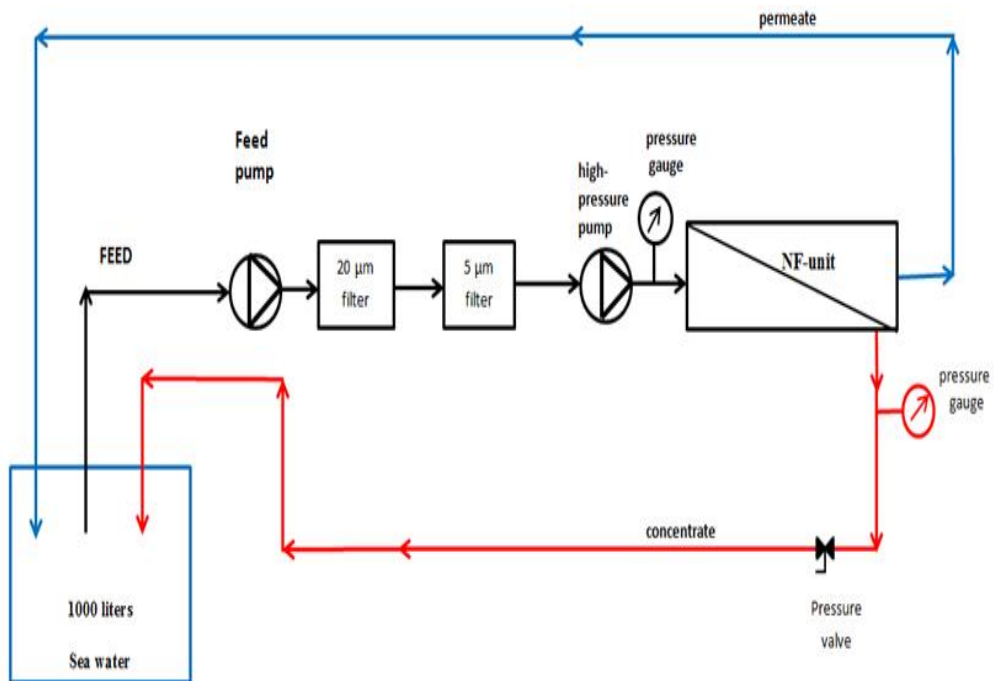
- 1000 liters of filtered seawater was circulated through the membrane by varying the feed pressure.
- Feed pressure was varied from 25 bar to 40 bar
- After each increase in pressure , the membrane was kept running for 20 minutes to get highest accuracy
- Flow rate for the permeate and retentate was measured with varying pressure
- Samples from both retentate and permeate was collected for ion chromatography test.
- Feed sea water sample were collected to measure the pH, conductivity, salinity, temperature and TDS
- pH, conductivity, salinity, TDS and temperature was measured for each sample.

The experimental setup for the membrane is shown in **Figure19**.



**Figure 19: Experimental setup for Filmtec 30 - 2540**

The schematic of the experimental setup is shown in **Figure 20**.



**Figure 20: Schematic of experimental setup for Filmtec SW 30-2540**

### 3.4 Calculation of Parameters

Membrane flux (J), membrane rejection (%) and recovery are calculated using the following formulas:

- **Membrane Flux (J)**  $\left[ \frac{L}{m^2hr} \right] = \frac{\text{Permeate flow rate (L/hr)}}{\text{Nominal membrane area}(m^2)}$

Where,

Membrane area for Nano- BW- 4040 = **7 m<sup>2</sup>**

Membrane area for Filmtec 30- 2540 = **2.8 m<sup>2</sup>**

- **Membrane Rejection (Robs)** [%] =  $\left( 1 - \frac{C_p}{C_0} \right) * 100$

Where,

C<sub>p</sub> = Salt concentration in the permeate

C<sub>0</sub> = Salt concentration in the feed

- **Recovery** =  $\left[ \left( \frac{F_p}{F_f} \right) * 100 \right]$

Where:

F<sub>p</sub> = Flow rate of permeate

F<sub>f</sub> = Flow rate of feed.

### 3.5 Analytical Methods for Seawater Characterization

Following analytical methods were used to determine the solute properties in feed, retentate and permeate solutions containing Na<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions.

#### 3.5.1 pH

pH was measured for each sample using a pH- meter (*WTW Multi 340i*). The pH meter was calibrated with two-pH buffer standard (pH 4 and 7).

#### 3.5.2 Total Salinity and Conductivity Measurement

A Conductivity meter (*WTW Multi 340i*) was used to measure the total salinity of the feed, retentate and permeate sample. The probe is capable of measuring the

conductivity of any solution from 1  $\mu\text{S}/\text{cm}$  to 500  $\text{mS}/\text{cm}$  to and salinity of the sample from 0 to 70.

### 3.5.3 Ion Chromatography for Ion Determination

Ion chromatography was used to measure concentrations of major anions, such as chloride and sulphate, as well as major cations such as sodium, calcium, and magnesium in the parts-per-billion (ppb) range.

- The ion chromatography machine used is *Dionex ICS-3000* and it uses the program Chromeleon.
- The samples from *Nano BW 4040* were diluted to 500 times its concentration, to get results that are more accurate, with distilled water using the dilution machine (**Figure 49 in Appendix 9**).
- The samples was filtered prior to evaluation with an ion chromatograph to remove sediments or other particulate matter, in addition to limit the potential for microbial variation before the sample is run. Diluted samples were collected using a sterile syringe rinsed with distilled water followed by rinsing with sample water and then filtered through 0.45 $\mu\text{m}$  (or smaller) filters. The sample was stored in marked glass tubes of 10 ml capacity and was stored cold until they were processed. The minimum sample used for analysis was approximately 5mL. The ion chromatograph machine is shown in **Figure 21**.



**Figure 21: Ion chromatography machine**

The samples were processed on the ion chromatograph for 26 hours. Each anion took 12 minutes and each cation took 30 minutes to be processed.

An ion chromatographic graph comprises of several peaks as output data. Each peak represents a separate ion from the sample solution. The elution time or the time it takes for the ion to move through the column, differs for each ion species as they elute from the column separately as the ionic strength of the eluent is increased. The concentration of the ions moving through the column at a specific time is represented by the area under each peak and can be related to the concentration of a specific species in the sample solution.

Ionic concentrations were calculated using the area under each peak, where a large area relates with a higher concentration of a particular ion species. Almost every ion chromatography machines provide software that calculates this area, which can be converted to ppm or other quantity using calibrated standard solutions. Synthetic seawater of known ionic concentration is used for comparing the ionic composition of samples. The area under the curve measured for each ion is compared with the reference area of the same ion in synthetic seawater. The composition of the synthetic seawater is shown in **Table 6**.

- The samples from **Filmtec SW 30-2540** was diluted to 200 times its concentration with distilled water using the dilution machine. The same procedure was done as above explained.

## 3.6 Chemicals Used for Sample Preparation

Chemicals were used for preparing synthetic seawater for ion chromatography and in altering the composition of the feed sample through the membrane.

### 3.6.1 Synthetic seawater

Synthetic seawater was made to use as a reference for ion chromatography analysis and is shown in **Table 6**.

**Table 6: Synthetic seawater composition**

Salt	mg/l	mole/l
NaCl	23.38	0.400
Na <sub>2</sub> SO <sub>4</sub>	3.41	0.0240
NaHCO <sub>3</sub>	0.17	0.002
KCl	0.75	0.010
MgCl <sub>2</sub>	4.24	0.0445
CaCl <sub>2</sub>	1.44	0.0129
MgCl <sub>2</sub> *6H <sub>2</sub> O	9.05	0.045
CaCl <sub>2</sub> *2H <sub>2</sub> O	1.91	0.013

### 3.6.2 Addition of Na<sub>2</sub>SO<sub>4</sub>

Total amount of 10.2 g of Na<sub>2</sub>SO<sub>4</sub> was added in the feed seawater in stages to alter the sulphate concentration in the feed.



## **Chapter 4: Results and Discussion**

Experiments were performed on normal filtered seawater. The results obtained from these experiments are discussed below.

## 4.1 Feed Properties

The main characteristics of the feed seawater used in the experiments are given below in **Table 7**.

**Table 7: Feed Characteristics**

Quality	Unit	Value
TSS	mg/l	0.000019
Turbidity	NTU	0.2523
TDS	mg/l	30200
pH		7.18

The results obtained from the TSS experiment are shown in **Table 26** in Appendix 1

### **Observations**

- TSS found to be negligible, so for further analysis on sample seawater, only TDS needed to consider.
- NTU value shows that the seawater sample have a very low turbidity. Extremely clear water can signify very acidic conditions or high levels of salinity.

## 4.2 Feed Properties of Na<sub>2</sub>SO<sub>4</sub> Sensitivity Experiments

Turbidity test results for the feed used for sensitivity analysis of NF performance with addition of Na<sub>2</sub>SO<sub>4</sub>, are presented below. The SO<sub>4</sub><sup>2-</sup> ion in the feed was increased from the base concentration level of **1.7 g/L** to **3.4 g/L** and **6.8 g/L** to evaluate the sensitivity of NF performance. The turbidity of the each feed stream indicates low range, which rules out any SO<sub>4</sub><sup>2-</sup> salt precipitation.

Turbidity of permeate and retentate samples were also tested corresponding to the case with permeate flow rate of *145 L/h*. The results obtained are shown in **Table 8**.

**Table 8: Seawater spiked with Na<sub>2</sub>SO<sub>4</sub>**

Sample	Feed original	Feed with 2x Na <sub>2</sub> SO <sub>4</sub>	Feed with 3 x Na <sub>2</sub> SO <sub>4</sub>
	NTU	NTU	NTU
Feed	0.2523	0.364	0.395
Retentate (145 L/h)		0.250	0.257
Permeate (145 L/h)		0.102	0.150

### Observations

- The turbidity of the feed samples is increasing for each case but it is still in the low range.
- There was no precipitation when seawater was spiked with sulphate.
- Very low NTU values can signify high saline or acidic conditions.

## 4.3 Nanofiltration Experiments

The performance of the NF membrane, *Nano- BW -4040*, with normal seawater has been evaluated by varying the flux. The various operating and tested quality parameters are presented in **Table 9**.

The nominal membrane area of the Nano- BW- 4040 is 7m<sup>2</sup>. The permeate flow rate was varied from 45 L/h to 145 L/h. Membrane flux is calculated by the method given in Chapter 3.

### 4.3.1 Performance Parameters with Normal Sea Water as Feed

The operating parameters and the calculated performance parameters are tabulated in **Table 9** and the material balance for the performance parameter is shown in **Table 27** in **Appendix 3**.

**Table 9: Performance parameters from NF experiments**

Flow rate (l/hr)			pH			Temperature (°C)	Conductivity(mS/cm)			Salinity			TDS(ppm)			Pressure(bar)		Flux (l/m <sup>2</sup> h)	Recovery %
Permeate	Retentate	Feed (SW)	Feed(SW)	Permeate	Retentate		Feed(SW)	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Retentate		
45	120	165	7.18	7.22	7.22	21	47.2	44.3	49	30.6	28.6	31.6	30200	28300	31300	3	3.9	6.43	27%
65	120	185	7.18	7.39	7.31	21		43.4	48.18		27.7	31.7		27800	30800	3.8	4.7	9.29	35%
80	120	200	7.18	7.34	7.41	21		42.9	49.2		27.5	31.8		27400	31500	4.5	5.6	11.43	40%
100	120	220	7.18	7.25	7.24	21		42.5	50.1		27.1	32.4		27200	32100	5.7	6.6	14.29	45%
115	120	235	7.18	7.21	7.25	21		42.8	51		27.2	33.2		27400	32600	6.6	7.5	16.43	49%
130	120	250	7.18	7.08	7.1	21		42.3	51.7		26.9	33.7		27100	33100	7.6	8.4	18.57	52%
145	120	265	7.18	7.14	7.12	21		42	51.5		26.7	33.4		26900	32900	8.2	9.1	20.71	55%

- ❖ The conductivity, salinity and TDS are measured under varying permeate flow rate.
- ❖ Pressure applied on feed, retentate and permeate is observed from the control panel.
- ❖ Flux and recovery of the membrane is calculated from the measured values

### **Ion concentration**

Ion chromatography were used to measure concentrations of major ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) required for smart water preparation, on feed, permeate and retentate samples in the parts-per-billion (ppb) range and is shown in **Table 10**.

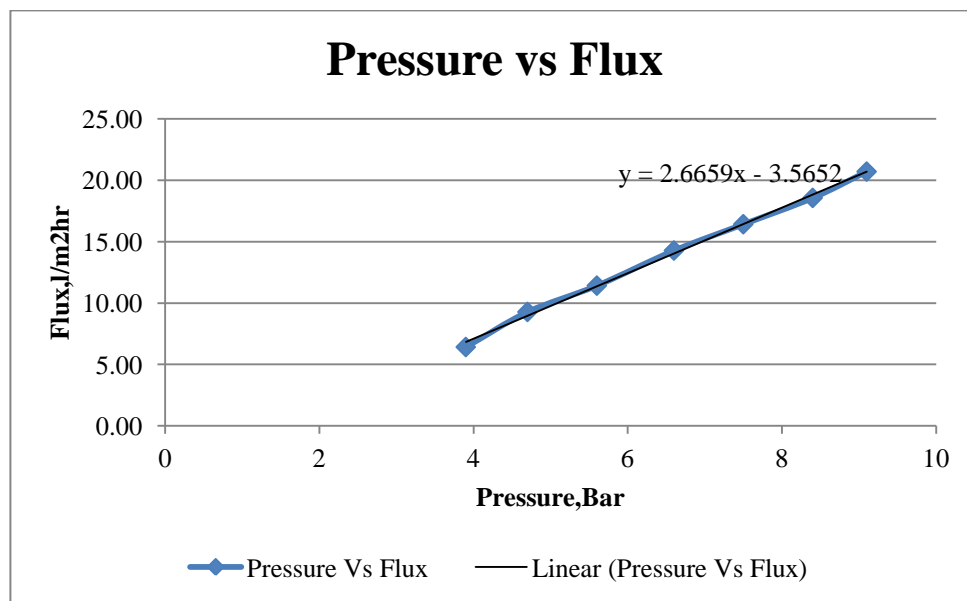
**Table 10: Concentration of individual ions calculated using ion chromatography**

Flow Rate (l/hr)	Chloride(ppm)			Sulphate(ppm)			Sodium(ppm)			Magnesium(ppm)			Calcium(ppm)			
	(Permeate)	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate
	16841			2362.0			9587.6			1249.5			410.4			
45		17647	16383		3385	53.5		9715	8931		1318	693.4		373.5	330	
65		17225	16342		3554	80.6		9718.9	9068		1340	629.1		384.3	352	
80		17825	16258		3846	27.1		9726.2	8905		1410	612.2		376.2	333	
100		21918	15644		4941	25.2		10000	8910		1787	542.3		448.6	314	
115		19277	15824		4785	26.4		10050	8872		1709	572.3		423.9	331	
130		18605	15673		4890	43.1		10500	8698		1720	507.8		437.1	275	
145		18426	15686		4745	51.7		9915	8721		1671	485.7		440.1	284	

- ❖ The material balance of each ions between the feed and the product streams are used to validate the ion chromatography results (**Table 28 - Table 32 in Appendix 4**).

### **Flux and Pressure Drop**

The calculated membrane flux values and their dependence on the pressure variations are presented in **Figure 22**.



**Figure 22: Pressure vs Flux for Nano – BW- 4040**

- ❖ The material balance across the membrane has been used to validate the flow rates, which are presented in **Table 27 in Appendix 3**.

