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Arash G Ghasemi

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Abstract

The thesis investigates the Effects of spiking phosphate on nanofiltration (NF) membrane ion separation for production of phosphate-containing designed water. Enhanced oil recovery in carbonate reservoir by seawater injection calls for modification of seawater ionic composition. Low concentration of monovalent ions (sodium and chloride) together with high concentration of divalent ions (sulfate, calcium and magnesium) are characteristics of this modified seawater known as designed water. Recent research findings show that increase in recovery is achievable when designed water contains phosphate. Ability of nanofiltration (NF) membrane to retain multivalent ions and permeate monovalent ions makes this separation process a suitable technique for production of designed water.

Effects of pressure, feed concentration and pH was experimented when phosphate chemicals were introduced into seawater as NANO-SW-2540 membrane feed. The membrane showed to reject ions in sequence of R(sulfate) > R(phosphate) > R(magnesium) > R(calcium) > R(chloride) > R(sodium). Increase in operational pressure led to a rise in permeate flux and rejection rates. Desirable recovery reduction was obtained by adding phosphate salts and increasing its concentration in membrane feed. Moreover, a downward trend was also observed in retention of normal seawater ions as a result of increasing concentration of phosphate salt in membrane feed resulted from screening phenomenon. Between the two phosphate salts, second one showed to contribute to higher phosphate rejection of 94 to 98% as well as higher monovalent permeation when its third dose was introduced into feed solution. Increasing pH of feed solution led to both higher recovery and ion permeation. Phosphate rejection ranged between 85 to 98% rejection at solution pH of 8 and decreased by about 40% when pH of feed was inclined to 11.

Keywords: *EOR, enhanced oil recovery, smart water, nanofiltration, membrane, phosphate*

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Abbreviations

AIM – *Advanced ion management*

AN – *Acid number*

CA – *Cellulose acetate*

D – *Dialysis*

ED – *Electrodialysis*

EOR – *Enhanced oil recovery*

GS – *Gas separation*

IC – *Ionic chromatography*

MF – *Microfiltration*

MW –*Molecular weight*

MWCO – *Molecular weight cutoff*

NANO-SW-2540 – Hydranautics NF module

NF – *Nanofiltration*

NTU – *Nephelometric turbidity unit*

OOIP – *Original oil in place*

PA – *Polyamide*

PAN – *Polyacrylonitrile*

PES – *Polyethersulfone*

PSF – *Polysulfone*

PSSF – *Polysulfone sulfonated*

PV – *Pervaporation*

PVA – *Polyvinyl alcohol*

RO – *Reverse osmosis*

SSW – *Synthetic seawater*

SW – *Seawater*

SW w/o SO_4^{2-} – *Seawater free of sulfate ion*

TDS – *Total dissolved solids*

UF – *Ultrafiltration*

Nomenclature

C_f – *Concentration of feed*

C_p – *Concentration of permeate*

C_r – *Concentration of retentate*

D_i – *Diffusion coefficient* ($m^2.s^{-1}$)

d_p – *Pore diameter (nm)*

J – *Flux* ($L.m^{-2}.hr^{-1}$)

K – *Boltzman constant* ($J.mol^{-1}.K^{-1}$)

L_p – *Hydraulic permeability constant* ($L.m^{-2}.hr^{-1}.bar^{-1}$)

pk_a – *Logarithmic acid dissociation constant*

Q_p – *Permeate flow rate* ($L.hr^{-1}$)

R – *Membrane rejection (%)*

r_h – *Hydrated radius (nm)*

r_i – *Stokes radius*

T – *Temperature (K)*

Δp – *Transmembrane pressure (bar)*

η – *Viscosity* ($Kg.m^{-1}.s^{-1}$)

Θ – *Contact angle*

Chapter 1: Introduction

1 Introduction

Production of oil from a reservoir is classified as primary, secondary and tertiary enhanced oil recovery. As the two first stages could only recover the existing oil in a reservoir up to 45% (Tzimas et al., 2005) various methods such as chemical process, thermal process, miscible process etc. have been applied to enhance the recovery known as tertiary or enhanced oil recovery (Green and Willhite, 1998).

Reserving around 50% of world's oil, reservoirs formed by carbonate rocks are of key significance. However, ultimate recovery from these types of reservoirs is below 30% (Cuiec, 1984; Treiber and Owens, 1972), which is due to reservoir's properties such as wettability and natural fractured (Høgnesen, 2005; Manrique et al., 2007). Carbonate rocks are believed to be oil-wet i.e. hydrocarbon spreads on the surface of carbonate rocks and negatively charge carboxylic adsorbs onto positively charged rock surface.

Flooding the reservoir with seawater as "smart water" is one of the tertiary methods that increases recovery by modifying the wetting properties of the reservoir. Sulfate ions act as wetness altering means. They initiate the mechanism of altering the wettability by decreasing rock surface positive charge and calcium and magnesium ions continue the procedure (Zhang et al., 2007). However, seawater flooding could result in scale formation due to high concentration of sulfate in seawater and high concentration of calcium in formation water. Moreover, recent research findings show that, enhanced oil recovery can be increased by adding phosphate and borate salts to seawater (Gupta et al., 2011).

In field of water treatment, membrane separation during last four decades has shown to be superior to other separation technology on many different levels. Most importantly, membrane as a selective barrier gives a good control over the concentration of dissolved particles on both permeate and retentate side, depending on the type of membrane that is used.

Nanofiltration (NF) membrane are believed to be proper choice, according to their pore size, when rejection of multivalent and permeating water and monovalent ions are the targets. The rejection from NF membrane then would be rich in concentration of crucial ions that are needed for enhanced oil recovery by flooding carbonate reservoirs. However, rejection of ions by NF membrane is not only a function pore size since membrane structure and more importantly, membrane surface charge play vital roles in ion separation by membrane.

The ability of phosphate containing brine to enhance oil recovery in carbonate rocks, together with NF theoretical abilities in ion separation was the basis of conducting this study. The following is a preliminary feasibility study of production of desired ionic composition from seawater containing phosphate by nanofiltration membrane.

1.1 Objective

The objective of this research is to:

- Find phosphate salts which are soluble in seawater.
- Determine the solubility limits of the salts.
- Investigate the fractionation behavior of nanofiltration membrane in separation of seawater in presence of different concentration of phosphate containing chemicals,
- Evaluate NF membrane ability to permeate monovalent ions and retain multivalent ions.
- Determine the effects of pressure, ionic strength, salt composition and pH in separation of seawater containing phosphate.

Chapter 2: Literature review

2 Literature review

A vast number of papers have been published on water-based enhanced oil recovery and modification of injected water for improving recovery from a reservoir. However, there has been a very few literature published regarding a recent study showing that recovery could be increased by 20% of original oil in place in a carbonate rock when injection water contained phosphate (Gupta et al., 2011). The review will focus on major themes which merged frequently throughout the existing publication. These themes are water-based enhanced oil recovery within carbonate reservoir including rock type, wettability, smart water etc. and membrane filtration related topics e.g. principle, classification, performance etc. Although these topics are presented in a variety of contexts, the paper will primarily focus on their application to the objectives of the thesis.

2.1 Enhanced Oil recovery from carbonate reservoir

Production of crude oil from an oil field usually consists of three phases: primary recovery, secondary recovery and enhanced (tertiary) recovery (EOR). During the first stage, underground pressure is the production’s driving force. This pressure declines over production lifetime and becomes inadequate to bring oil to the surface and consequently recovery fails. In order to overcome the pressure drop, during the second stage, several techniques such as water injection, steam injection etc. are practiced to maintain reservoir pressure. By the application of these methods, externally made pressure supersedes and/or increases the natural pressure existing in a reservoir. However, pressure alone would not result in maximum possible recovery and these two stages together could recover up to 35 to 45% of original oil in place (OOIP) (Tzimas et al., 2005). That is why enhanced oil recovery techniques are implemented to increase the production of the remaining oil in the reservoir an aiming at an additional 5 to 15% recovery (Tzimas et al., 2005).

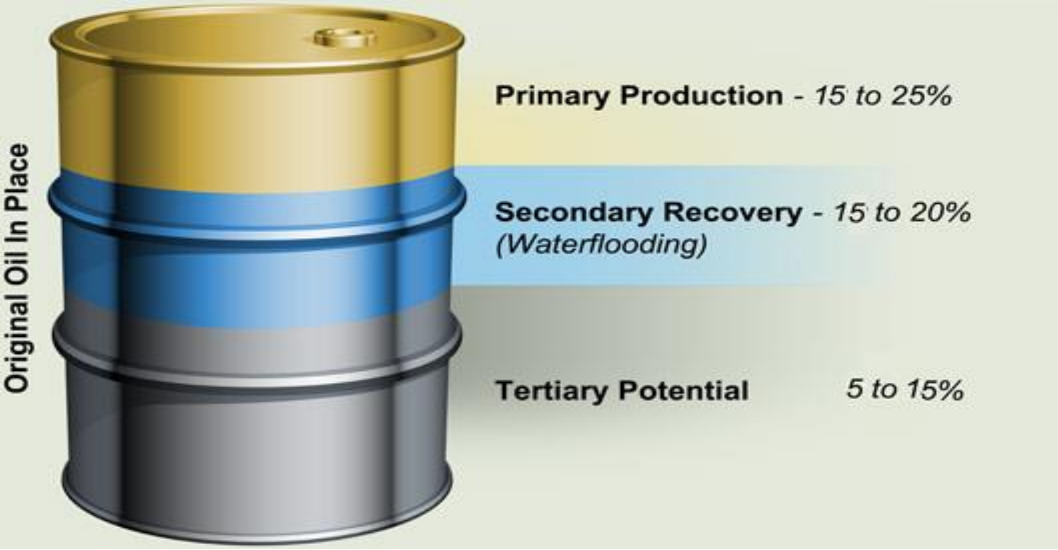


Figure 2.1 *Recovery potential in three production stages*

Tertiary recovery aims the remaining oil within the reservoir in order to increase the production and reservoir's lifetime. According to Green & Willhite (1998), EOR processes benefits from thermal energy, chemicals and miscible gases for oil displacement. The following are the main enhanced recovery techniques:

- *Thermal processes* target the viscosity of the oil in reservoir. By an increase in temperature, the fluid's viscosity decreases which results in better upward flow of oil. The temperature increase is achievable through steam injection, in-situ, in-situ energy generation by combustion etc. (Green and Willhite, 1998).
- *Chemical processes* use both phase behavior and interfacial tension (IFT) for easier oil displacement by injection of two types of chemical which are alkaline agents and surfactants (Green and Willhite, 1998).
- *Miscible processes* aim is to produce and increase miscibility of fluids within the reservoir by injection of either CO_2 or a same fluid as the solvent of hydrocarbon. This injection results in an alteration of the reservoir composition and consequently a better recovery (Green and Willhite, 1998).