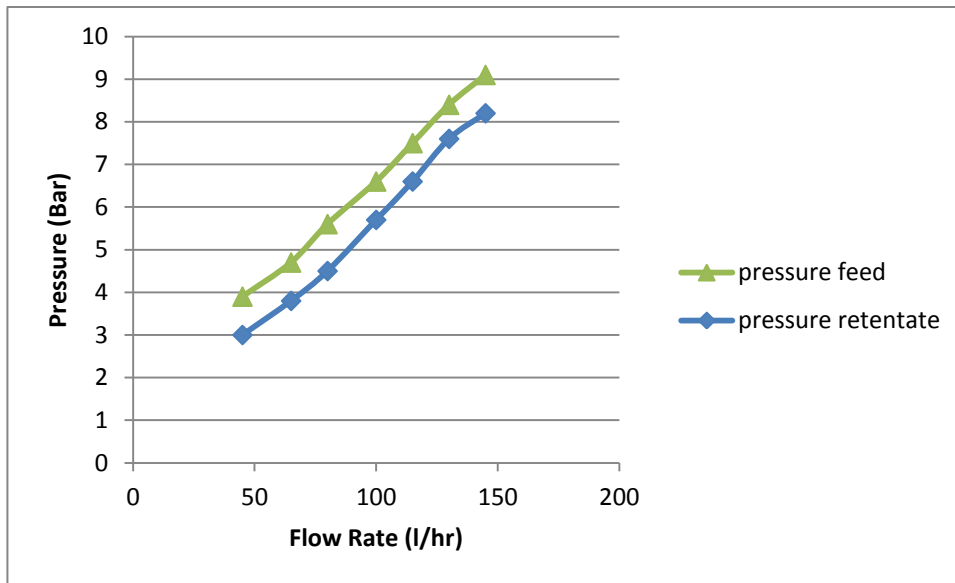
### **Observation**

- The flux increase linearly with increasing operating pressure, a typical characteristics of NF membrane
- The sharp slope of the flux curves indicates the characteristics of the NF membrane for high sensitivity of pressure on flux.
- The resistance to flow through the membrane is in the low range due to the wide pores compared to an RO.

- The operating pressure is much lower than the osmotic pressure of the feed stream since the NF membrane performance does not depend on osmotic pressure but rather on sieving of the ions.

### **Feed Pressure and Retentate Pressure**

The feed pressure and retentate pressure is plotted in **Figure 23**.



**Figure 23: Flow rate vs Pressure for SW with no spiking of sulphate**

- ❖ The pressures are measured at the feed inlet to the membrane and at the exit of retentate from the membrane.

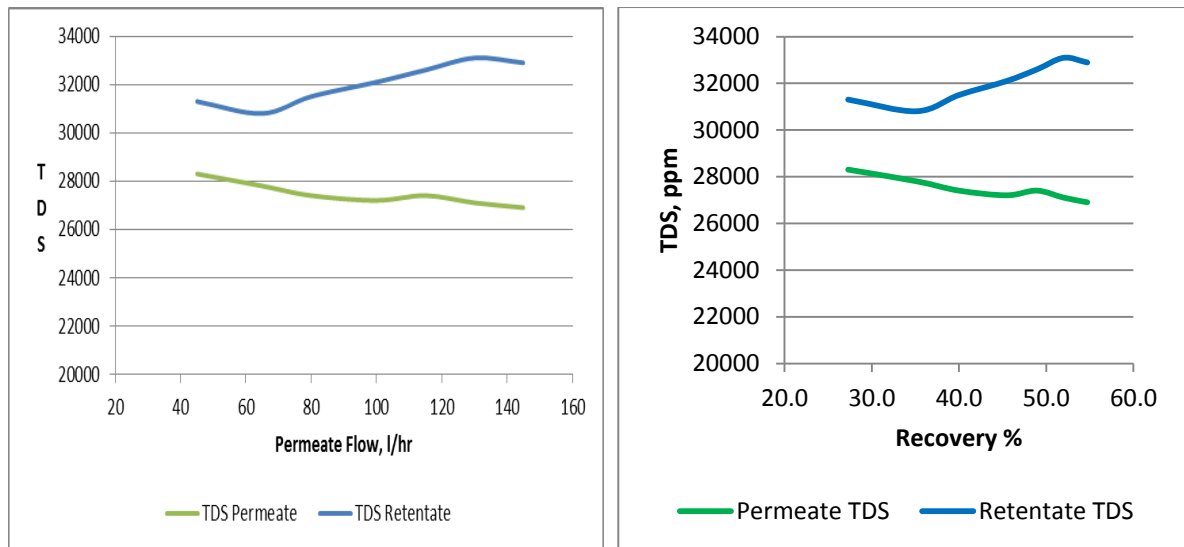
### **Observation**

- The difference between the pressures is the pressure loss in the membrane.
- The value is almost constant at around 1 bar since the retentate flow has been constant over the variation in flux (**Table 9**).
- The pressure difference should have increased at constant flux due to fouling on running the membrane for long duration. The current experiments were short duration and hence there is no fouling observed on the membrane.

### **Recovery and TDS**

The TDS of the samples is plotted against the permeate flow rate and recovery in **Figure 24**





**Figure 24: TDS vs Permeate flow rate and Recovery**

- Recovery is the ratio of permeate to feed in percentage.

### **Observation**

- The figure shows that with an increase in permeate flow rate, the TDS of the retentate first decreases and then reaches a peak and then decrease again.
- TDS of retentate maintains high level due to the effect of ions getting concentrated by lose of water through permeate.
- The peak in both figures can be due to the effect of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  since these ions shows a change in rejection (**Figure 25** [rejection] at the corresponding flow rates).

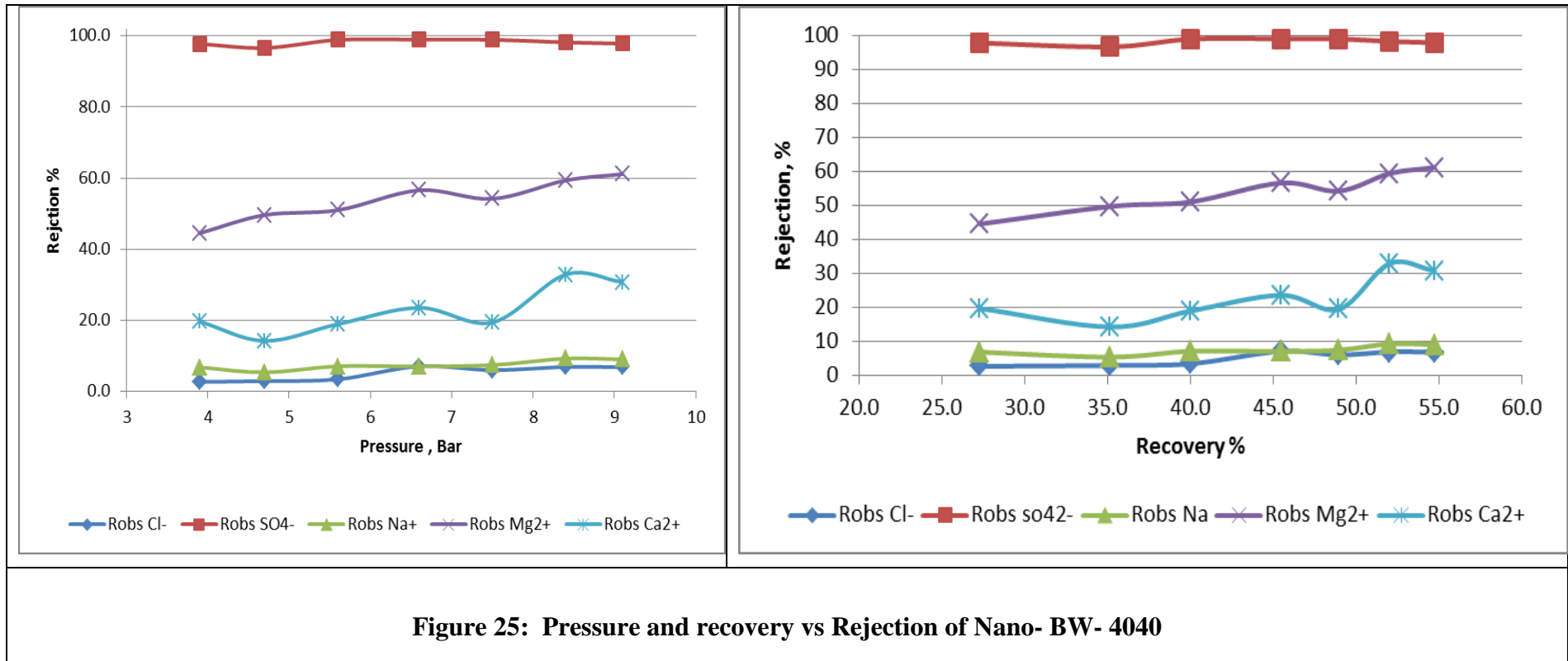
### **Rejection of Ionic Components**

The study of rejection of various ions is the focus in the report due to its importance in the design of smart water. The individual ion detection has been done for the permeate and retentate samples collected at various flux using ion chromatography. The ions in the feed also have been analysed. The pressure and rejection of ions are tabulated in **Table 11**.

**Table 11: Pressure vs Membrane rejection for Nano- BW- 4040**

Pressure, Bar	Rejection %				
	Chloride	Sulphate	Sodium	Magnesium	Calcium
3.9	2.7	97.7	6.9	44.5	19.7
4.7	3.0	96.6	5.4	49.7	14.3
5.6	3.5	98.9	7.1	51.0	19.0
6.6	7.1	98.9	7.1	56.6	23.6
7.5	6.0	98.9	7.5	54.2	19.5
8.4	6.9	98.2	9.3	59.4	32.9
9.1	6.9	97.8	9.0	61.1	30.7

The rejection of the membrane Nano- BW- 4040 vs pressure and recovery is plotted in **Figure 25**.



**Observation**

- From **Figure 25**, rejection of sulphate ions (divalent) is highest and that of monovalent chloride ions is the lowest, a typical characteristics of NF membranes
- The retention of the ions depends on the salt diffusion coefficient in water or molecular dimensions of hydrated ions. With reference to **Table 2**, the dimensions of the hydrated ions show that  $\text{Na}^+$  and  $\text{Cl}^-$  are smaller than  $\text{SO}_4^{2-}$ . This explains the low retention of  $\text{Na}^+$  and  $\text{Cl}^-$  and high retention of  $\text{SO}_4^{2-}$ .
- The small size and lower hydration energy (**Table 2**) helps  $\text{Na}^+$  to permeate easily even at lower pressure (diffusion controlled).
- The wide gap between sulphate and chloride retention is due to the following factors tabulated in **Table 12**.

**Table 12: Parameters affecting sulphate and chloride retention**

Parameters	Sulphate	Chloride	Retention Favors
Stoke radius	High	Low	Sulphate
Hydration energy	High	Low	Sulphate
Negatively charged membrane affinity	Favorable	Favorable	Chloride
Valency	High	Low	Sulphate

- Due to the comparatively higher size of  $\text{SO}_4^{2-}$  and the repulsive force from the negatively charged NF membrane, the retention is highest for sulphate ions.
- Then small sized chloride passes through the membrane pores and it maintains the charge balance. The retention should be lowest in order to satisfy the charge balance (to balance the high permeation of the counter ion,  $\text{Na}^+$  and high retention of co ion,  $\text{SO}_4^{2-}$ ) requirements.

- The above phenomenon is according to the mechanism of separation defined in Donnan exclusion theory (Gawaad, Sharma and Sambhi, 2011).
- The cations,  $Mg^{2+}$  and  $Ca^{2+}$  are retained based on comparatively higher sizes and in order to satisfy the charge balance to combine with retained  $SO_4^{2-}$  ions.
- However, the positive charge of the divalent cations creates a strong attractive force towards the negatively charged membrane and hence the retention is not at the highest level for  $Mg^{2+}$  and  $Ca^{2+}$ .
- The  $Mg^{2+}$  and  $Ca^{2+}$  also help in maintaining the electro neutrality condition to balance the excess counter ions,  $Cl^-$  in the permeate.
- Higher water flux leaves more ions behind during cross- flow. Salt rejection increases gradually with increasing the applied pressure. This can be explained by considering the salt transport through the membrane because of diffusion and convection, which occurs due to a concentration and pressure gradient across the membrane.

The higher-pressure helps to overcome the hydration energy (Table 2) required for the ions to break away from the solvent and move towards the pores of the NF membrane.

This explains the reason for increase in retention of  $Mg^{2+}$  and  $Ca^{2+}$  at higher pressures. The higher energy available from the convective force helps the solute ions to breaks away the bonding with solvent. Hence, the retention of ions increases and solvent permeates (higher flux and recovery).

- Rejection of  $Ca^{2+}$  ions is lower than that of  $Mg^{2+}$  ions. The lower rejection of  $Ca^{2+}$  compared to  $Mg^{2+}$  could be due to the lower Stock radius, lower hydration energy (Table 2) and higher affinity of  $Ca^{2+}$  towards the membrane.

The lower rejection of  $Ca^{2+}$  can also be explained according to Donnan exclusion theory. The negatively charged membrane will highly repel divalent anions such as  $SO_4^{2-}$  and results in poor retention of the counter ions such as  $Ca^{2+}$  (Ahmad et.al. 2004).

- *These results shows that the separation properties of the NF membranes are very selective and determined by the co- effect of the sieving effect through the nano-sized pores and the Donnan exclusion caused by the surface charge of NF membrane.*

### 4.3.2 Effect of Feed Ion Concentration on Membrane Properties

The sulphate concentrations in the feed have been increased, to two times and later to three times its concentration in seawater, by the addition of  $\text{Na}_2\text{SO}_4$ . This results in an increase in concentration of both sodium and sulphate in the feed samples when compared to normal seawater concentration.

#### A. *Seawater spiked with two times sulphate*

The objective was to investigate if there is any effect of added chemicals, on the behaviour of other ions as well as to observe membrane separation and its properties. The characteristic values obtained from analytical methods are shown in **Table 13**.

**Table 13: Performance parameters of addition of 2 \*SO<sub>4</sub><sup>2-</sup> on normal seawater**

Flow rate (l/hr)			Flux (lmh)	pH		Temperature (°C)	Conductivity(mS/cm)			Salinity			TDS(ppm)			pressure(bar)		Recovery %	
	Permeate	Retentate		Feed(SW)	Feed(SW)		Permeate	Retentate	Feed(SW)	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate		Retentate
80	120	200	11.4	6.96	6.97	6.94	21	50.2	44.8	52.5	32.7	28.7	34.2	32100	28700	33600	5.7	6.6	40%
100	120	220	14.3	6.96	7	7	21	50.2	43.8	53.2	32.7	27.9	34.8	28000	28000	34000	7	7.9	45%
115	120	235	16.4	6.96	7	6.99	21	50.2	43.6	53.7	32.7	27.8	34.9	27900	27900	34400	7.9	8.7	49%
130	120	250	18.6	6.96	6.98	6.98	21	50.2	43.3	54.1	32.7	27.6	35.4	27700	27700	34600	8.9	9.8	52%
145	120	265	20.7	6.96	7.04	7.03	21	50.2	42.9	54.6	32.7	27.4	35.8	27400	27400	34900	9.6	10.5	55%

- Added amount of  $\text{Na}_2\text{SO}_4 = 3.4 \text{ g/L}$  of seawater
- The mass balance for the above experiment is presented in **Table 34** is given in **Appendix 5**.

### Rejection of Ions

The calculated individual ion concentration is presented in **Table 14**.



**Table 14: Ion chromatography results with addition of  $2 \cdot \text{SO}_4^{2-}$  in the feed**

Flow Rate (l/hr)	Chloride(ppm)			Sulphate(ppm)			Sodium(ppm)			Magnesium(ppm)			Calcium(ppm)			
	(Permeate)	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate
		17184			6034.31			11012.41			1149.28			384.64		
80			17522	16840		8457	68.26		11503	9927		1444	462.85		410	231
100			17691	16806		9002	39.97		11505	9721		1499	392.69		424	213
115			17650	16403		9573	37.51		11664	9872		1600	368.27		439	226
130			17690	16513		9895	40.59		11717	9791		1620	385.75		448	234
145			18411	16450		10579	59.03		11918	9928		1683	343.60		449	241

Rejection rate of ions when spiked with two times sulphate is shown in **Table 15**.

**Table 15: Permeate flow vs Ion rejection for SW spiked with 2 \*SO<sub>4</sub><sup>2-</sup>**

Permeate Flow rate(L/hr)	Rejection %				
	Chloride	Sulphate	Sodium	Magnesium	Calcium
80	2.0	99.6	9.9	59.7	40.0
100	2.2	99.8	11.7	65.8	44.5
115	4.5	99.8	10.4	68.0	41.2
130	3.9	99.8	11.1	66.4	39.1
145	4.3	99.7	9.8	70.1	37.3

***B. Seawater spiked with 3 times sulphate***

Sulphate concentration on the feed was tripled on the third stage, to check if an increase in concentration of one sample has any effect on the separation of other constituents in the feed, as well as to observe any effect on membrane separation and its properties.

The characteristic values obtained from analytical methods are shown in **Table 16**.

**Table 16: Performance parameters with addition of 3\*SO<sub>4</sub><sup>2-</sup> in feed seawater**

Flow rate (l/hr)			Flux (lmh)	pH			Temperature (°C)	Conductivity(mS/cm)			Salinity			TDS(ppm)			pressure(bar)		Recovery %
Permeate	Retentate	Feed(SW)		Feed(SW)	Permeate	Retentate		Feed(SW)	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Retentate	
80	120	200	11.4	7.06	7.06	7.06	21	52.7	45.8	55.3	34.4	29.4	36.5	33700	29300	35400	6.7	7.6	40%
100	120	220	14.3	7.06	7.07	7.07	21	52.7	45.1	55.8	34.4	28.9	36.8		28900	35700	8	8.9	45%
115	120	235	16.4	7.06	7.06	7.04	21	52.7	44.8	56.4	34.4	28.6	37.2		28700	36100	8.8	9.7	49%
130	120	250	18.6	7.06	7.06	7.05	21	52.7	44.5	56.8	34.4	28.5	37.8		28500	36300	9.7	10.7	52%
145	120	265	20.7	7.06	7.07	7.08	21	52.7	43.9	57.9	34.4	28.1	38.3		28100	37000	10.7	11.5	55%

- Added amount of Na<sub>2</sub>SO<sub>4</sub> = 6.8 g/L of seawater
- The mass balance for three times spiked sulphate values are presented in **Table 35** in **Appendix 6**.

The individual ion concentrations calculated using chromatography readings are presented in **Table 17**.

**Table 17: Ion chromatography results with addition of 3\*SO<sub>4</sub><sup>2-</sup> in feed**

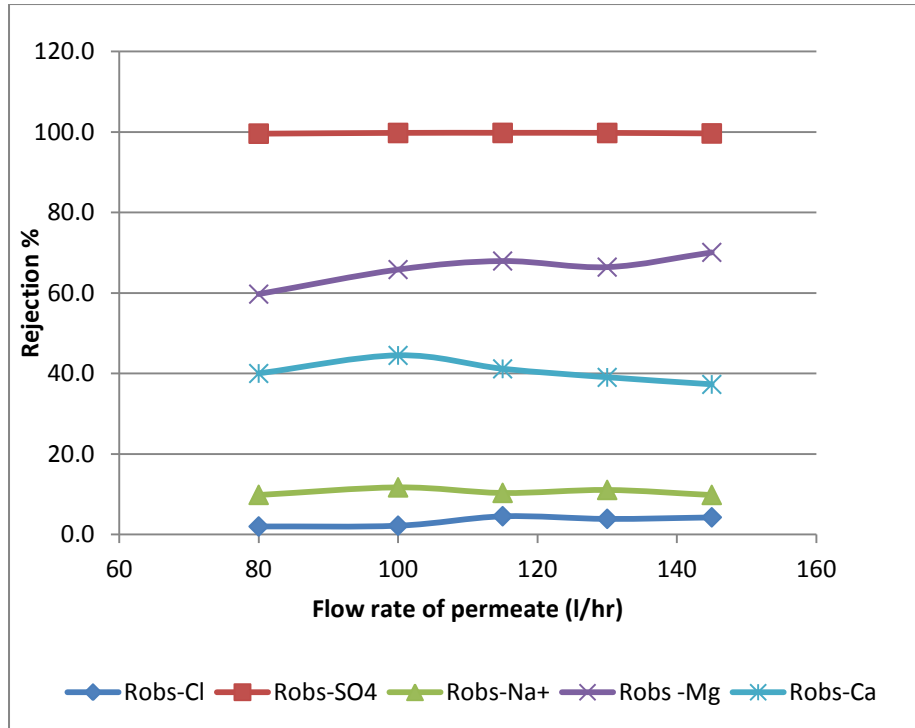
Flow Rate (l/hr)	Chloride(ppm)			Sulphate(ppm)			Sodium(ppm)			Magnesium(ppm)			Calcium(ppm)			
	(Permeate)	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate
		16774			8767			11679			1076			344		
80			17010	16096		12312	30		12185	9375		1534	462		402	246
100			17668	16405		13386	35		12695	9840		1533	437		422	273
115			17459	15778		13996	36		12763	9527		1602	421		414	257
130			17466	15996		14485	30		13209	9439		1646	378		452	246
145			17501	16398		15458	46		13715	9361		1743	503		439	258

Rejection rate of ion when spiked with three times sulphate is shown in **Table 18**.

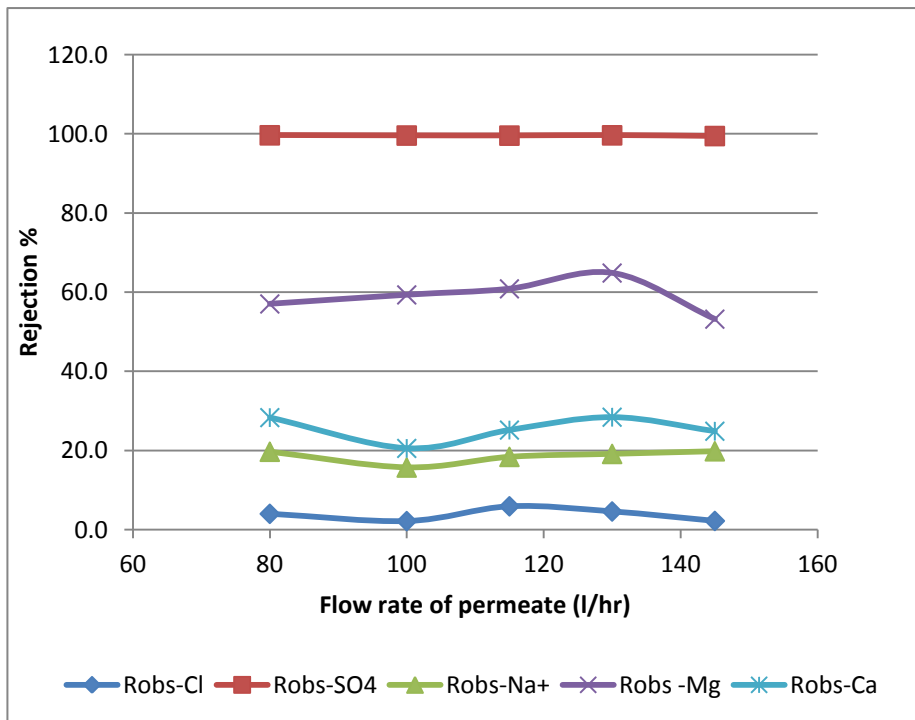
**Table 18: Rejection with addition of 3 times sulphate on seawater**

Permeate Flow rate(l/hr)	Rejection %				
	Chloride	Sulphate	Sodium	Magnesium	Calcium
80	4.0	99.7	19.7	57.1	28.3
100	2.2	99.6	15.7	59.4	20.6
115	5.9	99.6	18.4	60.9	25.2
130	4.6	99.7	19.2	64.9	28.4
145	2.2	99.5	19.8	53.2	24.9

The membrane rejection (Robs) % of ions in spiked seawater is plotted in **Figure 26** and **Figure 27**.

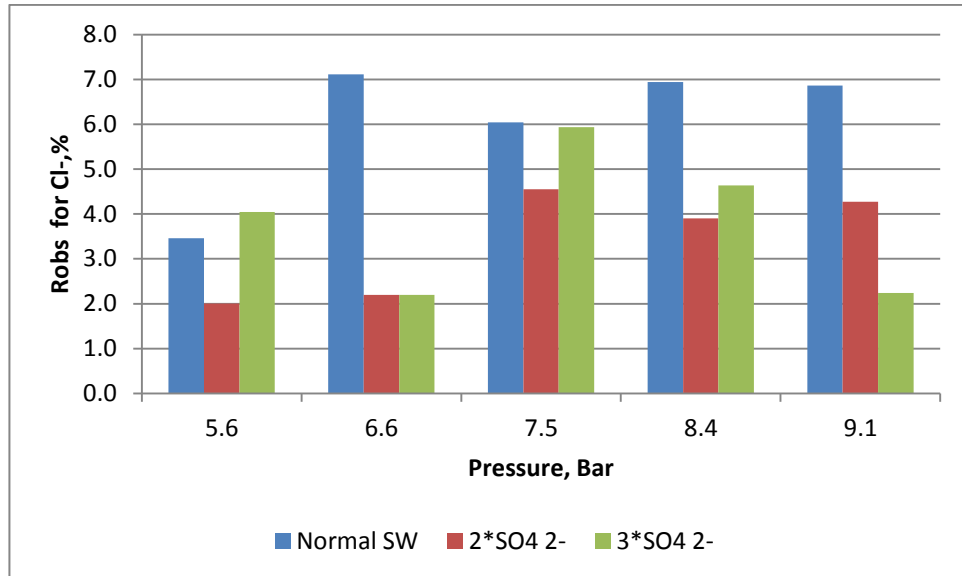


**Figure 26: Permeate flow rate vs Rejection for 2\* SO<sub>4</sub><sup>2-</sup>**



**Figure 27: Permeate flow rate vs Rejection for 3\* SO<sub>4</sub><sup>2-</sup>**

The rejection of monovalent ion,  $\text{Cl}^-$ , by the membrane Nano BW 4040, with increase in  $\text{Na}_2\text{SO}_4$  concentration, is plotted as a function of the operating pressure and is shown in **Figure 28**.



**Figure 28: Rejection of  $\text{Cl}^-$  ions in normal,  $2 \times \text{SO}_4^{2-}$ ,  $3 \times \text{SO}_4^{2-}$  seawater**

**Figure 28** presents the rejection of  $\text{Cl}^-$  ions at different concentrations of  $\text{SO}_4^{2-}$  in feed against the operating pressure for Nano- BW- 4040.

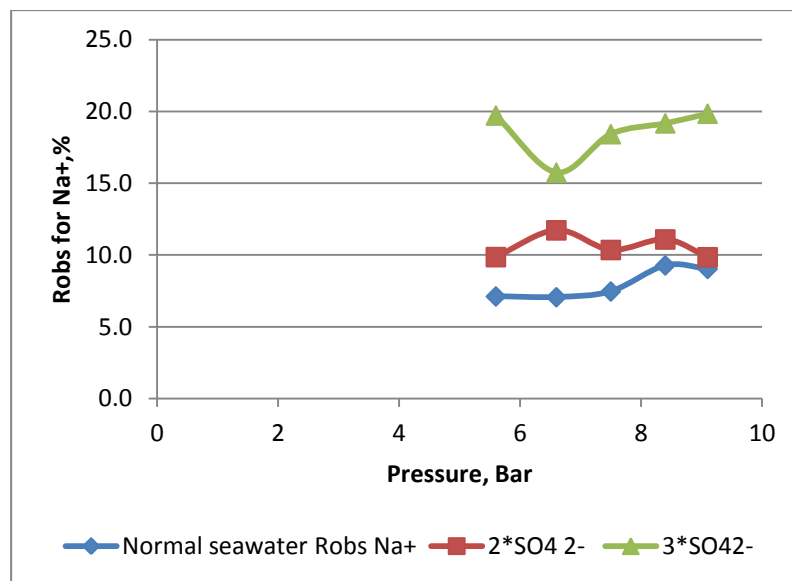
### Observations from the change in feed concentrations

- As observed from the **Figure 28**, the increase in  $\text{SO}_4^{2-}$  concentration leads to a decrease in  $\text{Cl}^-$  retention. *This seems that the presence of a high valence anion such as  $\text{SO}_4^{2-}$  drives more chloride into the membrane, thus decreasing its retention (Krieg et al. 2004).*
- There is an indication that the effect of membrane charge is being eliminated when the salt concentration is high enough (Scheap and Vandecastle, 2001). **Figure 26**, **Figure 27** and **Figure 28** shows that there is high rejection of ions at lower feed concentration and lower rejections at higher feed concentration, which are *characteristics of charged membrane (Peeters et.al. 1998)*. This confirms that NF membranes retentions are dependent on the feed concentration.

- When charge effects of the membrane play no role, it is assumed that ion diffusion is not hindered anymore and no steric hindrance is taken into account resulting in lower rejection of monovalent anions (Cl<sup>-</sup>) (Schaep and Vandecastle, 2001).
- Cl<sup>-</sup> retention decreases when the salt concentration increases. One reason is to maintain electro neutrality when divalent cation is permeated through the membrane (i.e. for every one Ca<sup>2+</sup> ion, two chloride ions have to be retained). However, with increases in sulphate concentration, sulphate effectively balances the calcium charge, resulting in a decrease in Cl<sup>-</sup> retention (Krieg et al. 2004).