- *Smart water* introduced by Austad and co-workers refers to seawater that can alter the wettability of the reservoir when injected. When a reservoir wetting property is altered from oil-wet to water-wet, recovery will be increased by spontaneous imbibition (Strand et al., 2006a; Zhang and Austad, 2006; Zhang et al., 2006).

When compared to other tertiary methods, smart water flooding benefits from advantages such as (Kokal and Al-Kaabi, 2010):

- High ultimate recovery by very low investment in an water flooding operation
- Faster payback by small gradual recovery
- Being practical from early life stage of a reservoir

Enhanced oil recovery techniques in order to be successful needs to be applied according to parameters such as characteristics of reservoir, field location etc. Rock composition is a decisive factor in oil recovery.

2.1.1 Carbonate rock

Reserving virtually 50% of the oil in world makes carbonate rocks a very important class of reservoirs. However, due to wetting properties, low permeability and being naturally fractured properties of these types of reservoir, the ultimate recovery would not proceed 30% (Cuiec, 1984; Treiber and Owens, 1972). Carbonate rocks are divided into three subclasses, which are:

- *Chalk* with coccoliths as its source of formation high porosity and low permeability (Cossé, 1993). Wettability of chalk is highly influenced by its outer organic layer (Andersen, 1995).
- *Limestone* with its large weight portion being composed by calcite ($CaCO_3$) forms many of oil reservoirs around the world (Gluyas and Swarbrick, 2013).
- *Dolomite* is a carbonate rock that contains dolomite mineral which is formed when calcium ion is replaced by magnesium ion in calcite (Strand, 2005).

Properties of reservoir rock influence the recovery in different levels and different wetting properties is one of the possible effects.

2.1.2 Wettability

In a three-phase medium consisting two immiscible fluids and a solid, the spreading and adhering tendency of either two fluids to the surface of a solid is termed wettability (Al-Garni and Al-Anazi, 2008). Wettability could be measured by quantitative methods such as contact angle, USBM (Anderson, 1986), Amott cell (Ma et al., 1999) and separation of sulfate and thiocyanate chromatographically (Strand et al., 2006b). The degree of wettability depends on the properties of the surface. Figure 2.2 illustrates the angle that is formed by the contact of a surface and a liquid droplet. The surface has either high or low wettability when the contact angle (θ) is below or above 90°, respectively.

Figure 2.2 *Schematic of surfaces wettability towards a liquid droplet. A surface with low wettability (left), a surface with high wettability (right).*

When a system in a reservoir rock is at equilibrium, the wetting fluid is placed on the pore walls and inside smallest holes. Whilst the non-wetting fluid is in pore bodies. Hence, oil-wet reservoirs have a noticeable amount of oil on their pore walls and inside their smallest holes. Consequently, it is considerably more difficult to recover oil from oil-wet reservoirs compared to water-wet reservoir. Figure 2.3 expounds oil-wet and water-wet rock grains. Between 80 to 90% of carbonate reservoirs have shown to be oil-wet (Høgnesen, 2005) which could be the reason to low recovery from carbonate reservoirs. Effects of seawater in changing wetting property of carbonate reservoirs is discussed later on this chapter.

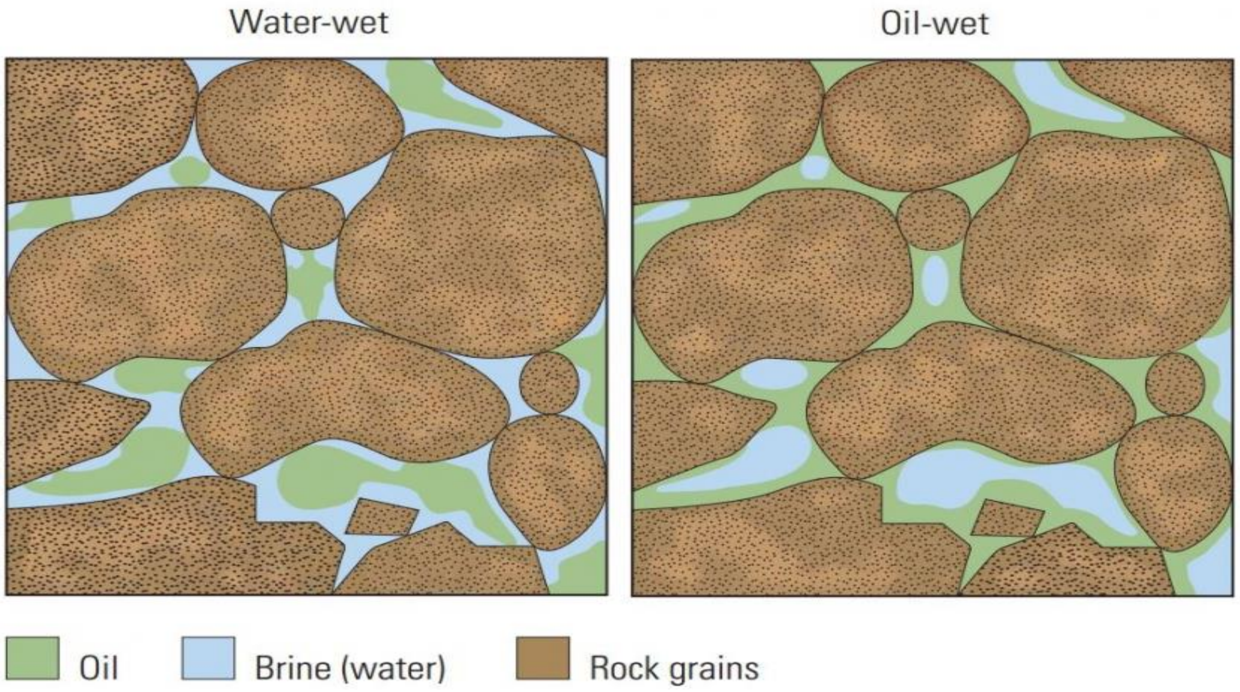


Figure 2.3 *Water-wet rock grains (left), oil-wet rock grains (right) (EPGEOLOGY, 2015)*

2.1.3 Smart water in carbonate reservoir

One of the methods in water-based enhanced oil recovery is injection of water that is optimized in terms of its ionic composition, in lieu of injection of any available water, to a reservoir. Different terms are used to refer to this modified water e.g. “Smart water $^{\text{TM}}$” by Saudi Aramco, “Designed water $^{\text{TM}}$” by Shell, “Advanced ion management (AIM) $^{\text{SM}}$” by Exxonmobil and “LoSal $^{\text{TM}}$” by British petroleum. The working theories of smart water in carbonate reservoirs include rock dissolution, surface ion exchange and in-situ surfactant formation. However, researchers believe that wettability alteration as a result of surface ion exchange is the dominant mechanism in oil recovery from carbonate rock by smart water. Wetting property of reservoir as a major obstacle regarding enhanced recovery, calls for modification of this factor. Sulfate has shown to be able to alter wettability of carbonate reservoir without being accompanied by any surfactants (Austad et al., 2005; Zhang and Austad, 2005). Since seawater contains a high concentration of sulfate it could be used as proper source of sulfate and it also includes low concentration calcium and magnesium ions. *Zhang et al.* (2007) suggested that in order for enhanced oil recovery to take place firstly, positively charged surface attract the negatively charged sulfate and this adsorption increases by increased temperature. Afterwards due to reduction in surface positive charge calcium ions co-adsorb to the surface. Moreover, magnesium ion can take calcium's place on the surface at high temperature. Finally these two divalent cations could bond with negatively charged carboxylic and result in extraction of detached hydrocarbon (Zhang et al., 2007). Figure 2.4 demonstrates the mechanism of wettability modification by seawater in a reservoir.

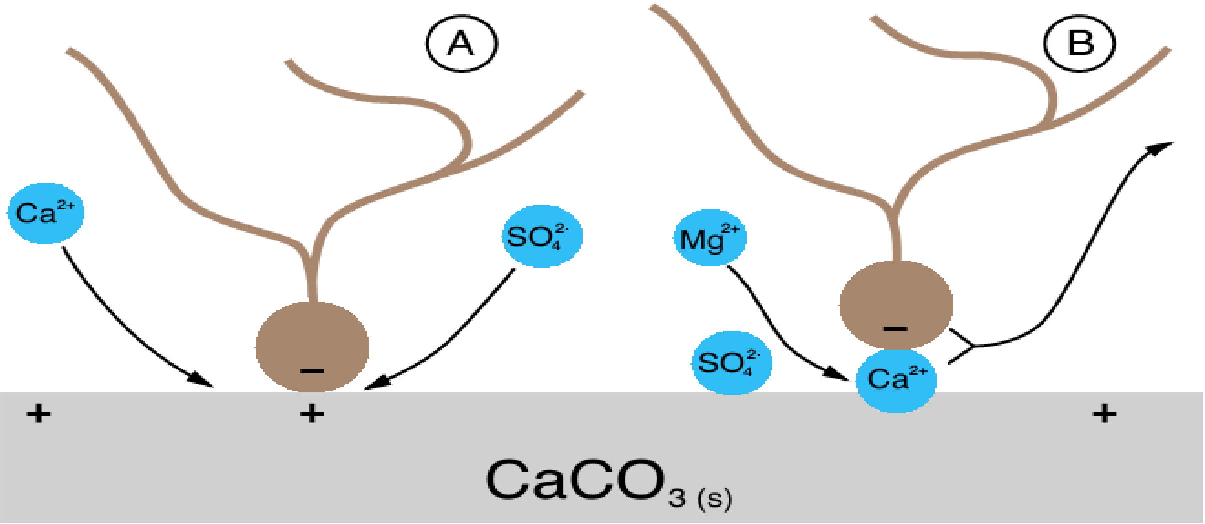


Figure 2.4 *Wettability modification schematic by seawater in a reservoir (A) Low temperature with* Ca^{2+} *and* SO_4^{2-} *as active ions (B) High temperature with* Mg^{2+}, Ca^{2+} *and* SO^{2-} *as active ions (Zhang et al., 2007).*

Further studies reported the importance of salinity and ionic composition of the injected seawater. Fathi *et. al* suggested that the access of potential determining ions such as SO_4^{2-} and Ca^{2+} to the calcite surface is affected by the concentration of non-active ions in the double layer (Figure 2.5). When seawater with low NaCl concentration was injected, instead of normal seawater, an increase of 29% was observed. This matter proved that apart from concentration of sulfate, calcium and magnesium ions, low concentration of monovalent i.e. NaCl is of key importance regarding modification of wettability within the reservoir (Fathi et al., 2010).