### Sodium ion rejection

The membrane rejection (R<sub>obs</sub>) % for sodium ions is plotted below in **Figure 29**

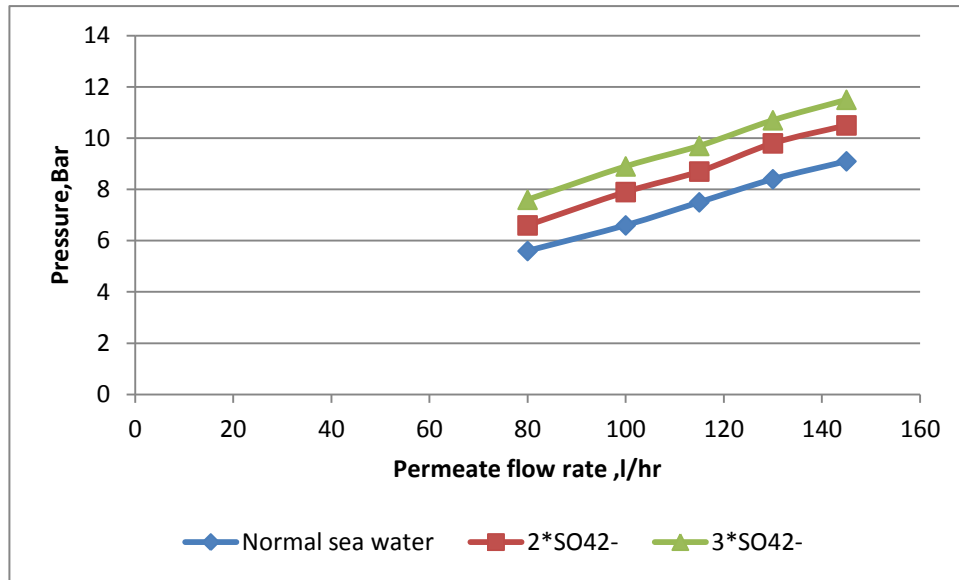


**Figure 29: Rejection of Na<sup>+</sup> ions in normal, 2\*SO<sub>4</sub><sup>2-</sup>, 3\* SO<sub>4</sub><sup>2-</sup> seawater**

From **Figure 29**, an increase in Na<sup>+</sup> rejection can be observed when normal seawater is spiked with sulphate. This can be due to the increase in sodium concentration, together with an increase in sulphate concentration, when Na<sub>2</sub>SO<sub>4</sub> is added to seawater.

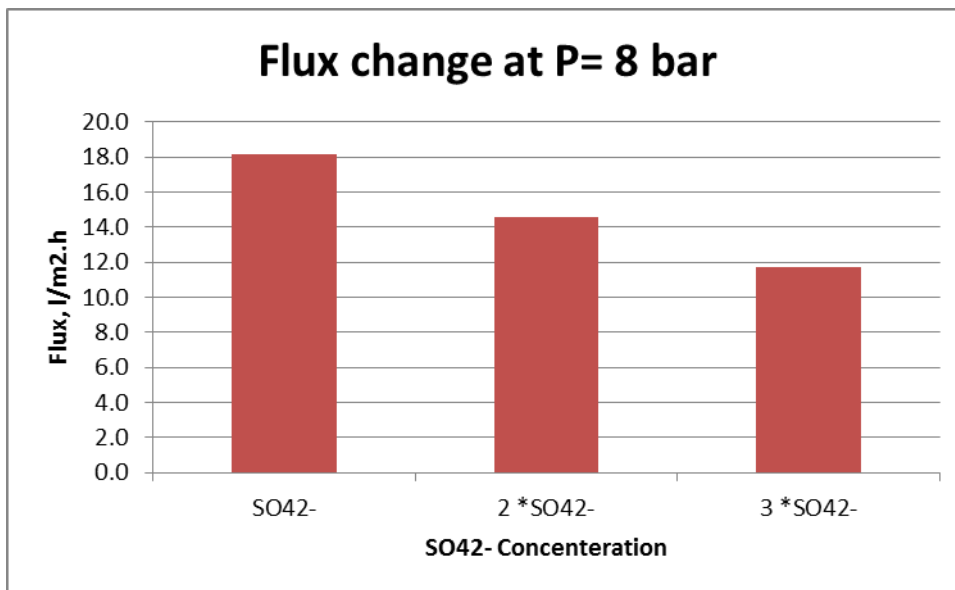
**Pressure vs Permeate flow rate**

The Pressure vs Permeate flow rate of all the three cases i.e. normal seawater, two times spiked and three times spiked seawater is plotted in **Figure 30**.



**Figure 30: Pressure vs Permeate flow rate for 3 cases**

The permeate flow is read from the **Figure 30** at a constant pressure (**8 bar**) and plotted below in **Figure 31** to show the effect of flux due to the  $SO_4^{2-}$  concentration change.



**Figure 31: Flux change Vs  $SO_4^{2-}$  concentration change**

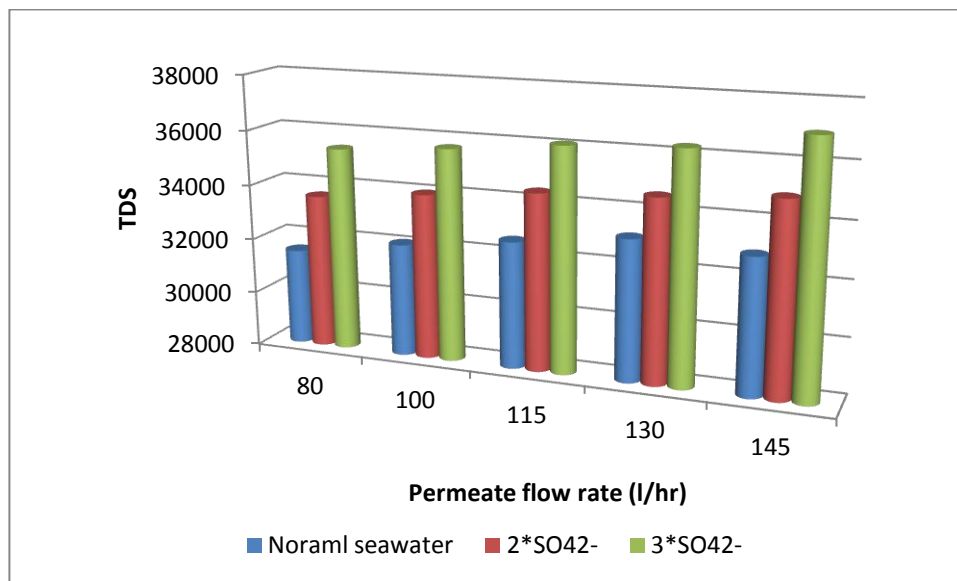


### Observation

- **Figure 30** shows that there is increase in pressure; at same permeate flow rates, with spiking of sulphate in normal seawater. In other words, the flux decreases as the concentration of  $SO_4^{2-}$  in the feed increases (**Figure 31**).
- The decrease in flux indicates an increase in resistance which could be due to membrane pore size reduction (concentration polarization), and change in physical property of solution (density and viscosity).

### Comparison of TDS for three samples

The measured **TDS** of retentate of normal seawater, twice and thrice spiked with sulphate retentate are plotted in **Figure 32**.



**Figure 32: Permeate flow rate vs TDS of three samples**

From **Figure 32**, it can be observed that the TDS level of the retentate increases with addition of  $Na_2SO_4$ , which is mainly due to the increase in feed TDS and lower rejection.

### 4.3.3 Summary of NF Experiment Analysis

- *The TDS in retentate still maintains high level (almost the level in feed) since the ions are getting concentrated due to the loss of water through permeate.*
- *NF is very selective due to the size and charge exclusion mechanism and the effect of operating parameters on these mechanisms.*
- *The selectivity of NF membrane to retain divalent ion is a favorable characteristics for smart water production.*
- *The low operating pressure of NF process makes it less energy intensive option.*

## 4.4 Reverse Osmosis (RO) Membrane Experiments

The results from RO membrane experiments are used to evaluate the option of mixing NF retentate with RO permeate for production of smart water. Performance of the RO membrane with normal seawater has been measured under different operating pressures. The RO membrane used is *Filmtec SW 30-2540*.

### 4.4.1 Experiment Results

The observed and calculated performance parameters of RO membrane at varying pressure are presented in **Table 19**.

**Table 19: Performance data of Feed, Retentate and Permeate at varying pressure**

Pressure (bara)	pH			Temperature (°C)	TDS(ppm)			Conductivity(mS/cm)			Salinity			Flow Rate (l/hr)			Flux (l/m <sup>2</sup> hr)
	Feed(SW)	Permeate	Retentate		Feed(SW)	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Feed(SW)	Permeate	Retentate	Permeate	Retentate	
	7.18			20.3	30,200			49			31.7						
25		7.5	8.0	20.3		4730	31,800		7.39	49.7		4.1	32.3	14.8	225.0	239.8	5.3
30		7.6	8.0	20.3		3890	32,000		6.08	50		3.3	32.6	30.0	225.0	255.0	10.7
35		7.7	8.1	20.4		2450	32,200		3.83	50.3		1.7	32.7	34.6	225.0	259.6	12.4
40		7.6	8.0	20.1		1620	33100		2.53	51.76		1.2	33.86	52.3	225.0	277.3	18.7

#### 4.4.1.1 Membrane Flux

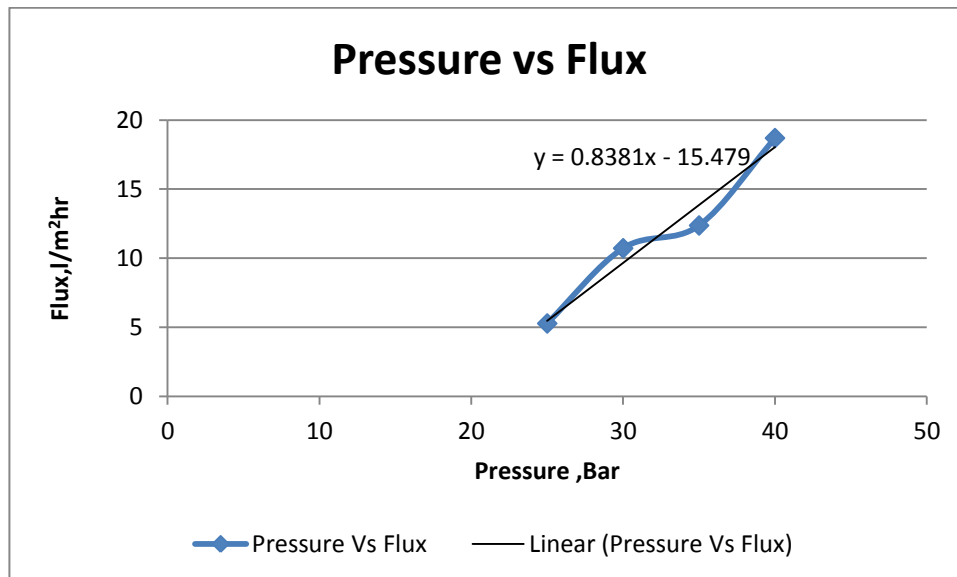
Membrane flux is calculated using the formula,

$$\text{Membrane Flux (J)} \left[ \frac{\text{L}}{\text{m}^2\text{hr}} \right] = \frac{\text{Permeate flow rate (L/hr)}}{\text{Nominal membrane area (m}^2\text{)}}$$

- ❖ For pressures below 25 bars, the flux was extremely low to be measured.
- ❖ Pressure applied to the membrane was lower than the osmotic pressure exerted by seawater resulting in no permeate.
- ❖ The feed pressure applied should be higher than the osmotic pressure, characteristic of an RO membrane.

The mass balance for the above experiment is shown in **Table 36** in **Appendix 8**.

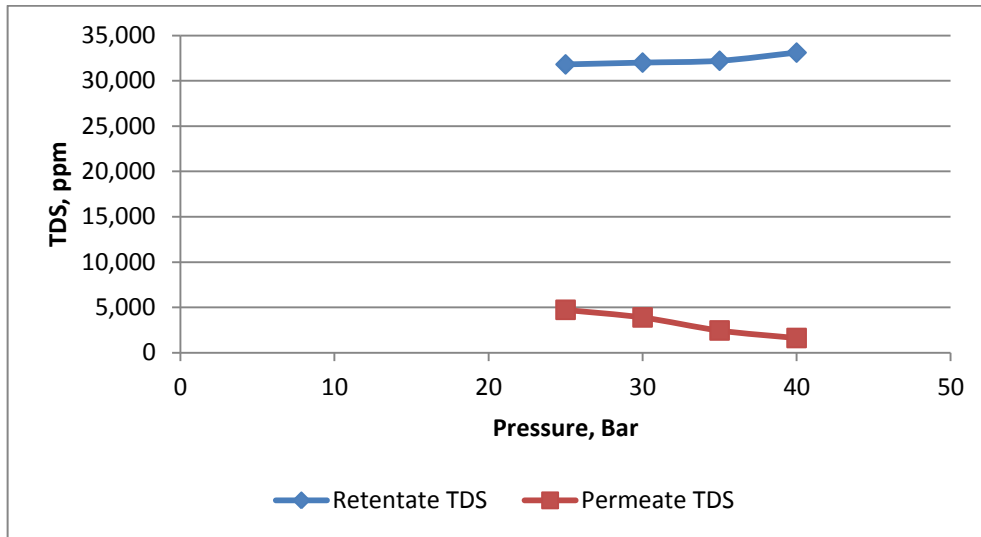
The obtained membrane flux values and their dependence on varying pressure are presented in **Figure 33**.



**Figure 33: Pressure vs Flux for Filmtec SW 30 - 2540**

- ❖ Pressure applied on RO membrane is greater than the osmotic pressure of seawater

Pressure vs TDS of retentate and permeate from the RO membrane is shown in **Figure 34**.



**Figure 34: Pressure vs TDS from Filmtec SW 30 - 2540**

- ❖ TDS of permeate from SW 30 2540 is very low in the range of 1500-4700 ppm approximately.
- ❖ TDS of retentate is almost the same as that of the feed TDS. This is due to the loss of water through the permeate resulting in concentrating the dissolved solids in the retentate.

#### 4.4.1.2 Rejection of Ionic Components

The performance of the membranes is evaluated using ion retention at different operating conditions (varying the pressure, change in permeate flux) and the characteristics of the membranes are compared.

Ion chromatography were used to measure concentrations of major ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) required for smart water preparation ,on feed , permeate and retentate samples in the parts-per-billion (ppb) range and is shown below in **Table 20**.

Concentration of sulphate was not able to determine due to the absence of sulphate in reference synthetic seawater.

**Table 20: Composition of ions when SW30- 2540 membrane is used**

Pressure(Bar)	Chloride(ppm)			Sodium(ppm)			Magnesium(ppm)			Calcium(ppm)		
	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate	Feed SW	Retentate	Permeate
	14229.4			8578.5			1011.4			322.4		
25		16460.4	1453.4		10240.4	1543.8		1212.2	0.4		416.9	31.0
30		16843.4	966.0		10335.9	883.4		1257.6	24.1		414.3	23.2
35		17514.5	721.8		10760.9	1073.3		1304.3	10.5		428.4	16.6
40		17535.5	585.9		10610.1	856.7		1292.0	9.0		422.7	20.6

Rejection rate calculated from the ionic chromatography values is presented in **Table 21**.

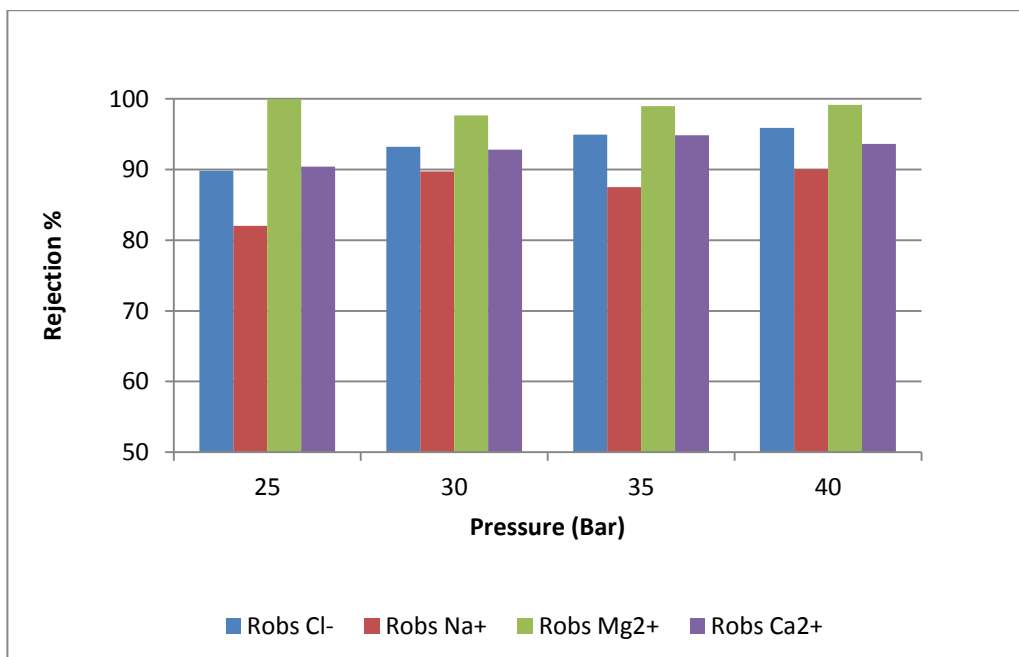
**Table 21: Pressure vs Membrane rejection for SW 30- 2540**

Pressure(Bar)	Rejection %			
	Cl-	Na+	Mg <sup>2+</sup>	Ca <sup>2+</sup>
25	89.7	82.0	99.9	90.3
30	93.2	89.7	97.6	92.8
35	94.9	87.4	98.9	94.8
40	95.8	90.0	99.1	93.5

Following assumptions were made from the above results:

- Magnesium, calcium and chloride ions are having the highest rejection of above 90%.
- Very less concentration of ions are present in permeate.
- The TDS of the permeate is low enough to use as potential mixing constituent to produce smart water.

The rejection of the RO membrane for seawater is plotted against the operating pressure as shown in **Figure 35**.



**Figure 35: Pressure vs Membrane rejection for Filmtec SW- 30- 2540**

From **Figure 35** it is obvious that rejections increases with the increasing operating pressure and in some cases reach a threshold.

- Ion rejection efficiency increases with operating pressure because the water flux increases linearly with increase in operating pressure while permeation of ion is only a function of feed concentration and is independent of the operating pressure (Ahmed et al, 2004).
- The rejection of most of the ions are higher at all pressures for Filmtec SW 30 2540 which indicates very less permeation of ions in the RO membrane.

#### 4.4.1.3 Recovery

The recovery of the membrane Filmtec SW 30-2540 is shown is tabulated in **Table 22**.

**Table 22: Recovery of SW 30 2540**

Pressure (Bar)	Permeate flow rate(l/hr)	Feed flow rate(l/hr)	Recovery %
25	14.8	239.8	6.2
30	30.0	255.0	11.8
35	34.6	259.6	13.3
40	52.3	277.3	18.9

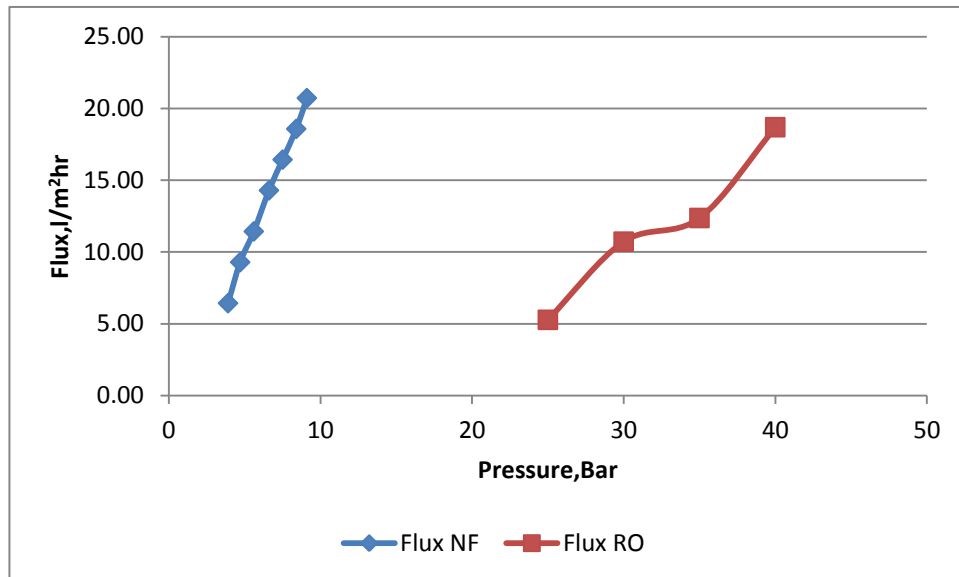
## 4.5 Comparison between NF and RO

The experiments done with NF membrane and RO membrane are compared below to help understand how the combination works.



### 4.5.1 Effect on Flux

The effect of pressure on the flux for both the membranes is shown in **Figure 36**.



**Figure 36: Flux vs Pressure for NF and RO**

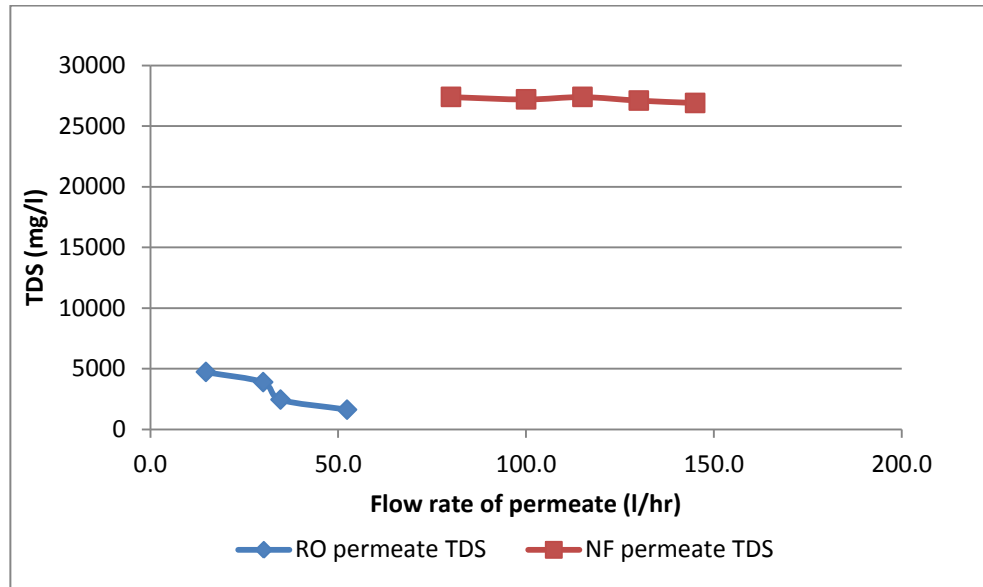
- ❖ For an approximate flux of  $20 \text{ L/m}^2\text{hr}$ , the pressure applied is higher for RO and lower for NF membranes
- ❖ The relation between flux and pressure is linear for NF membranes.

#### **Observation**

- High flux at low pressure is advantageous when large quantity of water needs to be treated.
- Resistance to flow through the membrane is high for RO and low for NF.
- Recovery from the RO membrane is very low (i.e. from 6-19 %) at higher pressure when compared with the NF membrane, which have higher recovery (i.e. from 27-55 %) at a lower pressure. This low recovery makes the RO process less economical.

### 4.5.2 Effect on TDS

The comparison for the membranes on TDS as a function of permeate flow rate is shown in **Figure 37**.



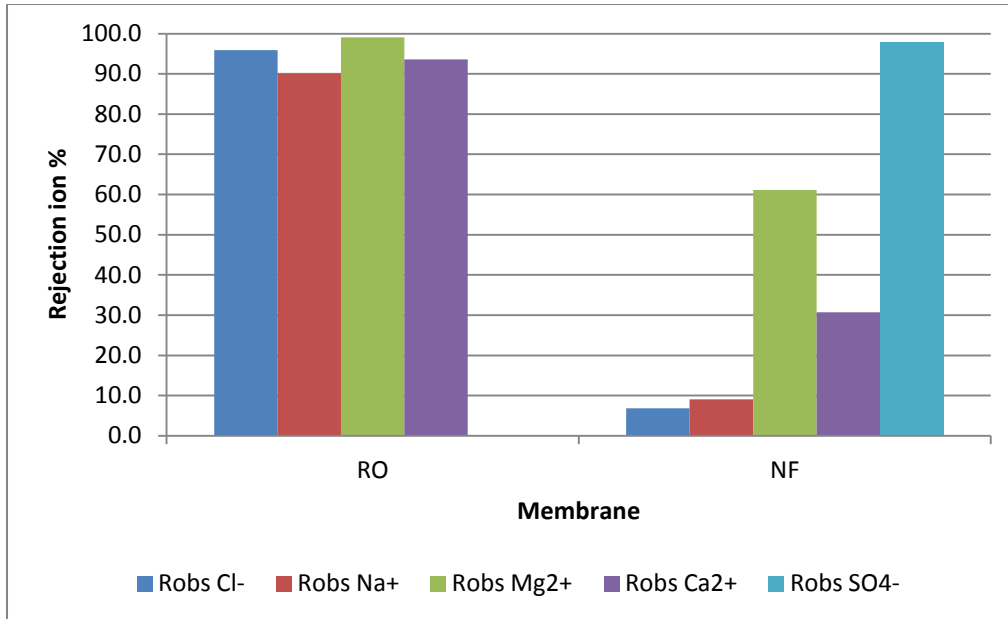
**Figure 37: TDS vs permeate flow rate**

#### Observation

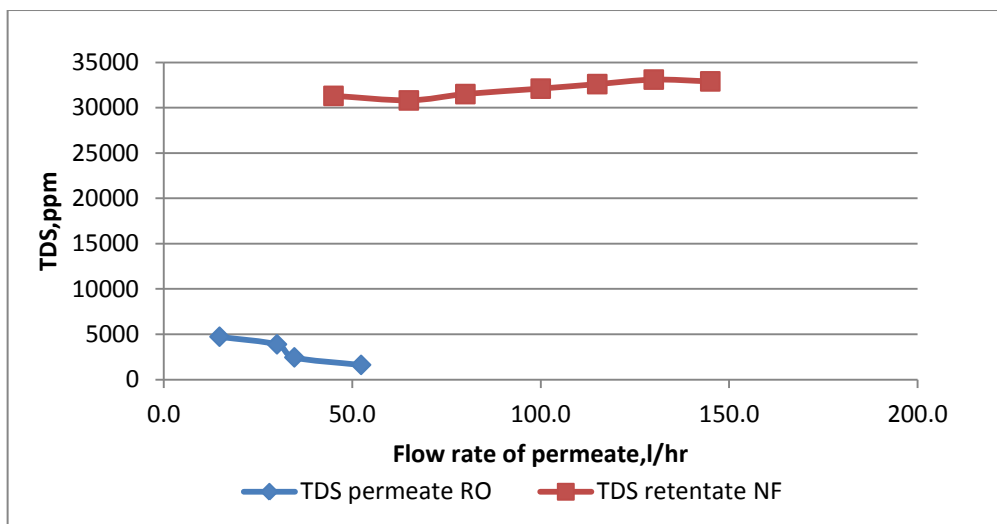
- ❖ RO permeate TDS level is very low due to higher rejection of all ions in the feed.
- ❖ The TDS of permeate from NF is almost the same as that of feed seawater.

### 4.5.3 Membrane Ion Rejection Comparison

The ion rejections of NF and RO membranes are compared in **Figure 38**.



**Figure 38: Membrane ion rejection comparison**



**Figure 39: Combination of TDS of NF retentate and RO permeate**

**Observation**

- ❖ TDS of permeate from RO is very low compared to TDS of retentate from NF in **Figure 39**.
- ❖ The RO permeates mostly only the solvent and much of the solutes are rejected from the membrane, which makes the low TDS of permeate.
- ❖ The TDS level of feed and the product streams of NF do not have the wide difference as in RO.

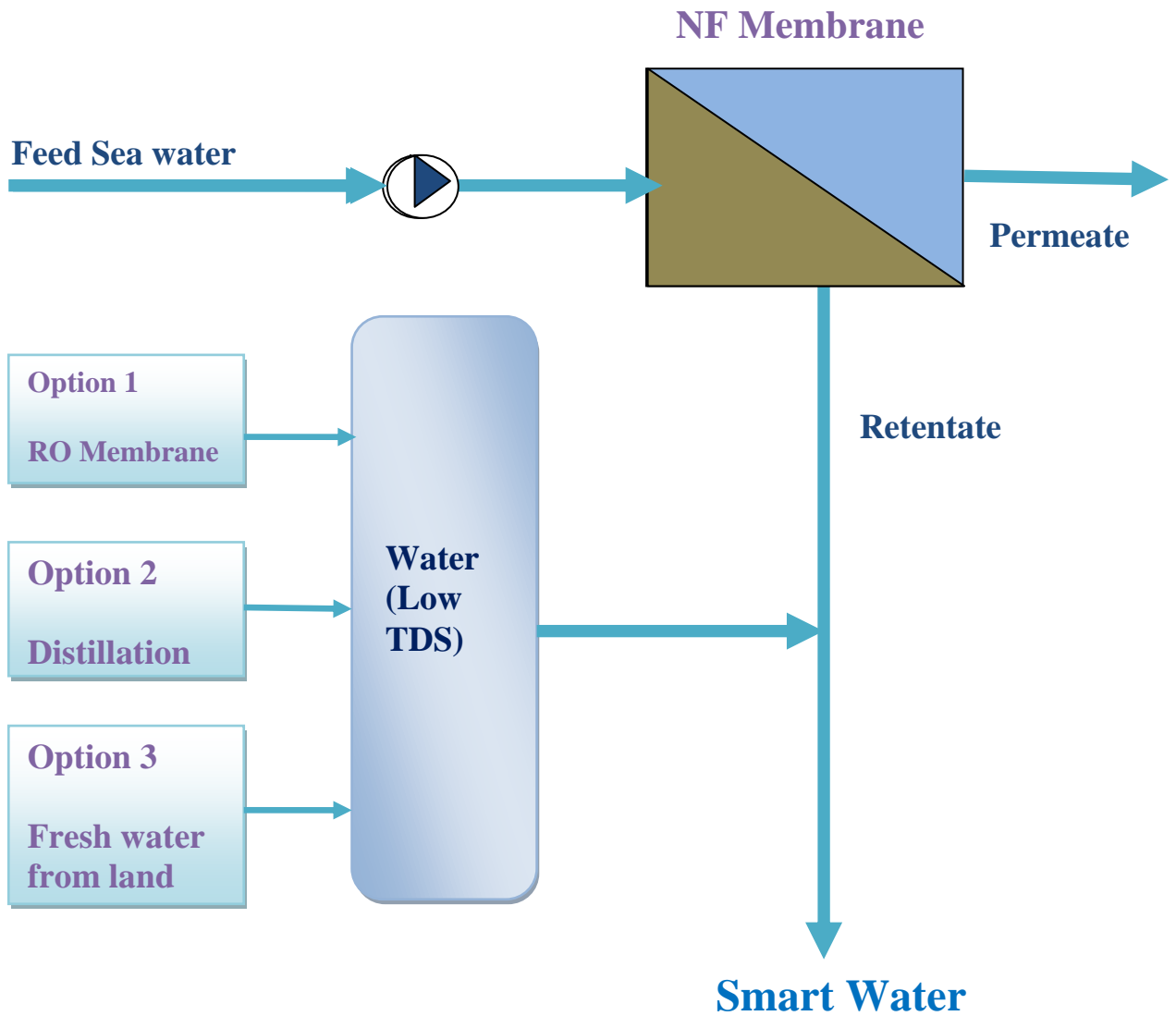
- ❖ The size and charge exclusion mechanism in NF makes it very selective and susceptible to operating parameter changes.
- ❖ The selectivity of NF on rejection combined with the low TDS of permeate from RO makes the combination a potential option for smart water production.
- ❖ RO rejects most of the ions from feed water at a high level whereas NF is very selective in rejecting the ions, which is evident from **Figure 38**.
- ❖ The predominant retention of divalent ion in the retentate of NF makes it a desirable constituent for smart water.