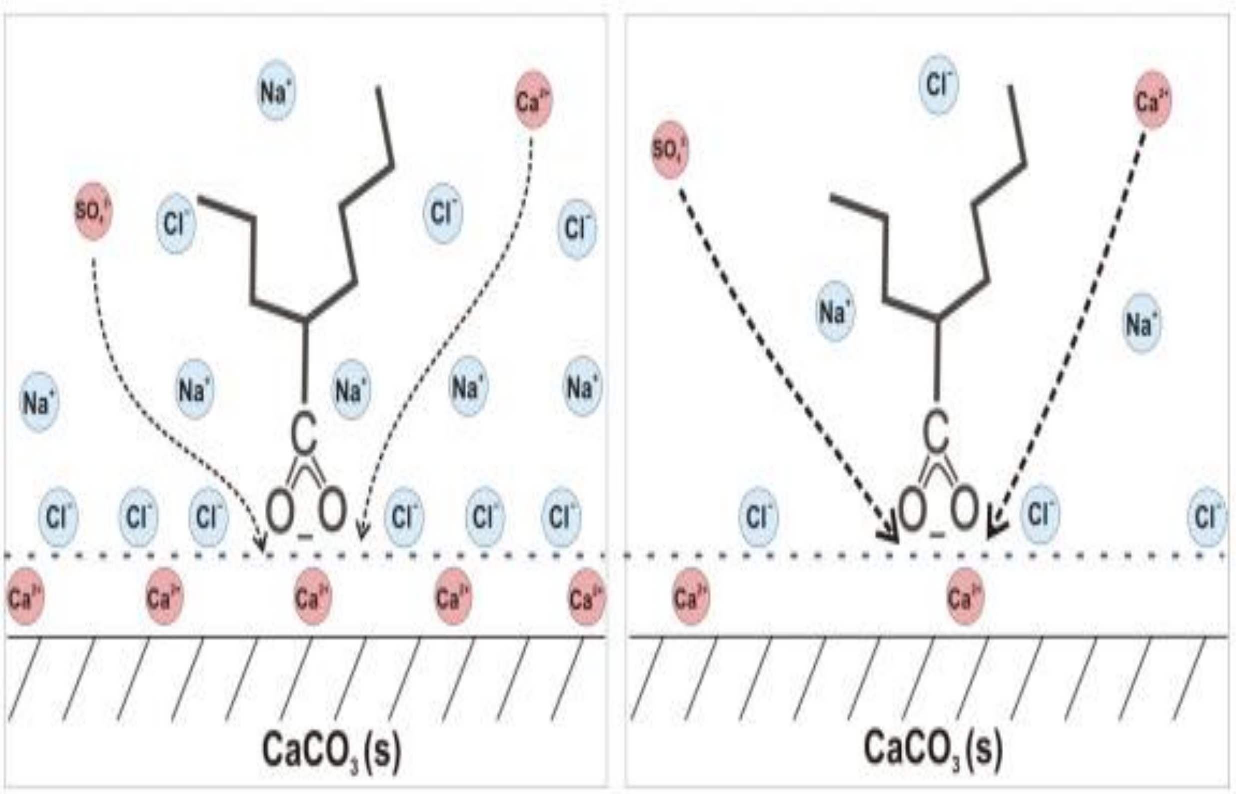


Figure 2.5 *Potential determining ions access to calcite surface in presence of high NaCl concentration (left), low NaCl concentration (right) (Fathi et al., 2010).*

Gupta *et. al* investigated the effects of phosphate containing brine in oil recovery from limestone reservoir. The study showed over 20% OOIP incremental recovery (Figure 2.6) when a phosphate salt were added to a modified seawater (Gupta et al., 2011)

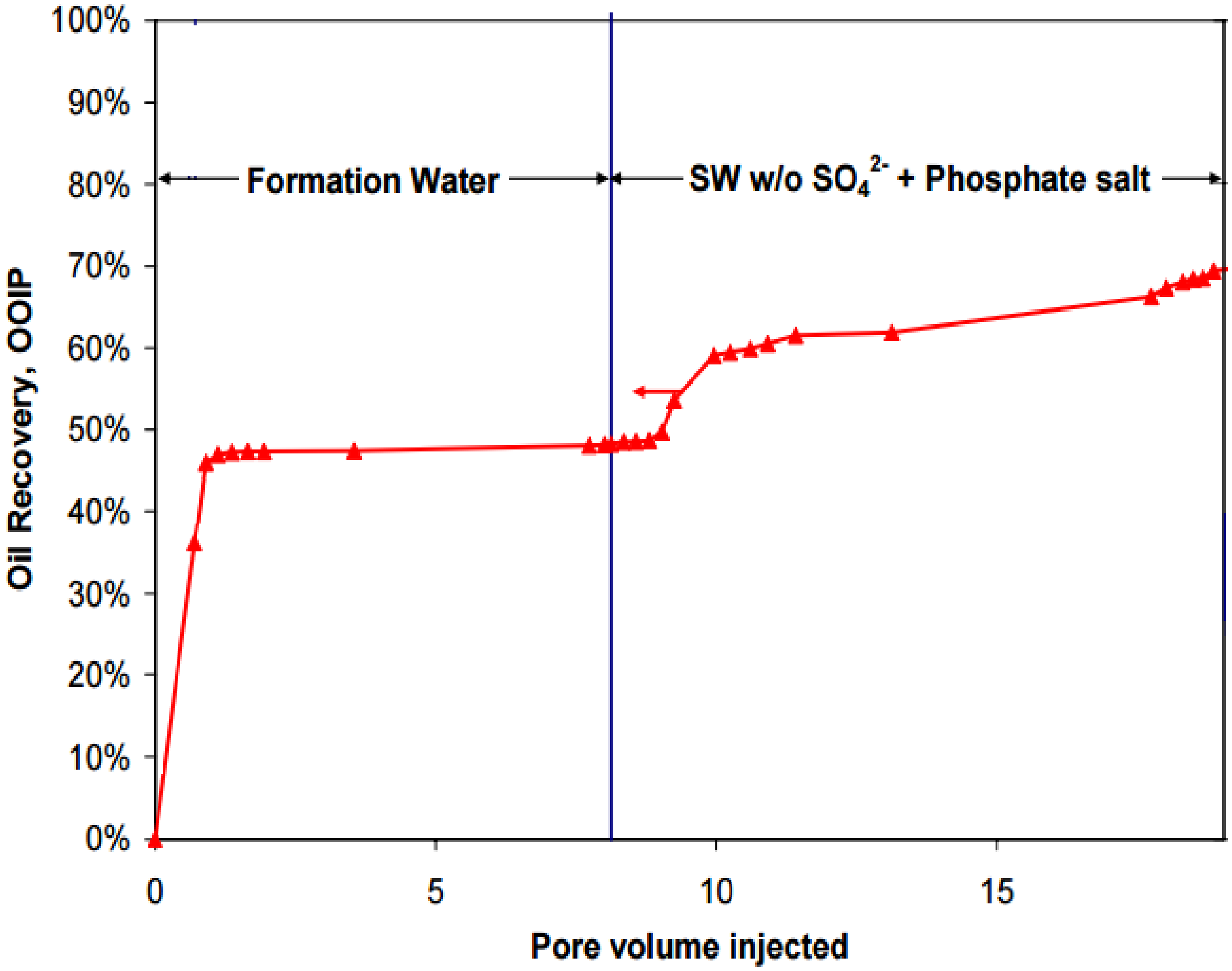


Figure 2.6 *Oil recovery by imbibing phosphate-containing seawater in a limestone core (Gupta et al., 2011).*

Along with other researchers Gupta *et. al* believed that wettability alteration is the dominant mechanism responsible for enhanced recovery with smart water. When phosphate is one of the ions existing in smart water in lieu of sulfate, the recovery mechanism in carbonate rocks would be akin to the mechanism that applies for sulfate. The multivalent orthophosphate ions compete with the acid group of the crude oil to be adsorbed by the calcite surface, following which the divalent cations compete to attach to the rock surface to balance the system's electrostatic charge, resulting in detachment of acid group from the carbonate surface and wettability alteration. One can argue that higher affinity of phosphate to positively charged carbonate rock surface compared to sulfate leads to superior phosphate adsorption. High affinity of phosphate for calcite was reported in a study regarding removal of phosphate species from solution by adsorption onto calcite (Karageorgiou et al., 2007). This matter could be considered as the major contributing factor to more successful oil recovery when phosphate is added to seawater that is free of sulfate.

2.1.4 Phosphate

Phosphate as an inorganic compound is an orthophosphoric acid (H_3PO_4) derivative salt known with the empirical formula PO_4^{3-}, having molar mass of 94.97 g/mol. The four oxygen atoms surround the central phosphorus atom forming a tetrahedral arrangement. Phosphoric acid in an aqueous environment can release up to three of its hydrogen molecules. The trivalent anion is the conjugate base of the hydrogen phosphate ion that is the conjugate base of dihydrogen phosphate ion, which in turn is the conjugate base of phosphoric acid. Negatively charged oxygen of phosphate anions can form phosphate salts by bonding with positively charged ions. Phosphates are mostly not soluble in water at standard temperature and pressure.

The fraction of phosphate species within an aqueous solution depends on solution's pH. The speciation diagram given in Figure 2.7 is obtained using logarithmic acid dissociation constant (pk_a) of three equilibrium equations given below:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad pk_{a1} = 2.12$$ *Equation 2.1*

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad pk_{a2} = 7.21$$ *Equation 2.2*

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad pk_{a3} = 12.67$$ *Equation 2.3*

The correlation between pH and pk_a of an equilibrium equation for weak acid dissociation is given by Henderson–Hasselbalch equation:

$$HA \rightleftharpoons H^+ + A^-$$

$$pH = pk_a + log(\frac{[A^-]}{[HA]}) \qquad \textit{Equation 2.4}$$

Where, [HA] and [A^-] are concentration of the weak acid and conjugated base, respectively. According to Henderson-Hasselbach equation when pH is equal to pk_a concentration of weak acid and its conjugated base should be roughly equal.

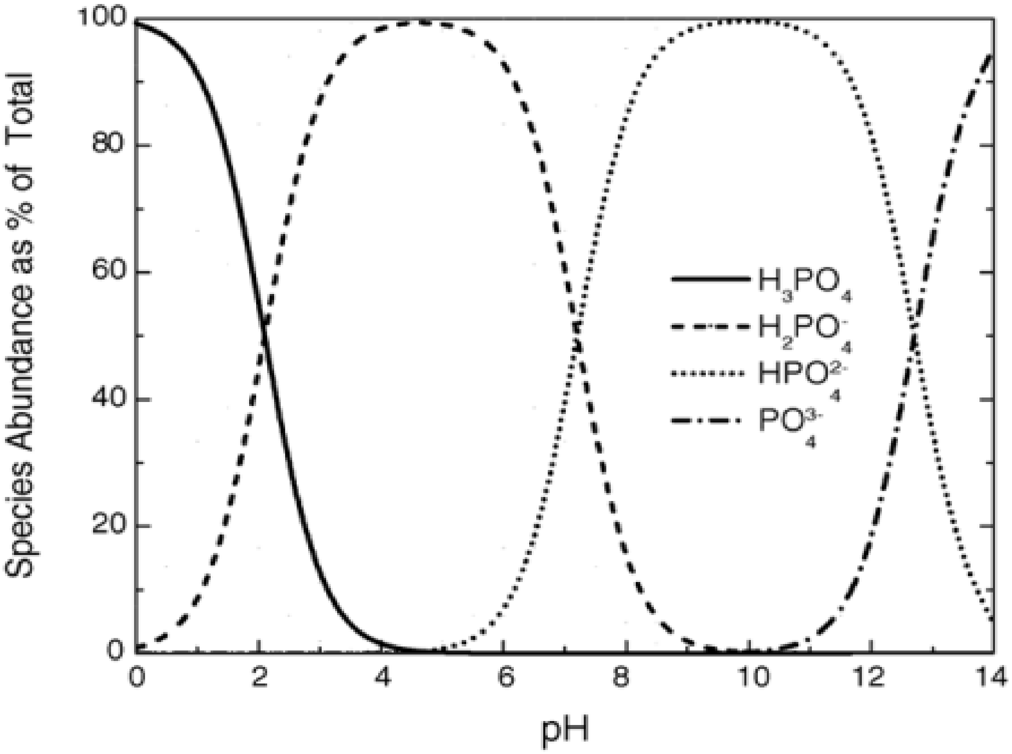


***Figure 2.7** Species abundance of phosphate, as a percentage of the total concentration at various pH (Hanrahan et al., 2005).*

Using the graph given in Figure 2.7 one can estimate the percentage of phosphate species that coexist at a given pH within an aqueous solution. For instance, trivalent anion of phosphate (PO_4^{3-}) is only produced when solution's pH is above 11.

2.1.5 Seawater ionic composition and quality

Saline water of oceans covers around 70% of the earth surface (Pidwirny, 2010). This would make seawater an available and inexpensive source of desired chemicals such as sulfate and calcium for offshore oil fields processes e.g. smart water flooding for enhanced oil recovery. However, seawater in order to be used for oil recovery purposes, as discussed in section 2.1.3, needs to be modified in terms of its ionic composition and the desired modification are unachievable without basic understanding of seawater chemistry and salt composition.

Water constitutes more than 96% of seawater. Nevertheless, the small amount of exacting salts in seawater results in seawater properties to slightly deviate from water properties. Moreover, the ions initiate the wettability alteration mechanism. Thus, the measurements of salinity, conductivity, total dissolved solids and turbidity test are both inevitable and crucial steps towards seawater modification.

2.1.5.1 Salinity

Salinity or saltiness in seawater is defined as the total amount of salts and dissolved inorganics in grams that exist in a kilogram (a liter) of seawater and it is usually presented in parts per thousands (‰). Several approaches towards measuring seawater's salinity are based on chlorinity and conductivity. All these measurement methods work well due to constancy of seawater composition, i.e. seawater abundant ions being independent of salinity and having little to no variation in different location (Stewart, 2008). Seawater salinity is generally assumed 35‰ although slight variation is likely due to precipitation and evaporation, dilution by river runoff etc. at different locations. Ionic composition in terms of molar concentration and mass concentration of seawater is available in Table 2.1.

Table 2.1 *Standard mean chemical composition of sea water (Salinity = 35) (Dickson and Goyet, 1994).*

Species	mol·kg-soln^{-1}	g·kg-soln^{-1}	mol·kg-H_2O^{-1}	g·kg-H_2O^{-1}
Cl^-	0.54586	19.3524	0.56576	20.0579
SO_4^{2-}	0.02824	2.7123	0.02927	2.8117
Br^-	0.00084	0.0673	0.00087	0.0695
F^-	0.00007	0.0013	0.00007	0.0013
Na^+	0.46906	10.7837	0.48616	11.1768
Mg^{2+}	0.05282	1.2837	0.05475	1.3307
Ca^{2+}	0.01028	0.4121	0.01065	0.4268
K^+	0.01021	0.3991	0.01058	0.4137
Sr^{2+}	0.00009	0.0079	0.00009	0.0079
$B(OH)_3$	0.00032	0.0198	0.00033	0.0204
$B(OH)_4^-$	0.00010	0.0079	0.00010	0.0079
CO^*2	0.00001	0.0004	0.00001	0.0004
HCO_3^-	0.00177	0.1080	0.00183	0.1117
CO_3^{2-}	0.00026	0.0156	0.00027	0.0162
OH^-	0.00001	0.0002	0.00001	0.0002
sum of column	1.11994	35.1717	1.16075	36.4531
ionic strength	0.69734		0.72275	

2.1.5.2 Conductivity

Conductivity is the ability of an object to conduct electricity. Seawater as an electrolyte solution is a good conductor of electricity due existence of ionized salts.

Seawater’s conductivity is directly proportional to the salinity and total dissolved solids, as higher salinity increases the concentration of charged species within seawater, which results in a more powerful electricity current and higher conductivity. Water’s conductivity is usually measured using a probe containing two electrodes within a specific distance; as a result, the conductivity is expressed in millisiemens per centimeter (mS/cm). Figure 2.8 shows the principle of conductivity measurement. Seawater’s conductivity is generally around 50 mS/cm, which is one million times higher than the conductivity of deionized water (Masters and Ela, 2008).

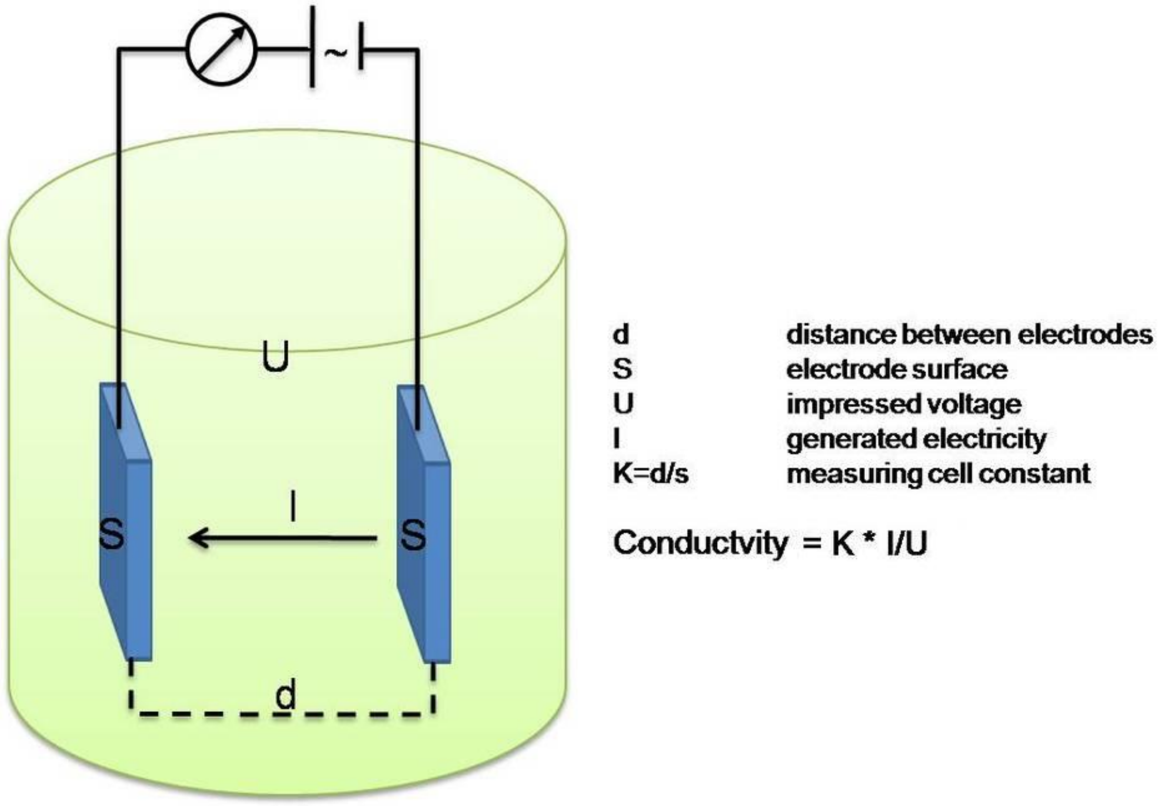


Figure 2.8 *conductive measuring principle (Hoberg, 2015)*

2.1.5.3 Total dissolved solids (TDS)

Total dissolved solids (TDS) is a measurement of water quality by the existing amount dissolved inorganic charged ions and organics within specific volume of water. TDS is expressed in mg/l or part per million (ppm) (Masters and Ela, 2008).