## 4.6 Smart Water Formulation

In order to attain the TDS of smart water from retentate of NF, the retentate should be diluted with low TDS water. The low TDS water can be produced from a number of options. The options considered in this thesis are given below:

- 1) Combination of NF retentate and RO membrane permeate
- 2) Combination of NF retentate with Distillation
- 3) Combination of NF retentate and fresh water from land

The options evaluated in this report are presented schematically in **Figure 40**.



**Figure 40: Different methods to reduce TDS**

- ❖ Fresh water from land can be used in places where there is no scarcity of water.
- ❖ The choice between RO and distillation need to be taken after considering the economic aspects.

## **Chapter 5: Economic Analysis of Smart Water Production Options**

In order to reduce the TDS of NF retentate to the required range of smart water, different combinations are considered. The amount of low TDS water required to mix with NF retentate is calculated by TDS balance. Power consumed is calculated using the flow rates and applied pressure to determine the viable option.

***Assumptions:***

- ❖ *Basis target TDS for smart water is taken as 10000 ppm*
- ❖ *Highest pressure (9.1 Bar) and flow rate (145 L/h) is selected from the experimental data for the NF case.*
- ❖ *Highest pressure (40 Bar) and flow rate (277 L/h) is selected from the experimental data for the RO case.*

## **5.1 Smart Water Option 1: NF Retentate + RO Permeate**

In this option, permeate of the RO process is mixed with retentate of NF to bring down the TDS to target of 10000 ppm for smart water.

The schematic of the proposed process is as given below in **Figure 41**.

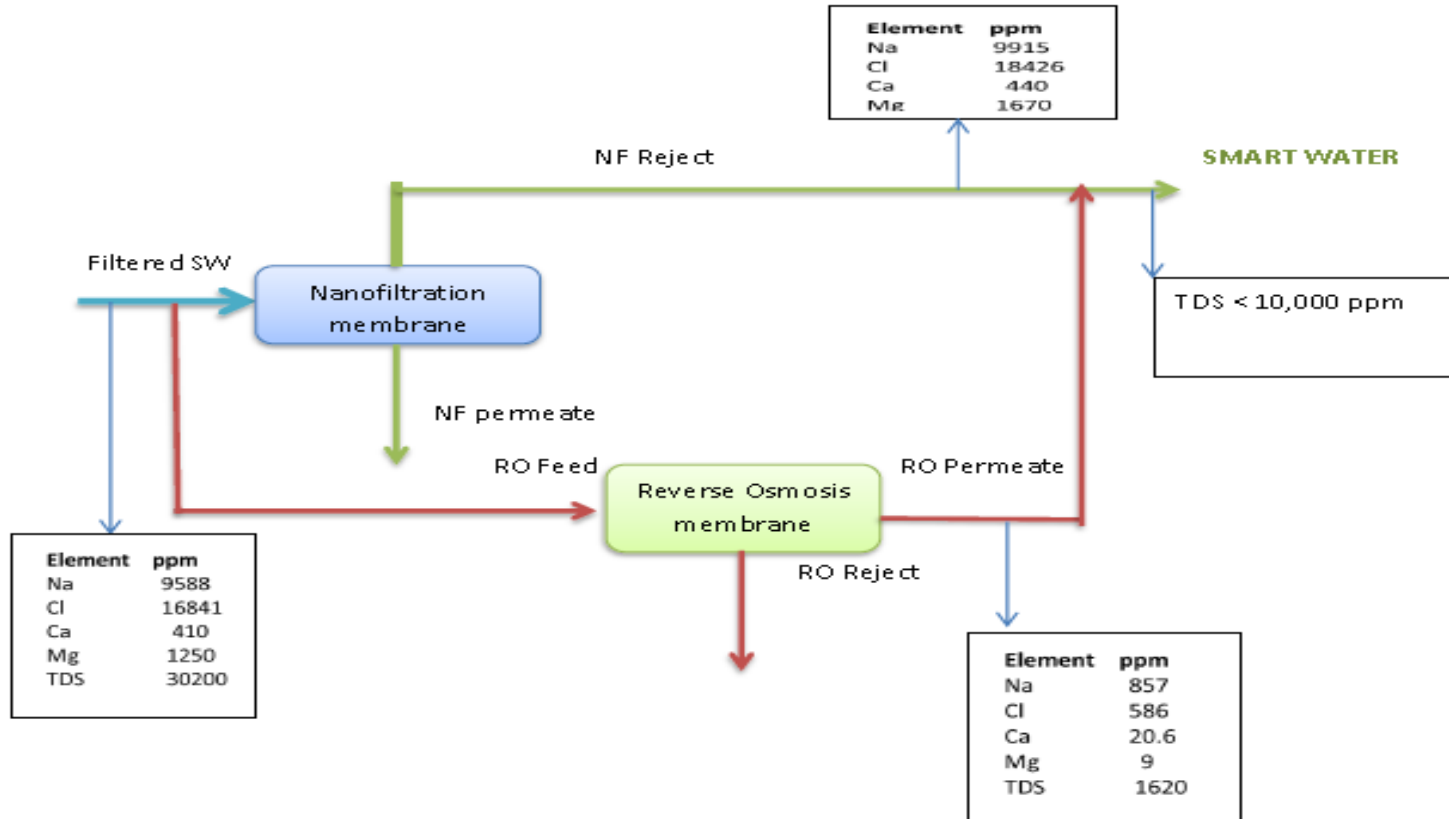


Figure 41: Proposed combination of NF and RO membrane



The results obtained from Nano BW 4040 and Filmtec SW 30 -2540 is combined to perform a TDS balance. The amount of low TDS water required for dilution is calculated from the TDS balance and is shown in **Table 23**.

$$\text{➤ } (Q_r, \text{ retentate from NF} * \text{TDS of retentate}) + (Q_p \text{ permeate from RO}, X * \text{TDS permeate}) = (Q+X)*10000$$

where,

X is the amount of permeate from the RO system mixed with retentate from NF.

**Table 23: TDS Balance for NF +RO**

Q <sub>r</sub> (NF)	120	l/hr
TDS r(NF)	32900	mg/l
TDS p (RO)	1620	mg/l
TDS (Smart Water)	10000	mg/l
Q <sub>p</sub> (RO)	328	l/hr
Recovery of RO	18.9	%
Feed flow rate to RO	1745	l/hr

**Result:** From **Table 23**, the feed flow rate of RO required for the dilution is equal to **1745 L/h**.

## 5.2 Smart Water Option 2: NF Retentate+ Fresh Water

The amount of low TDS water required for dilution is calculated from the TDS balance and is shown in **Table 24**.

$$\text{➤ } (Q \text{ retentate from NF} * \text{TDS of retentate}) + (Q \text{ fresh water}, X * \text{TDS fresh water}) = (Q+X)*10000$$

where,

X is the amount of fresh water from land, mixed with retentate from NF

**Table 24: Calculation of amount of fresh water required**

Freshwater TDS	1000	mg/L
Q <sub>r</sub> (NF)	120	L/h
TDS <sub>r</sub> (NF)	32900	mg/L
TDS Smart water	10000	mg/L
Q(fresh water)	305.3	L/h

*Assumption 1: TDS of fresh water = 1000 ppm or mg/L.*

**Result:** From **Table 24**, the required amount of fresh water for dilution is **305.3 L/h**.

### 5.3 Smart Water Option 3: NF + MSFD (Multi Stage Flash Distillation)

The amount of low TDS water required for dilution is calculated from the TDS balance and is shown in **Table 25**.

$$\text{➤ } (Q \text{ retentate from NF} * \text{TDS of retentate}) + (Q \text{ distillation} * \text{TDS distillation}) = (Q+X)*10000$$

where:

X is the amount of water from distillation, mixed with retentate from NF.

**Table 25: Calculation of amount of water from distillation**

MSFD water TDS	150	mg/l
Q <sub>r</sub> (NF)	120	l/hr
TDS <sub>r</sub> (NF)	32900	mg/l
TDS Smart water	10000	mg/l
Q(MSFD)	279	l/hr

*Assumption 2: TDS of seawater from distillation = 150 ppm or mg/L.*

**Result:** From the mass balance, amount of water required for dilution is **279 L/h.**

## **5.4 Energy Consumption**

The energy consumed in each case is tabulated in **Table 26**

**Table 26: Power consumption**

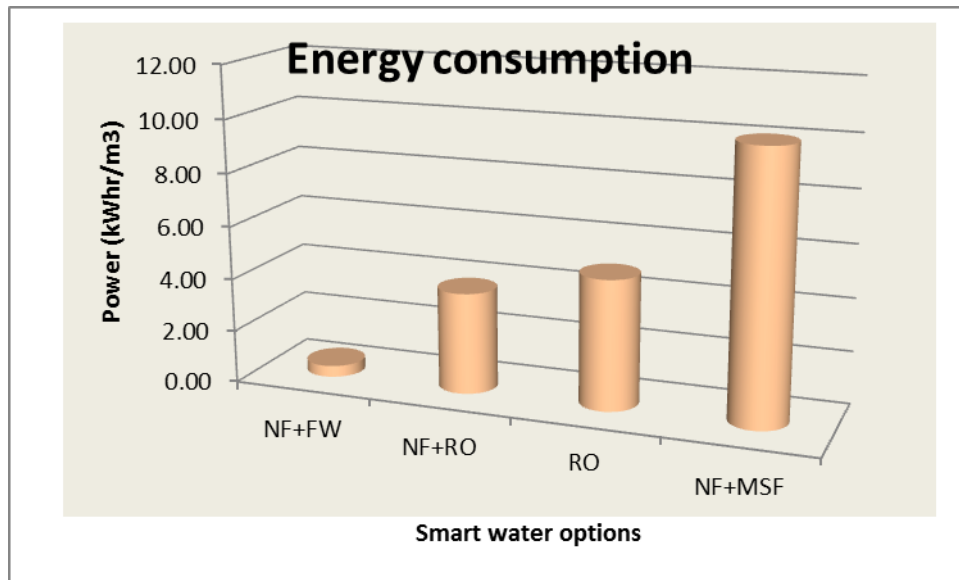
Options	Configuration		Pressure	Feed Flow	Retentate Flow	Permeate Flow	Smart water produced	Power	Power consumed/(m <sup>3</sup> /hr smart water)
			bar	l/hr	l/hr	l/hr	l/hr	Watt	kWhr/m <sup>3</sup>
Base case		RO	40	277.3		52.3	52.3	256.76	<b>4.91</b>
Option 1	NF+RO	NF	9.1	265	120		120	111.64	0.93
		RO	40	1735		328	328	1606.48	4.90
		Net					448	1718.13	<b>3.84</b>
Option 2	NF+FW	NF	9.1	265	120		120	111.64	0.93
		FW	5	305.3			305.3	70.67	0.23
		Net					425.3	182.31	<b>0.43</b>
Option 3	NF+MSF	NF	9.1	265	120		120	111.64	0.93
		MSF		279			279	3906	14
		Net					399	4017.64	<b>10.07</b>

- Power consumed for the above combinations are calculated from the equation,

$$Power(Watt) = \frac{Feed\ flow\ rate\ \left(\frac{m^3}{sec}\right) * Feed\ pressure(Pa) * 100}{Efficiency, \eta(\%)}$$

- An energy recovery factor of 50 % is applied for the RO process (i.e.50 % of the energy required for feed pump is recovered from the retentate).
- Pump Efficiency,  $\eta$ , is assumed as 60 %.

The result of the above calculation is presented below in **Figure 42**.



**Figure 42: Power consumed by different combinations with NF**

### Observation

- From above economic analysis of different options, it can be concluded that the combination of NF with fresh water is the best, in terms of energy consumption for smart water production.
- However, due to the constraints on availability of fresh water and its socio-environmental impact, the combination process of NF and RO is proposed as the most feasible process for producing the smart water.

- The energy consumption of RO is directly related to the concentration of salts, since a higher salt concentration results in higher osmotic pressure.
- NF + RO are best suitable due to relatively compact space, weight and lower power consumption.
- Thermal based methods(MSFD) are not suitable offshore due to large space, weight and energy consumption
- There can be other expenditures associated with all the options. The cost effectiveness will apparently depend on the amount and timing of the incremental recovery.

## **Chapter 6: Conclusions and Recommendations**

Production of low salinity seawater with varying ionic composition, using nano membranes in carbonate reservoir is discussed. The performance of the membranes was measured in terms of flux and rejection, under different operating conditions such as feed solution composition, feed characteristics and recovery rate. The experimental results showed that the rejections of salts increased with the feed pressure and decreased with the increase in salt concentration.

The thesis also includes a technical-economical study comparing RO and NF processes for salt separating efficiency. The study included the performance of NF and RO modules and the obtained results were evaluated in terms of output, desalination efficiency and energy requirements. A sharp reduction of TDS of filtered SW was found with the performance of RO module. NF was observed to be an effective method to perform partial desalination of seawater, at lower applied pressure resulting in high flux. The amounts of mineral salt removal with the Nano- BW- 4040 membrane were in the range of 75 and 95 %. From the experiments, the following results can be concluded:

1. According to the objective of the thesis, it is observed that smart water, for EOR can be produced from SW using nanomembranes.
2. The predominant retention of divalent ions ( $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) in the retentate of NF makes it a desirable constituent for smart water.
3. NF membrane retains 95-99% sulphate, 55-70% magnesium ion and 20-45% calcium ions in the retentate.
4. Low to moderate salinity and high presence of divalent ions are the characteristics of smart water. In order to meet this requirement, various mixing options with NF retentate have been evaluated.
5. A combination of NF and RO process is selected as the economically feasible option with lowest socio-environmental impact and lower power consumption.
6. Smart water production by membranes require only fewer chemicals, making the process environmental friendly.



**Recommendations**

- 1) NF experiments with change in pH of feed solution can be done in order to study the retention characteristics resulting from charge exclusion mechanism.
- 2) Experiments with different NF membrane types help to understand the ion rejection and can analyze the possibility of lower TDS retentate.
- 3) Exact smart water formulation can be adjusted by spiking after membrane treatment, if needed.