2.1.5.4 Turbidity

Turbidity is the degree of clearness of a specific volume of water from suspended particles. How much a sample water can pass the light through itself depends on the sample's contaminants, which is the basis of turbidity test. The more pure the water is the less it scatters the light wave emission (Water.epa.gov, 2015a). The device that is used to measure turbidity is called nephelometer and it is expressed in Nephelometric turbidity unit (NTU). Figure 2.9 shows the principle of turbidity measurement.

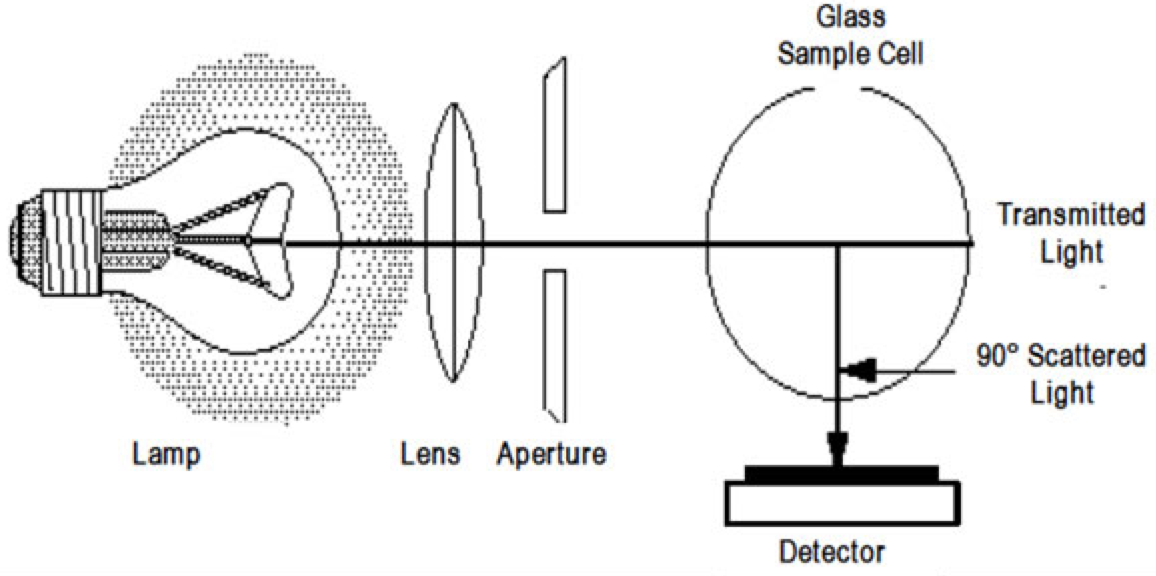


Figure 2.9 *Schematic of turbidity measurement principle (Sadar, 1998)*

Standards regarding drinking water differs from country to country. For instance in US the turbidity of a plant outlet drinking water must be less than 0.3 NTU 95% of the times and should not exceed 1 NTD when conventional or direct filtration methods are used (Water.epa.gov, 2015b). Seawater generally does not include a large amount of suspended particles and it has a low turbidity although adding specific salt to seawater can increase turbidity due to precipitation.

2.2 Membrane separation

A selective interphase between two phases next to each other, which regulates the transport of substances between the two sections, is called membrane. Membrane technology is a separation process benefiting from its selectivity of the barrier to separate the inlet feed flow. Unlike other thermal separation processes, membrane separation operations are efficient when used at low temperatures, resulting in lower energy consumption. This type of separation is a straightforward process that does not require large footprint and it can be easily combined with other equipment in order to be upgraded (Cheryan, 1986).

The basis of modern membrane science in laboratory was developed by 1960 but it was the development of Loeb-Sourirjan process for achieving defect-free and high-flux RO membranes that resulted in transforming laboratory scale membrane separation to industrial scale membrane. Nowadays, membrane separation technology is being used in vast number of industries from medicine to chemical application (SIDNEY and SRINIVASA, 1963).

2.2.1 Principle

Membrane separates the feed stream into two phases. When the feed contains different components membrane simply allows one or few the components pass through while it rejects the other components transport through the membrane. Different driving forces such as concentration gradient, pressure gradient, electrical potential gradient or temperature gradient together with selectivity of membrane results in a separation and division of feed stream into two stream, the concentrate stream (retentate) which is the rejected side and the permeate stream. Figure 2.10

represents a membrane process concept. Each of these two stream could be the favorable product considering the application.

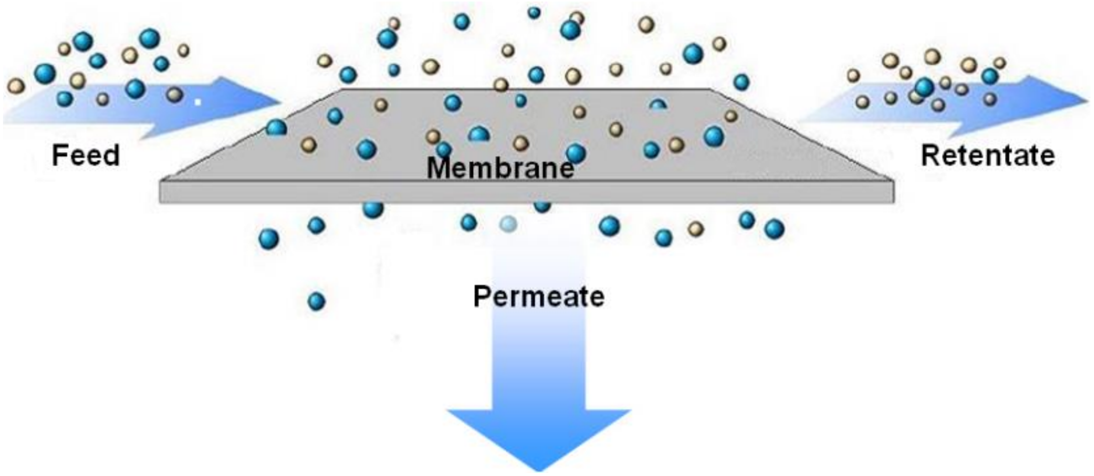


Figure 2.10 *Schematic of a membrane separation concept (Schmeling et al., 2010)*

The membrane separation purposes are normally purification of feed, achieving a high concentration solution and fractionation of a mixture into two or more favorable components (Cheryan, 1986). The end-use and application objective are decisive factors in terms of choosing a suitable membrane processes and the membrane itself. For instance, a membrane that is used for removal of large particulates will fail to produce potable water. Different membrane type and operation will be discussed in the following sections.

2.2.2 Membrane processes and driving forces

Driving forces are a basis for classification of membrane operations. Different membrane processes with regard to their driving forces are:

- *Electrically driven processes,* in which electrical potential difference induces the driving force for ionic transport e.g. electrodialysis and membrane electrolysis.
- *Concentration driven processes***,** which are dialysis and osmosis. These processes benefit from concentration gradient. In osmosis, osmotic

pressure gradient (π) is the driving force. This gradient is due to the difference in chemical potential and solute concentration across the semi-permeable membrane (Cath et al., 2006)

- *Pressure driven processes* use pressure difference between feed and permeate stream across the membrane to make the solvent pass through the membrane. The size, shape and charge of particles and dissolved content along with the pore size of membrane results in the separation. Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and reverse osmosis (RO) are the four main membrane processes in this category. As the pore size decrease from MF to RO, more pressure is needed for the separation and the concentration of retentate side increases. Moreover, rejection flux, which is dependent on applied pressure, will decrease (Shih, 2005). Table 2.2 shows the values for applied pressure and their correlated fluxes for different membranes.

Table 2.2 *Molecular weight cut off, flux range and used pressure range in MF, UF, NF and RO membrane processes (Van der Bruggen et al., 2003).*

Membrane operation	Pressure range (bar)	Hydraulic permeability range ($L.h^{-1}.m^{-2}.bar^{-1}$)	MWCO (Da)
MF	0.1 - 2	> 1000	$> 10^6$
UF	1 - 5	10 - 1000	1000-300000
NF	3 - 20	1.5 - 30	200-1000
RO	5 - 120	0.05 - 1.5	< 200

2.2.3 Membrane classification

The classification of membrane is typically according to membranes' separation mechanism, structure and material, and configuration, which will be discussed in the following sections.

2.2.3.1 Separation mechanisms

Different morphology of membrane results in different separation mechanism. Porous character of the membrane could be a basis for classification membrane barrier as Table 2.3 shows classification of membrane according to barrier porosity and transfer mechanism.

Table 2.3 *Classification of membranes and membranes transfer mechanisms (Ulbricht, 2006).*

Membrane barrier porosity	*Transfer mechanism*		
	Viscous flow/size exclusion	*solution/diffusion*	*Electrochemical exclusion*
Non-porous		Reverse Osmosis (RO) Pervaporation (PV) Gas separation (GS)	Electrodialysis (ED)
Microporous pore diameter $d_p \leq 2$ nm	Nanofiltration (NF)	Nanofiltration (NF)	Dialysis (D)
Mesoporous pore diameter $d_p = 2–50$ nm	Ultrafiltration (UF)	Dialysis	Electrodialysis
Macroporous pore diameter $d_p = 50–500$ nm	Microfiltration (MF)		

- *Porous membranes'* selectivity and transport rate are under the influence of sieving exclusion due to pore size and the viscosity of flow. However, performance of porous membrane could be altered by the interaction between membrane and solutes like rejection of monovalent ions in aqueous solution by NF membranes as a result of their Donnan potential (Ulbricht, 2006).
- *Non porous membranes'* transport mechanism is described by solution/diffusion model
- *Ion-exchange membranes* are either negatively charged, positively charged or bipolar and the transport mechanisms through these types of membranes are solution/diffusion model with Donnan effect for nonporous membrane and electrokinetic mechanism for porous membrane.

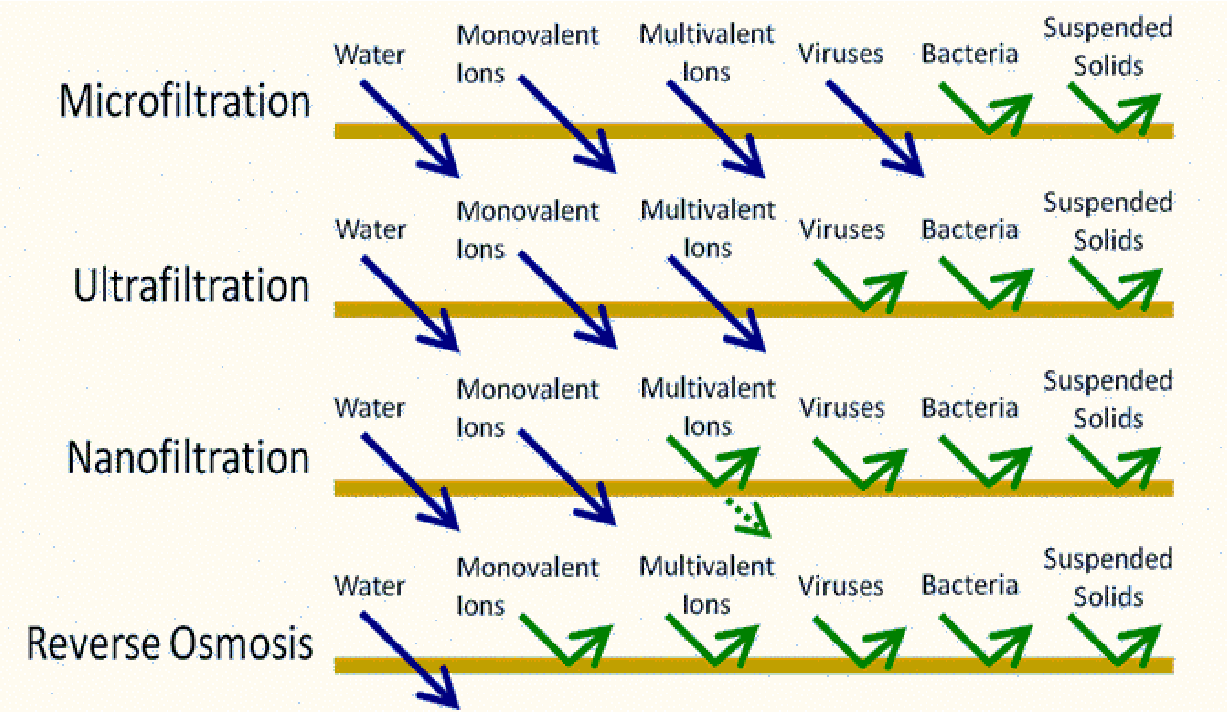


Figure 2.11 *Membrane separation characteristic (aquaclearllc.com, 2015).*

Nanofiltration membrane separation mechanism

Physiochemical characteristics of both solutes and membrane are factors that dictates the separation mechanism in NF membranes. From physical selectivity point of view size exclusion and charge repulsion lead to separation while solvation energy, hydrophobic interaction or hydrogen bonding are chemical selectivity factors that regulates fractionation.

Sieving effect refers to separation occurring due to size difference between solutes and pore size of membrane. When a solute's molecular weight (MW) is less than membrane's molecular cut-off (MWCO) it will pass through membrane's pore otherwise it will be rejected. This mechanism mostly controls the separation of uncharged molecules. Sieving come about by convection through pressure difference and diffusion through concentration gradient across the membrane (Košutić and Kunst, 2002; Van der Bruggen et al., 1999). Charged compounds separation, on the other hand, is controlled by both electrostatic interaction between membranes and the compound and size difference. Surface charge of a NF membrane is an influential factor in separation mechanism. NF membrane surface is mostly charged and this charge results in repulsion between membrane and ions with the same charge which are called co-ions (Schaep et al., 1999). This type of ion separation is based on Donnan exclusion mechanism (Childress and Elimelech, 2000). In this mechanism by rejections of co-ions, counter-ions are retained to maintain electroneutrality condition. Rejection of multivalent ions and more efficiently multivalent co-ions is much higher than monovalent ions due to larger charge interaction (Van der Bruggen et al., 2004). There are several factors affecting Donnan effect such as salt concentration, co-ion and counter-ion valance and the fixed charge concentration of the membrane. Formation of a counter-ion shield on NF membrane is likely by increasing the salt concentration which leads to less repulsion forces consequently less rejection (Afonso et al., 2001). Moreover, an increase in co-ion valance and a decrease in counter-ion valance results in an increase rejection (Yaroshchuk, 2001). For instance, using a negatively charged membrane should result in more rejection of Na_2SO_4 compare to NaCl due to their anion charge density and rejection of Na_2SO_4 is more than $CaSO_4$ due to their cations charge density. Diffusivity could affect the rejection sequence when ions have the same valance. Retention of an ion is likely to be more when the ion has low diffusivity and high stokes radius. This radius, which is indirectly proportional to diffusion coefficient, can be calculated through Stokes-Einstein, which is given by:

$$r_i = \frac{KT}{6\pi\eta D_i} \qquad \textit{Equation 2.5}$$

In which T is temperature (K), K is Boltzman constant (J/mol.K), η is viscosity (Kg/m.s) and D_i is diffusion coefficient (m^2/s).

Hydration energy is another parameter that is needed to be taken into account in rejection of ions, which are dissolved in water. This energy could be considered as the required forced to put the solute through the membranes' pores. In this way, ions are less retained when they have lower hydration energy (Pontalier et al., 1997). Hydration energy and hydrated radius have showed to be the decisive parameter in separation of ions with the same charge by nanofiltration membrane. Table 2.4 presents thermodynamic values of hydration and hydrated radius for different ions. Furthermore, dielectric exclusion is another explanation to separation of nanofiltration membrane. Different dielectric constants at the interfaces of membrane and solvent induce interaction between ions with bound electric charges. This phenomena brings about dielectric exclusion (Yaroshchuk, 2001; Szymczyk et al., 2006). The separation mechanism of NF membrane is more complicated when a mixture of salts and ions is spiked to the feed stream. For instance increasing the concentration of low permeable co-ions could result in higher permeability of monovalent ions (Tanninen et al., 2006). Moreover, all the mentioned mechanisms plus membrane and solute properties seems to be only a part of existing explanation and there are still NF membrane separation mechanisms that are unidentified.

Table 2.4 *Thermodynamic quantities for ion hydration and hydrated radius at 298.15 K (Marcus, 1997; Lv et al., 2008; Kiriukhin and Collins, 2002).*

Ion	Δ_{hydr} H$^{\infty}$ (KJ. Mol^{-1})	Δ_{hydr} S$^{\infty}$ (J. K^{-1}. Mol^{-1})	Δ_{hydr} G$^{\infty}$ (KJ. Mol^{-1})	Hydrated radius (nm)
H^+	-1103	-131	-1064	0.28
Li^+	-531	-142	-489	-
Na^+	-416	-111	-383	0.36
Mg^{2+}	-1949	-331	-1850	0.43
Ca^{2+}	-1602	-252	-1527	-
Cl^-	-367	-75	-345	0.33
$H_2PO_4^-$	-522	-166	-473	0.302
SO_4^{2-}	-1138	-249	-1064	0.38
HPO_4^{2-}	-1170	-272	-1089	0.327
PO_4^{3-}	-2879	-421	-2773	0.34

2.2.3.2 Membrane structure

Membranes come under three categories regarding the uniformity of their pore structure within the membrane. These three classes of membranes are symmetric, asymmetric and composite membranes. Figure 2.12 shows these types of membrane structure.

- *Symmetric membranes'* pore diameter and pore cross section are homogenous across the membrane.
- *Asymmetric membranes* are composed of a very thin and dense layer (0.1-1.0 microns) called skin on a highly porous and much thicker substrate (100-200 microns) called the support layer. This type of membrane has displaced asymmetric membranes since they have higher fluxes.
- *Thin film composite membranes* includes two layers or more with different structure. These types of membranes are superior than asymmetric

membranes since thin film composite membranes have higher permeation and rejection rate (due to lower thickness) and they also reduce pressure drop across the membrane (Ulbricht, 2006).

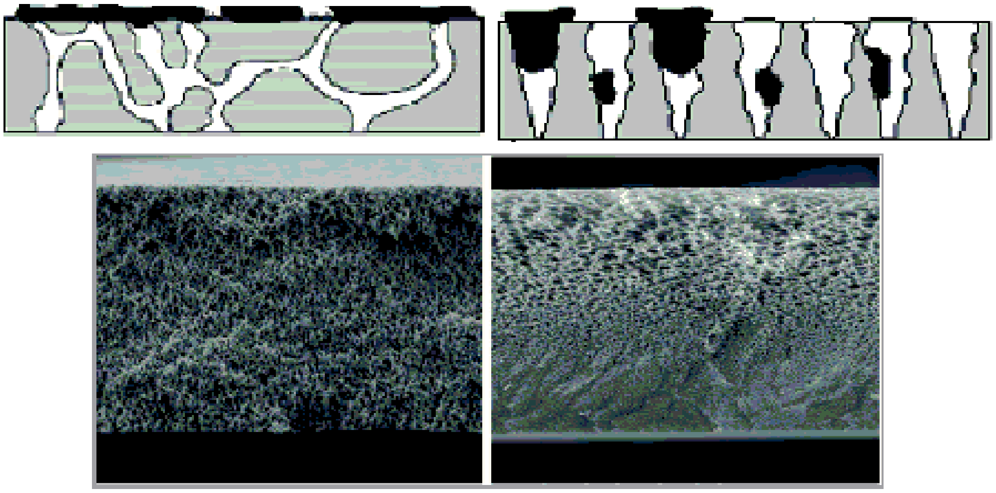


Figure 2.12 *Symmetric membrane structure (left) and asymmetric membrane structure (right) (Wu et al., 2007).*

2.2.3.3 Membranes materials

Materials that are used in membrane fabrication could come under organic, inorganic and hybrid categories. Cellules acetate, aromatic polyamides and polysulfone are good example of polymer (organic) class while ceramic, metal and glass are typical materials that are used in production of inorganic membranes. In comparison of these two classes of membranes, it is noteworthy to mention that inorganic membranes can be applied in a more hostile environment e.g. high temperature, high and low pH range. These high mechanical and chemical stabilities results in a longer lifetime. However, organic membranes are cheaper and superior than inorganic ones in terms of pore properties and surface modification potential (Cheryan, 1986). In addition to these two classes, organic-inorganic hybrid membranes has shown to be advantageous in terms of selectivity and flux while offering proper thermal and chemical stability (Sforca et al., 1999). Classification of these membrane is based on the interaction and bonding of organic and inorganic material which are either Van der Waals forces and hydrogen bonds or covalent (Cot et al., 2000).