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## Appendices

### Appendix 1: Analysis of Total suspended solids (TSS)

**Table 27: Analysis of Total suspended solids (TSS)**

Trial 1		Trial 2	
Weight of dish 1(g)=	91.51	Weight of dish 2 (g)=	132.94
Weight of dish 1 + filter(g) =	91.6639	Weight of dish 2 + filter(g) =	133.0934
Weight of filter 1 (g)=	0.1539	Weight of filter 2 (g)=	0.1534
<b>After 1 hour drying</b>			
Weight of dish 1 + filter(g) =	91.6657	Weight of dish 2 + filter(g) =	133.0954
Weight of filter 1 (g)=	0.1557	Weight of filter 2 (g)=	0.1554
Difference in weight of filter 1 (g)=	0.0018	Difference in weight of filter 2 (g)=	0.002
<b>Average weight of the filter (g) =</b>	<b>0.0019</b>		
<b>TSS</b>	<b>0.000019</b>		

**Volume of sample used = 100 ml**

## Appendix 2 : Membrane Specification for Nano-BW-4040



Membrane Element		NANO-BW-4040								
<b>Performance:</b>	<b>MgSO<sub>4</sub></b> Permeate Flow (Nominal): MgSO <sub>4</sub> Rejection (Nominal):	2000 gpd (7.6 m <sup>3</sup> /d) 99.7% (99.5% minimum)								
<b>Type</b>	Configuration: Membrane Polymer: Nominal Membrane Area: Feed/Brine Spacer Thickness:	Spiral Wound Composite Polyamide 75 ft <sup>2</sup> (7 m <sup>2</sup> ) 34 mil (0.87 mm)								
<b>Application Data*</b>	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 <sup>3</sup> /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.										
<b>Test Conditions</b>	The stated performance is based on the following test conditions:  2000 ppm MgSO <sub>4</sub> 130 psi (0.9 MPa) Applied Pressure 77 °F (25 °C) Operating Temperature 15% Permeate Recovery 6.5 – 7.0 Feed pH									
<table border="1"> <thead> <tr> <th>A, inches (mm)</th> <th>B, inches (mm)</th> <th>C, inches (mm)</th> <th>Weight, lbs. (kg)</th> </tr> </thead> <tbody> <tr> <td>40.00 (1016)</td> <td>3.95 (100.3)</td> <td>0.75 (19.1)</td> <td>8 (3.6)</td> </tr> </tbody> </table>			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)
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)							
<p><b>Notice:</b> 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.</p> <p>Hydranautics believes the information and data contained herein to be accurate and useful. The information and data are offered in good faith, but without guarantee, as conditions and methods of use of our products are beyond our control. Hydranautics assumes no liability for results obtained or damages incurred through the application of the presented information and data. It is the user's responsibility to determine the appropriateness of Hydranautics' products for the user's specific end uses.</p> <p style="text-align: right;">12/15/10</p>										

**Figure 43: Specifications of NANO BW 4040 membrane**

### Appendix 3: Mass balance for characterisation of samples from Nano- BW-4040

**Table 28: Mass balance (TDS) of experiments with Nano BW 4040**

TDS (Feed),mg/l	Feed Flow rate[l/hr]	TDS = Feed TDS *flow rate[mg/hr]	Permeate[mg/l]	Permeate flow rate [l/hr]	TDS of permeate = Permeate tds*flow rate (Permeate)[mg/hr]	Retentate[mg/l]	Retentate Flow rate [l/hr]	TDS of retentate = Retentate tds*flow rate (Retentate)[mg/hr]	TDS of permeate +TDS of retentate[mg/hr]	balance	balance error w.r.t feed%
30200	165	4983000	28300	45	1273500	31,300	120	3756000	5029500	46500	0.933173
30200	185	5587000	27800	65	1807000	30,800	120	3696000	5503000	-84000	-1.50349
30200	200	6040000	27400	80	2192000	31,500	120	3780000	5972000	-68000	-1.12583
30200	220	6644000	27200	100	2720000	32,100	120	3852000	6572000	-72000	-1.08368
30200	235	7097000	27400	115	3151000	32,600	120	3912000	7063000	-34000	-0.47908
30200	250	7550000	27100	130	3523000	33100	120	3972000	7495000	-55000	-0.72848
30200	265	8003000	26900	145	3900500	32,900	120	3948000	7848500	-154500	-1.93053



## Appendix 4: Mass balance for each ion from chromatographic results

Mass balance for each ions from chromatographic results on stage one by Nano BW 4040

**Table 29: Mass balance for chloride**

Permeate Flow rate (l/hr)	Mass balance for chloride on stage 1			
	TDS = Feed TDS *flow rate[mg/hr]	TDS of permeate*flow rate +TDS of retentate*flow rate[mg/hr]	Balance	Balance error % w.r.t.feed
45	2778783.2	2854925.6	-76142.4	-2.7
65	3115605.4	3129167.7	-13562.3	-0.4
80	3368222.0	3439605.5	-71383.5	-2.1
100	3705044.2	4194560.2	-489516.0	-13.2
115	3957660.9	4132944.9	175284.1	-4.4
130	4210277.5	4270033.0	-59755.5	-1.4
145	4462894.2	4485511.8	-22617.6	-0.5

**Table 30: Mass balance for sulphate**

Permeate Flow rate (l/hr)	Mass balance for sulphate on stage 1			
	TDS = Feed TDS *flow rate[mg/hr]	TDS of permeate*flow rate +TDS of retentate*flow rate[mg/hr]	Balance	Balance error % w.r.t.feed
45	389721.0	408556.3	18835.3	-4.8
65	436959.9	431751.4	5208.5	1.8
80	472389.0	463730.8	8658.2	-14.6
100	519627.9	595436.5	75808.5	-4.0
115	555057.1	577286.8	22229.7	-0.3
130	590486.3	592386.4	-1900.1	7.8
145	625915.5	576939.4	48976.1	7.8

**Table 31: Mass balance for sodium**

Permeate Flow rate (l/hr)	Mass balance for sodium on stage 1			
	TDS = Feed TDS *flow rate[mg/hr]	TDS of permeate*flow rate +TDS of retentate*flow rate[mg/hr]	Balance	Balance error % w.r.t.feed
45	1581951.85	1567677.19	14274.66	0.90
65	1773703.59	1755704.72	17998.87	1.01
80	1917517.40	1879539.46	37977.93	1.98
100	2109269.14	2091015.87	18253.27	0.87
115	2253082.94	2226279.27	26803.67	1.19
130	2396896.74	2390737.35	6159.40	0.26
145	2540710.55	2454387.28	86323.27	3.40

**Table 32: Mass balance for magnesium**

Permeate Flow rate (l/hr)	Mass balance for Magnesium on stage 1			
	TDS = Feed TDS *flow rate[mg/hr]	TDS of permeate*flow rate +TDS of retentate*flow rate[mg/hr]	Balance	Balance error % w.r.t.feed
45	206169.2	189408.0	16761.2	8.1
65	231159.4	201659.0	29500.5	12.8
80	249902.1	218127.2	31774.9	12.7
100	274892.3	268652.5	6239.8	2.3
115	293635.0	270869.1	22765.9	7.8
130	312377.6	272394.3	39983.3	12.8
145	331120.3	270916.6	60203.7	18.2

**Table 33: Mass balance for calcium**

Permeate Flow rate (l/hr)	Mass balance for calcium on stage 1			
	TDS = Feed TDS *flow rate[mg/hr]	TDS of permeate*flow rate +TDS of retentate*flow rate[mg/hr]	Balance	Balance error % w.r.t.feed
45	67708.4	59645.1	8063.3	11.9
65	75915.5	68985.5	6930.0	9.1
80	82070.8	71746.0	10324.8	12.6
100	90277.9	85189.9	5088.0	5.6
115	96433.2	88875.7	7557.6	7.8
130	102588.5	88248.1	14340.4	14.0
145	108743.9	94019.5	14724.4	13.5

## Appendix 5: Mass balance for characterisation of 2\* SO<sub>4</sub><sup>2-</sup> samples

**Table 34: Mass balance performed for 2\*SO<sub>4</sub><sup>2-</sup> spiked seawater**

TDS (Feed),mg/l	Feed Flow rate[l/hr]	TDS = Feed TDS *flow rate[mg/hr]	Permeate[mg/l]	Permeate flow rate [l/hr]	TDS of permeate = Permeate tds*flow rate (Permeate)[mg/hr]	Retentate[mg/l]	Retentate Flow rate [l/hr]	TDS of retentate = Retentate tds*flow rate (Retentate)[mg/hr]	TDS of permeate +TDS of retentate[mg/hr]	balance	balance error w.r .t feed%
32100	200	6420000	28700	80	2296000	33600	120	4032000	6328000	-92000	-1.43302
32100	220	7062000	28000	100	2800000	34000	120	4080000	6880000	-182000	-2.57717
32100	235	7543500	27900	115	3208500	34400	120	4128000	7336500	-207000	-2.74408
32100	250	8025000	27700	130	3601000	34600	120	4152000	7753000	-272000	-3.38941
32100	265	8506500	27400	145	3973000	34900	120	4188000	8161000	-345500	-4.0616

## Appendix 6: Mass balance for characterisation of $3 \cdot \text{SO}_4^{2-}$

**Table 35: Mass balance for  $3 \cdot \text{SO}_4^{2-}$  spiked seawater**

TDS (Feed),mg/l	Feed Flow rate[l/hr]	TDS = Feed TDS *flow rate[mg/hr]	Permeate[mg/l]	Permeate flow rate [l/hr]	TDS of permeate = Permeate tds*flow rate (Permeate)[mg/hr]	Retentate[mg/l]	Retentate Flow rate [l/hr]	TDS of retentate = Retentate tds*flow rate (Retentate)[mg/hr]	TDS of permeate +TDS of retentate[mg/hr]	balance	balance error w.r .t feed%
33700	200	6740	29300	80	2344	35400	120	4248	6592	-148	-2.19585
33700	220	7414	28900	100	2890	35700	120	4284	7174	-240	-3.23712
33700	235	7919.5	28700	115	3300.5	36100	120	4332	7632.5	-287	-3.62397
33700	250	8425	28500	130	3705	36300	120	4356	8061	-364	-4.32047
33700	265	8930.5	28100	145	4074.5	37000	120	4440	8514.5	-416	-4.65819

## Appendix 7: Chromatography results

### Chromatography results

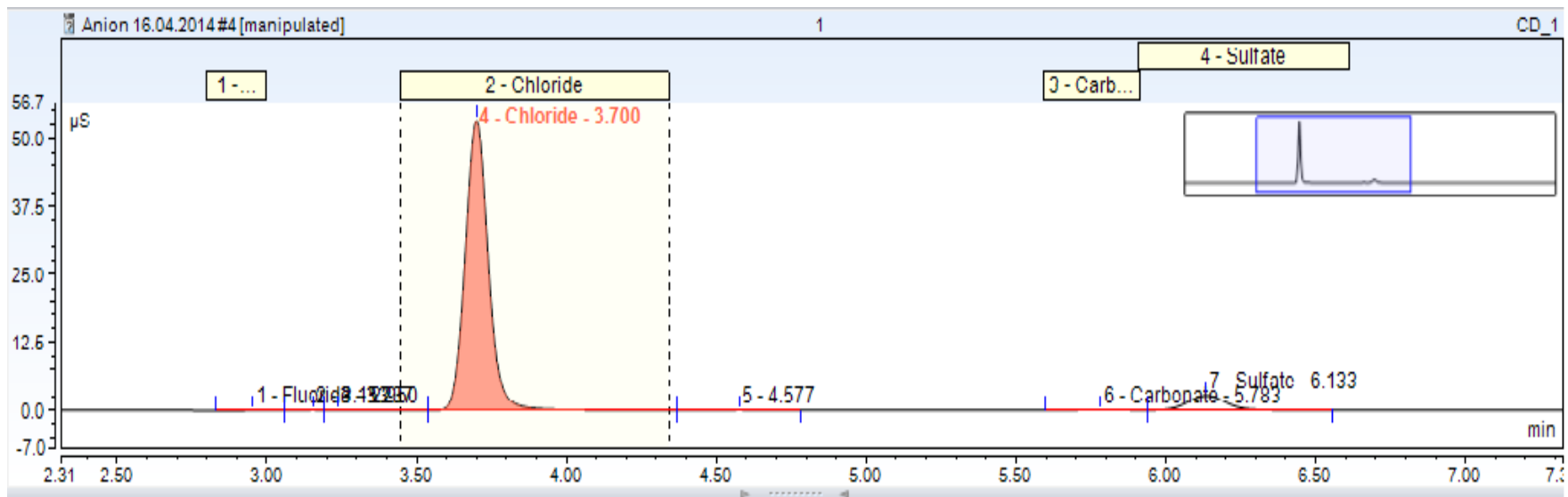


Figure 44: Anions (Cl-) present in feed seawater

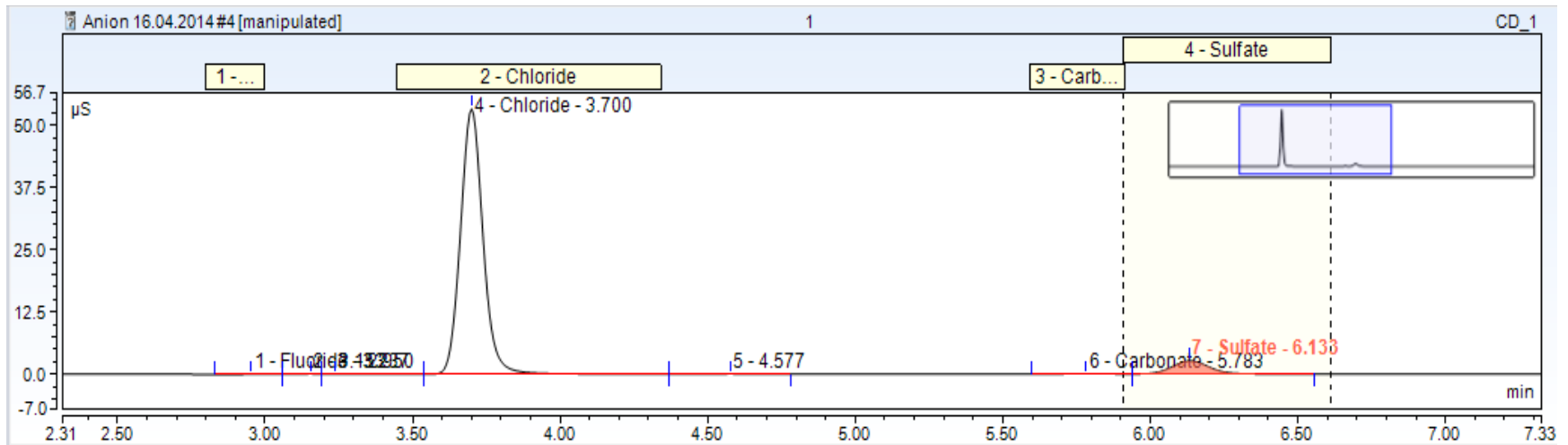


Figure 45: Anions present in feed seawater ( $\text{SO}_4^{2-}$ )