2.2.4 Membrane shape and design

Membranes in order to be applied in an operation need to be housed in modules and the design of these modules are reliant on the shape of membrane. Different modules are as follows:

- *Flat sheet module* contains a channel in which membranes with flat rectangular shape are placed. As the feed is pumped to the channel, separation takes place and permeate will be collected through the existing cut at the bottom of the frame. The main disadvantages of this module are low hydraulic pressure and large footprint due to low packing density.
- *Spiral wound module* are manufactured by sticking the edges of several flat sheet membrane together with their active layer facing outward and a spacing mesh in between. These membranes are then glued and rolled up around a pierced central tube. Permeate then will be collected from the central tube as the feed is pumped through the membrane. This module configuration results in an easier maintenance and smaller footprint compare to other modules while it suffers from flow complexity and cleaning difficulties.
- *Tubular module* includes several non-self-supporting tubular shape membranes enclosed in a PVC or stainless still shell. When feed goes through one end of this module the permeate will be collected on the shell side and the retentate will leave the membranes from the other end. These modules have a low packing density but they are easy to clean.
- *Hollow fiber module* follows the same concept as tubular module. However, existence of self-supporting in hollow fiber module is the key difference that separates the two modules. High packing density is the advantage of this

module while being prone to plugging is the main drawback when using hollow fiber module.

Figure 2.13 illustrates four membrane design modules.

Figure 2.13 *Membrane design modules. Flat sheet module (top left), spiral wound module (top right), tubular module (bottom left) and hollow fiber (bottom right).*

2.2.4.1 Nanofiltraion membrane structure

NF membranes are either asymmetric or thin film composite. The dense thin layer on the surface of porous layer in thin film composite membrane results in higher permeability and salt rejection compared to asymmetric membrane (Yang et al., 2007). Homogeneous asymmetric NF membranes are resulted from polymer phase inversion and polysulfone cellulose acetate are the most common materials used in this class. Whilst, thin film composite NF membrane is prepared by polarization of thin film on top of a porous substrate. This class benefits from reacted polyamide to a charge group such as carboxylic group for its surface layer and polysulfone, polyacrylonitrile, polyethersolfune etc. are commonly used as substrate material. Once these membranes are prepared, they will be packed to either spiral wound, tubular or flat sheet modules. Information regarding some of the nanofiltration membrane manufacturers are available in Table 2.5.

Table 2.5 *Main manufacturers of Nanofiltration membranes (Ben Farès, 2006).*

Manufacturer	Material	Configuration
Advance Membrane Technology (United States)	PSSF	Spiral
Dow chemical (Denmark)	PA	Spiral
Filmtec (United States)	Diverse	Diverse
UOP fluid system (United States)	CA-PA	Spiral
Hoechst (Germany)	CA-PES	Flat sheet /spiral
Hydranautics (United States)	Composite	Spiral
Kalle (Germany)	CA-PA	Plat/Spiral
Koch membrane systems (Germany)	Diverse	Diverse
Membrany (Russia)	Diverse	Diverse
Millipore (United States)	PA	Plat/spiral
Nitto-Denko (Nitto Electrical Industriel) (Japan)	PVA-PSF	Diverse
North Carolina SRT (United states)	Diverse	Plat
NWW acumen (United states)	PS	Spiral
Osmonics Desalination Systems (United states)	CA-PA	Spiral
Osmota (Germany)	Composite	Diverse
Stork Friesland (Canada)	PA	Tubular
Orelis (France)	Zircon	Diverse
Tami (France)	Ceramic	Tubular
Toray (Japen)	PA-PES	Spiral
Tri-Sep (United states)	PA	spiral
US Filter SCT (United states, France)	Titan	Tubular
X-Flow (Netherland)	PES	Spiral

Polysulfone (PSF), polyethersulfone (PES), Polyamide (PA), Polysulfone sulfonated (PSSF), Polyvinyl alcohol (PVA).

2.2.5 Nanofiltration membrane (NF)

Nanofiltration membrane deploys pressure induced by a pump on the feed stream or suction on permeate side to separate the inlet stream constituent. This type of membrane's properties lie between ultrafiltration and reverse osmosis. The term nano identifies the pore size of this permeable membrane. Having pore size around 1 nm and molecular weight cut-off between 200 to 1000 Da, this membrane allows water and nanoparticles to get through and rejects the rest. This property results in higher quality of NF permeate compare to ultrafiltration while having a lower quality than reverse osmosis. Moreover, existence of pore gives an edge to nanofiltration when contrasted with reverse osmosis regarding their operating pressure range. However, aside from pore size, the electrostatic charge of the NF membrane's surface is a decisive factor in terms of transmitting and rejection of ions, as discussed in section 2.2.3.1 and 2.2.7. High flux, high rejection, low operational pressure and low investment are some of NF membrane advantages.

2.2.6 Application of nanofiltration membranes

Nanofiltration membrane were being used in potable water industry for hardness reduction and water softening purposes. This usage resulted in NF membranes being referred to as softening membranes (Van der Bruggen and Vandecasteele, 2003). Over the course of time, use of these membranes has shown to be advantageous when (Rautenbach and Gröschl, 1990):

- Rejection of multivalent ions is the goal while retention of monovalent is inessential.
- Separation of low molecular weight organic from monovalent salts is favorable.
- Lower permeate quality with reduction of operational pressure compare to RO is required.

Benefiting from fractionation and selective removal of pollutants in a complex stream, application of these membranes is popular in several industries. Separation of pharmaceuticals (Yoon et al., 2007), recovery of metal from wastewater (Fane et al., 1992), virus removal (Hoffer et al., 1995), demineralization in dairy industry (Frappart et al., 2006) etc. are some of the application of these membranes. Moreover, nanofiltration membrane plays a crucial role in desalting processes.

2.2.7 Nanofiltration membrane surface characterization

NF membrane surface properties play a vital role in fractionation of the inlet feed stream. Permeability, solute selectivity and rejection ratio are main properties of a membrane defined by its surface. Parameters that are mainly used for characterization of a membrane and its properties are molecular weight cut-off (MWCO), contact angle and surface charge.

2.2.7.1 Molecular weight cut-off

The fundamental of MWCO is based on the idea that heavier molecules are larger than lighter molecules. Hence, by an increase in solutes MW they are more retained by membrane according to membrane pore size. Different manufacturers use different definition for their membranes' MWCO. However, MWCO is defined as MW of a solute that is rejected at 90 percent (Van der Bruggen et al., 1999).

2.2.7.2 Hydrophobicity

When a water droplet is placed on a surface they form an angle, which defines a surface hydrophobicity. A surface is hydrophilic if this angle is more than 90 degrees and hydrophobic when the angle is less than 90 degrees. High permeability and low fouling are hydrophilic surface advantages (Pearce, 2007), while hydrophobic surface benefits from higher chemical and mechanical stability and high salt rejection (Mulder, 2003).

2.2.7.3 Membrane charge

Membrane surface obtains electrical charge when contacted by electrolyte medium through various mechanisms e.g. adsorption of electrically charged components such as ions and charged macromolecules and dissociation of functional group.

When counter-ions attracted by membranes surface they form a double layer. A plane of shear separates the mobile and immobile part of the double layer. The Electrical potential at the shear plane is called zeta potential. The fact that determination of the electrical potential of the surface of membrane cannot be done experimentally, is why zeta potential is of key importance. Determination of zeta potential is possible through measurements such as streaming potential, sedimentation potential, electro-osmosis or electrophoresis (Hunter, 2013; Elimelech et al., 1998; Schaep and Vandecasteele, 2001).

2.2.8 Membrane performance and effective parameters

Performance of a membrane is commonly attributed to flux and salt rejection of the membrane. These two parameters are under the influence of several factors such as pressure, temperature, feed concentration, membrane area etc. Flux (J) is the rate of solvent transport per unit area per unit time and is given by:

$$J = \frac{Q_p}{A} \qquad \textit{Equation 2.6}$$

In which J is flux ($L.m^{-2}.h^{-1}$), Q_p is permeate flowrate ($L.h^{-1}$) and A is membrane area (m^2). Permeate flux when pure water is used, as membrane's feed is directly proportional to transmembrane pressure according to Darcy's law:

$$\frac{J}{\Delta p} = L_p \qquad \textit{Equation 2.7}$$

Where L_p is constant hydraulic permeability ($L.m^{-2}.h^{-1}.bar^{-1}$) that reflects the porous structure of the membrane (Košutić et al., 2006).

Membrane's rejection is defined as the portion of a target solute, which is retained by the membrane (desalting) and is given by:

$$R = \left(1 - \frac{C_p}{C_f}\right) * 100 \qquad \textit{Equation 2.8}$$

Where R is the rejection percentage, C_p is concentration of the target solute in permeate and C_f is concentration of the target solute in feed stream.