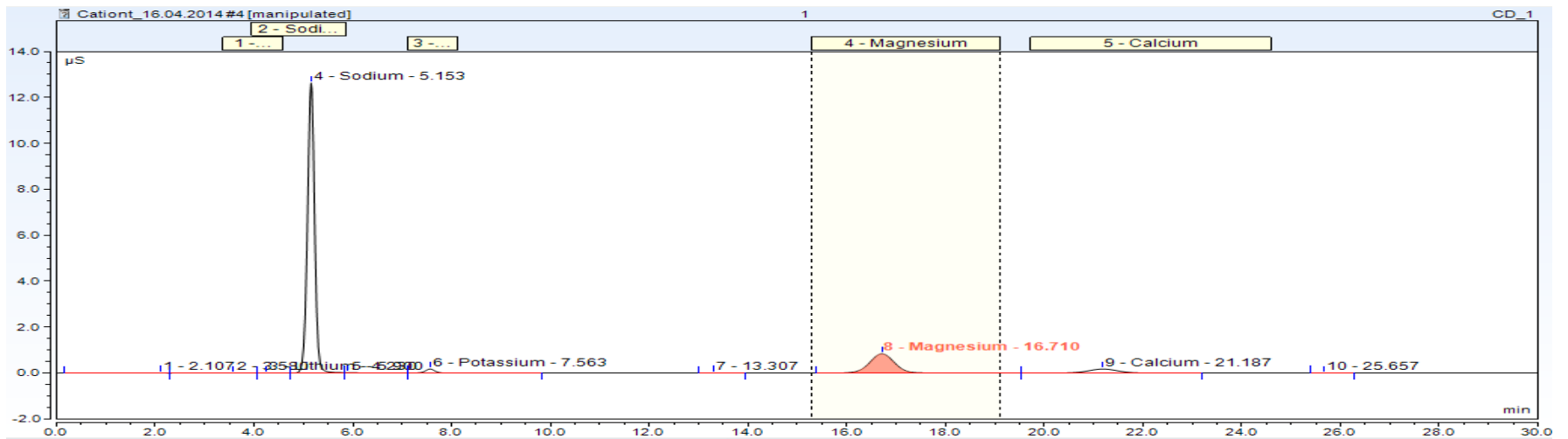
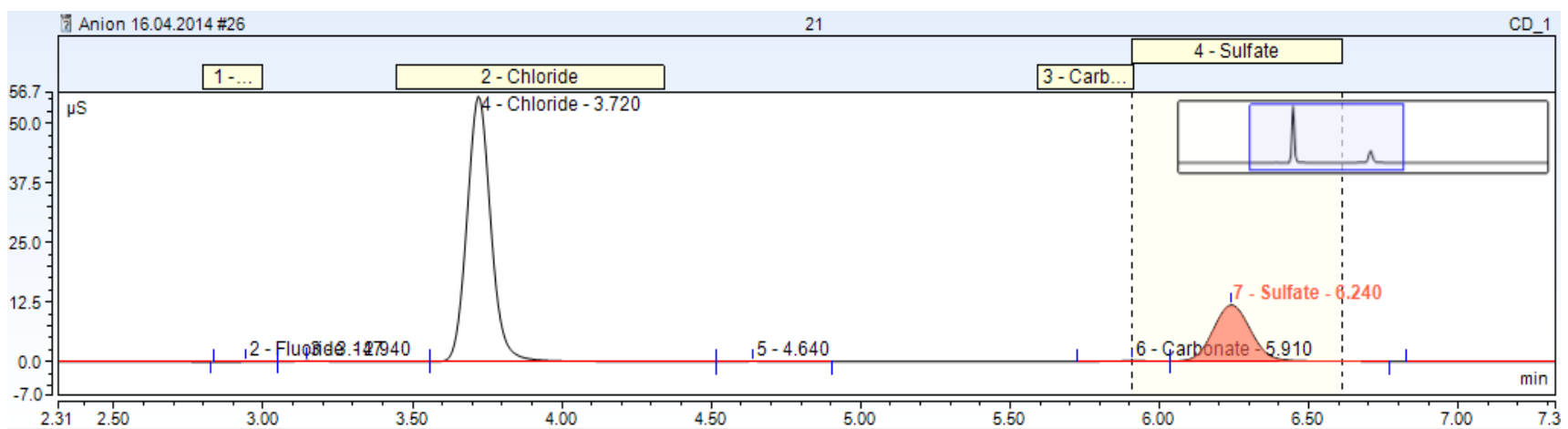
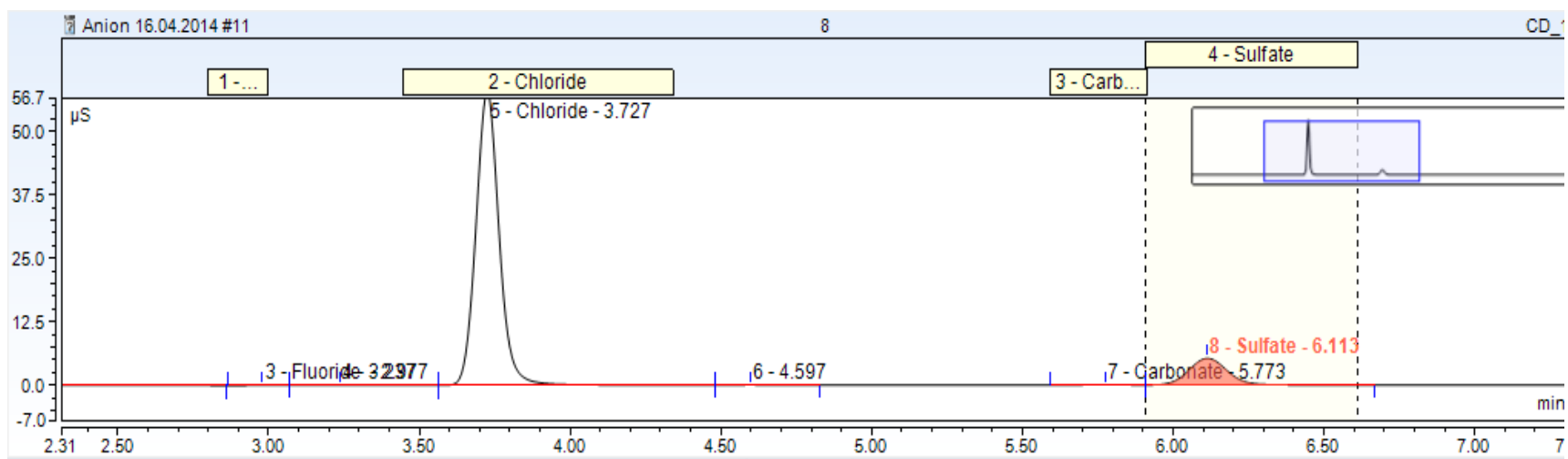


Figure 46 : Cations present in feed seawater





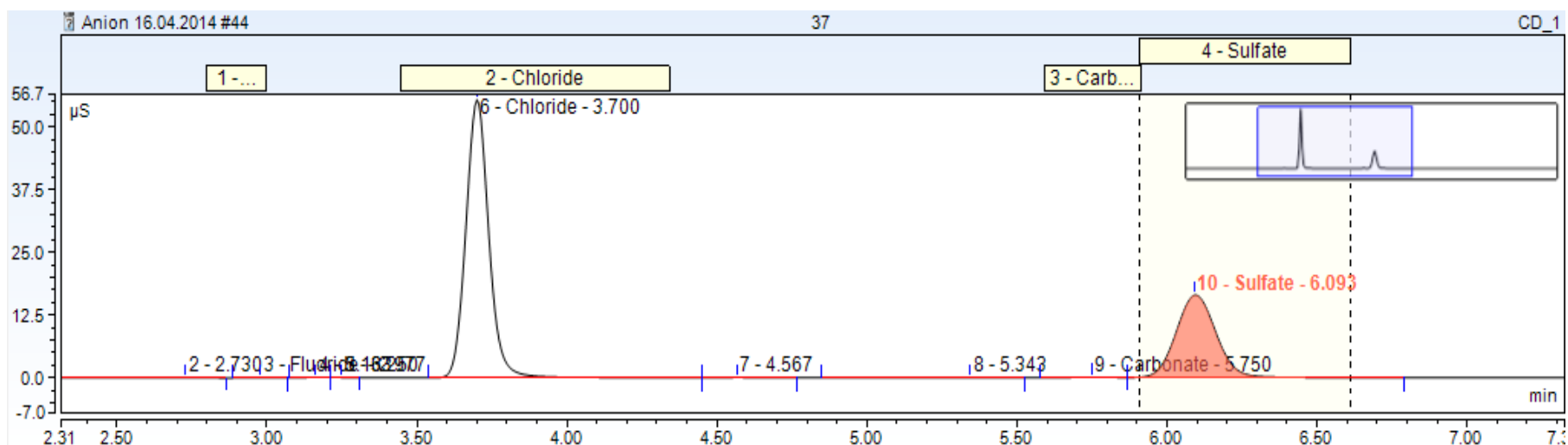
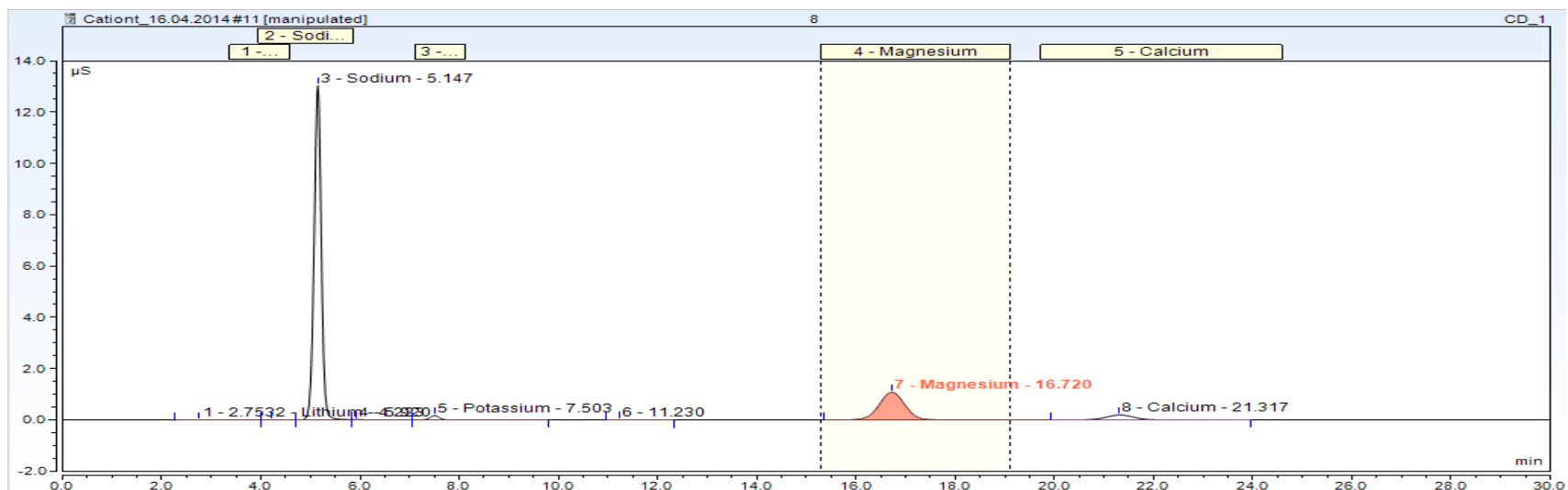


Figure 47: Anions at 145L/hr for feed,  $2 \cdot \text{SO}_4^{2-}$  and  $3 \cdot \text{SO}_4^{2-}$



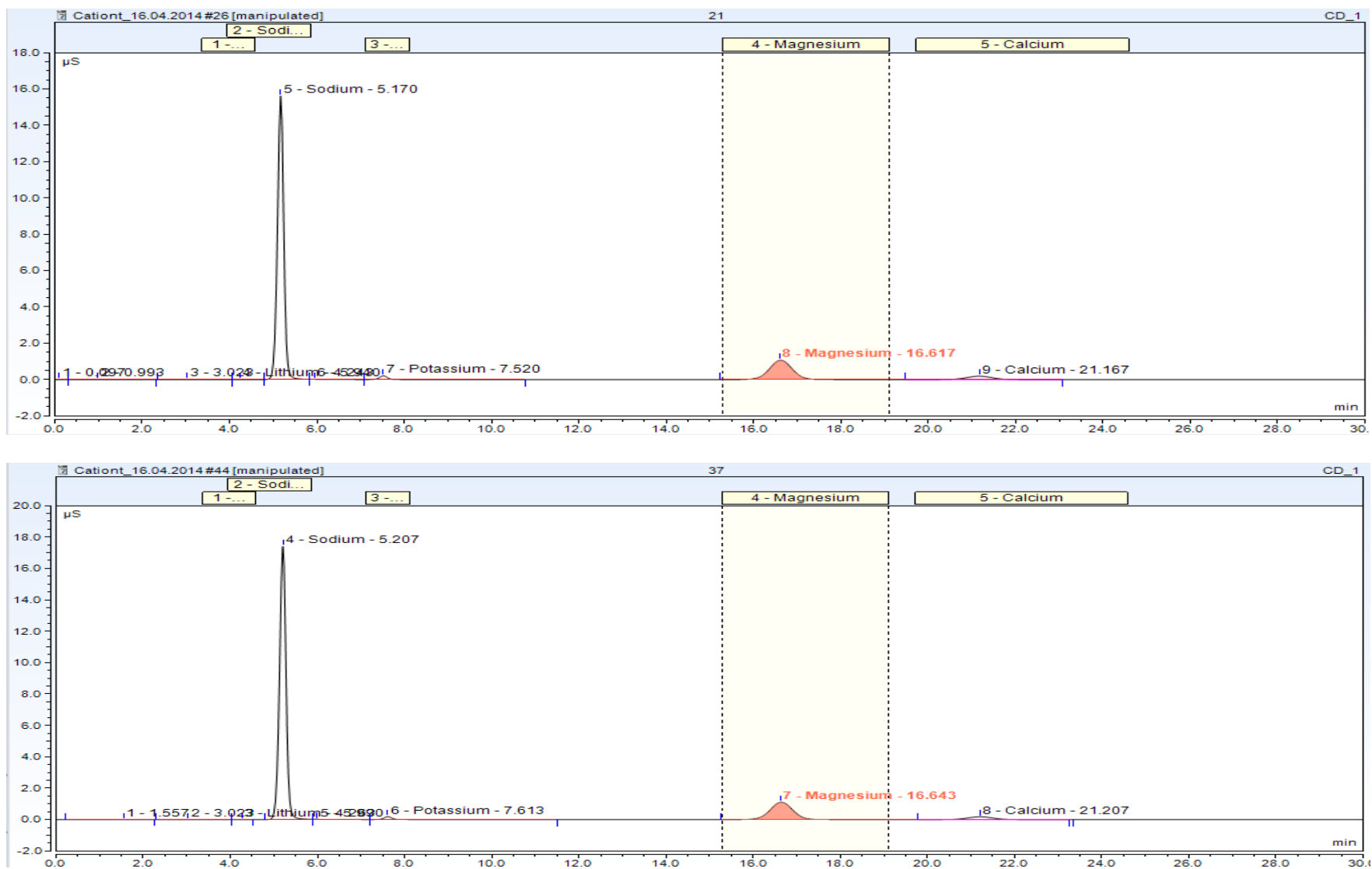


Figure 48: Cations at 145L/ hr for feed,  $2 \cdot \text{SO}_4^{2-}$  and  $3 \cdot \text{SO}_4^{2-}$

## Appendix 8: Mass balance for RO experiments

**Table 36: Mass balance for pressure change from RO experiments**

TDS (Feed),mg/l	Feed Flow rate[l/hr]	TDS = Feed TDS *flow rate[mg/hr]	Permeate[mg/l]	Permeate flow rate [l/hr]	TDS of permeate = Permeate tds*flow rate (Permeate)[mg/hr]	Retentate[mg/l]	Retentate Flow rate [l/hr]	TDS of retentate = Retentate tds*flow rate (Retentate)[mg/hr]	TDS of permeate +TDS of retentate[mg/hr]	balance	balance error w.r .t feed%
31300	239.75	7504303.3	4730.0	14.75	69786.89	31,800	225	7155000	7224786.89	279516.39	3.7247481
31300	255.00	7981500.0	3890.0	30.00	116700.00	32,000	225	7200000	7316700.00	664800.00	8.32926142
31300	259.62	8125961.5	2450.0	34.62	84807.69	32,200	225	7245000	7329807.69	796153.85	9.79765708
31300	277.33	8680290.7	1620.0	52.33	84767.44	33,100	225	7447500	7532267.44	1148023.26	13.2256314

## Appendix 9: Dilution Machine



**Figure 49: Dilution machine**