Most important parameters regarding performance and operation of a NF membrane are:

- *Pressure* plays a vital role in NF membrane as it is the driving force of the process. Favorable separation could be achieved by NF membranes at pressures more than 10 bar.
- *Temperature* is indirectly proportional to viscosity. Hence, by an increase in temperature the viscosity of the aqueous medium decreases and membrane’s flux increases. High temperature could also slightly effect the membrane’s morphology by increasing the mean radius of the membrane’s pore while simultaneously decreasing pore density that can affect the rejection characteristic of membrane (Sharma and Chellam, 2005).
- *Salinity* of the feed solution when increased results in a decrease of the rejection of monovalent ions. This is due to increase of charged pore radius resulted from increase in ionic strength. This effect is more significant on monovalent than multivalent (Xu and Lebrun, 1999; Jitsuhara and Kimura, 1983).
- *pH* can affect the membrane’s performance in several ways. For instance, at neutral to high pH surface of a NF membrane is commonly negatively charge and low pH results in membrane’s losing its charge. pH also can affect membrane pores depending on membrane’s material. Aside from membrane itself, pH could affect the solubility and dissociation state of ions leading to a change in rejection rate of the ions (Teixeira et al., 2005; Bellona et al., 2004)
- *Crossflow velocity* can increase the flux by reducing fouling when it is increased. However, increase of crossflow velocity increases the pressure drop. Moreover, intensifying cross flow velocity over its mechanical stabilities could result in premature failure of the membrane (Koyuncu, 2002).
- *Recovery rate* of feed water recovery has showed to be effective in a rejection of total hardness. Research findings indicate that increase in recovery rate

leads to a higher diffusion across the membrane. This increase could pose major problems such as stronger concentration polarization, solute adsorption onto membrane surface etc. all able to affect membrane's performance adversely (Chellam and Taylor, 2001; Lhassani et al., 2001).

Chapter 3: Methodology

3 Methodology

In order to achieve the objectives of the study mentioned in section 1.1, the experiment were broken down into three steps including chemical selection, membrane separation and ionic analysis by ion chromatography. All the experiments were carried out at university of Stavanger.

3.1 Chemical selection

Phosphate salts are not highly soluble in water and their solubility is even less in seawater. Thus, several phosphate salts were studied regarding their solubility in water at different temperature and three of those were selected for further solubility observation test in seawater.

3.1.1 Sample preparation

Based on solubility in water, different amounts of phosphate salts were added to one liter of seawater in order to estimate lower and higher limits of the chemicals concentration in seawater before they precipitate.

3.1.2 Turbidity test and pH

A calibrated HUCH 2100N Turbidimeter was used for turbidity measurements. Sample containers were inverted a few times to ensure homogeneity and they were poured into rinsed sample cells. The sample cells were wiped clean by a lint free cloth before placing them into the cell compartments. Afterwards, the readings from the device were each logged as the each samples turbidity. Finally, every samples' pH were measured using a VWR pH 1100L. Figure 3.1 and Figure 3.2 show pictures of the applied turbidimeter and pH meter, respectively.

Figure 3.1 *HUCH 2100N Turbidimeter*

Figure 3.2 *VWR pH 1100L pH meter*

3.2 Membrane separation

The experimental setup for membrane separation included a tank, a high-pressure pump for running the feed and producing trans-membrane pressure, a high-pressure holder for the nanofiltration membrane and a pressure gauge. In order to maintain feed concentration both permeate and concentrate flow were recirculated to the feed tank. Figure 3.3 illustrates a schematic diagram of the experimental setup. A spiral-wound nanofiltration membrane manufactured by Hydranautics (nito denko Co.)

NANO-SW-2540 with membrane active area of 2.3 m^2 and nominal divalent ion ($MgSO_4$) rejection rate of 99.8% was used. The experiments were carried out at ambient temperature .Total recirculation of the concentrate and the permeate flow were applied to maintained feed concentration. Pressure and volumetric flow rate were adjusted using the pump's outlet valve. Membrane's specification sheet is available in Appendix I on page 84. Laboratory setup of the experiment is demonstrated in Figure 3.4.

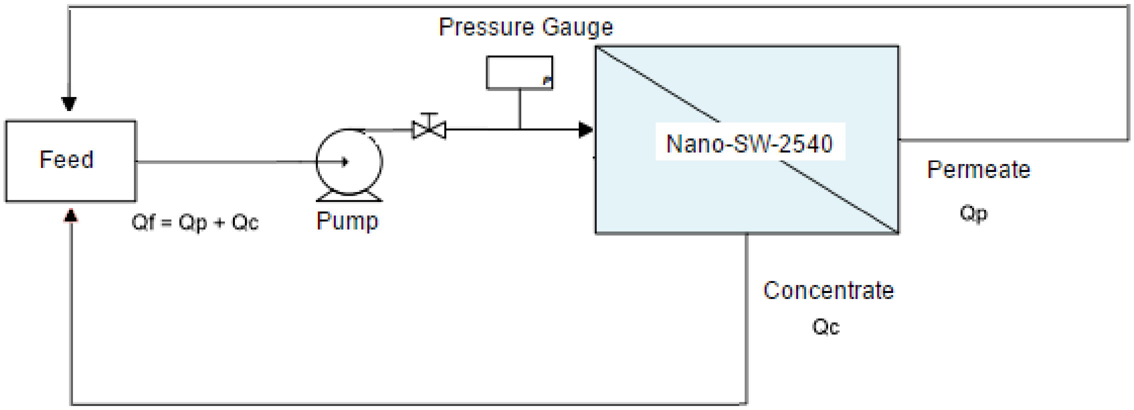


Figure 3.3 *Schematic diagram of the NF membrane separation setup*

Firstly, the feed tank was filled with 120 liter of seawater. Having the feed, permeate and retentate tubes submerged into the seawater tank unit was turned on at 6 bar. Pressure was increased by 2-bar increment at 20 minutes intervals to 16 bar. Two sets of sample were taken from feed before starting up the unit and two sets of samples were taken from permeate and rejection pipes at end of each interval.

Figure 3.4 *Membrane unit, feed tank and feed, permeate and retentate pipes*

TDS, salinity, conductivity, temperature and pH of the first set of samples were measured using a VWR CO 3100L TDS meter (Figure 3.4) and pH 1100L pH meter. Both devices' probe, before and after being placed into samples' container, were washed using distilled water in order to prevent any error caused by contamination. The second set of samples were preserved for ionic analysis that is explained in section 3.3.

Figure 3.5 *VWR CO 3100L TDS meter*

In order to investigate the effect of phosphate in ion separation of the membrane three doses of each chemical were added to seawater feed. In three first experiments 0.13, 0.18 and 0.21 grams of first chemical per liter of seawater were used to create the desired phosphate concentration within the seawater as the membrane's feed stream. Similarly, in second three experiments 0.13, 0.18 and 0.20 grams of second chemical per liter of sweater feed were used. In order to investigate effect of PO_4^{3-}, 400 grams of NaOH was added to 92 liters of seawater to adjust high pH solution. Afterwards first dose of second chemical were added to the solution.

It is noteworthy to mention that operating pressure range for the second dose of first chemical was from 8 to 18 bar due to a technical problem with the unit's pump.

3.3 Ionic analysis

The second sets of samples from membrane separation experiment were taken to ion chromatography (IC) laboratory at Petroleum department at University of Stavanger for ion analysis. Ion chromatography was used to calculate the concentration of each ion within all the samples. Ionic analysis of samples was performed using Dionex ICS-3000 and ICS-5000 machines linked to Thermo Scientific™ Dionex™ Chromeleon™ software (Figure 3.6).

***Figure 3.6** Dionex ICS-5000 chromatography machine*

These machines are designed for ion analysis of high quality water. Thus, the high TDS samples from membrane separation had to be diluted 500 times using automatic dilution software (GX-271) before being analyzed by the chromatography machines. Figure 3.7 shows dilution machine linked to a computer.

Figure 3.7 *Dilution device linked to GX-271 software*

It was also required to have a few reference samples with known ionic composition for data analysis. Therefore a synthetic sweater (SSW) containing 2 g/L of phosphate salt was made and diluted 500 times to be used as reference sample. Composition of the SSW is available in Table 3.1 below.

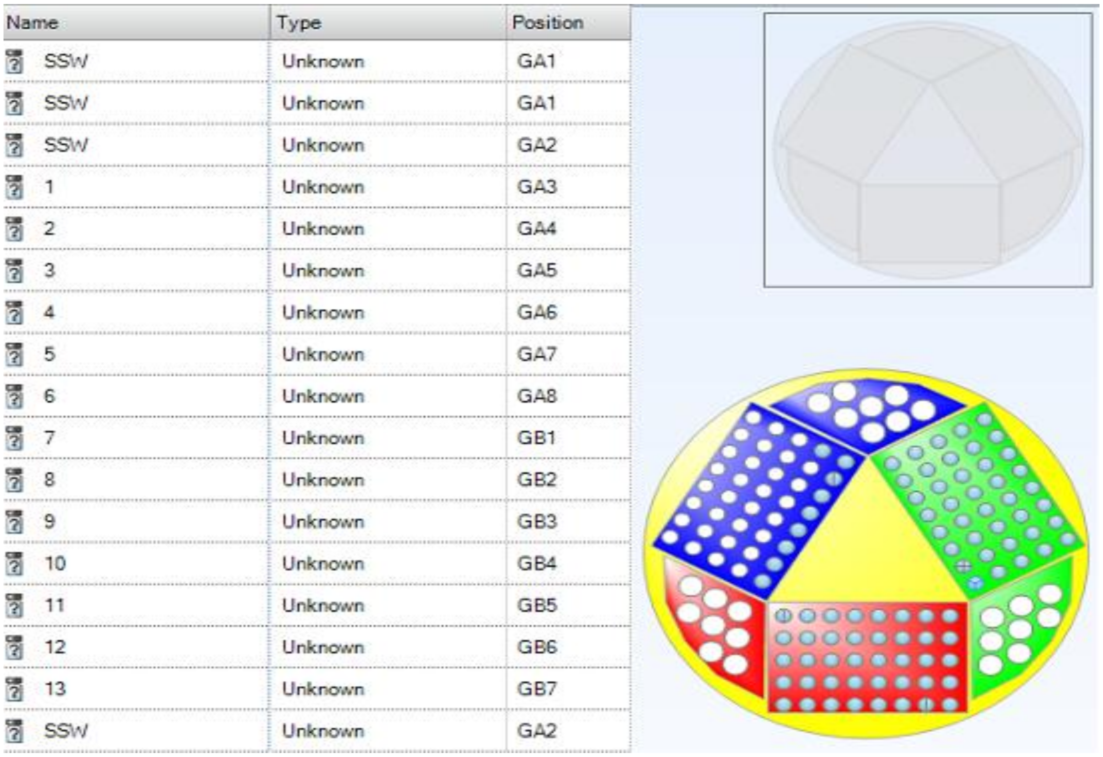
Table 3.1 *Chemical composition of Synthetic seawater used as referance for ionic chromatography.*

Chemical	**Concentration (g/l)**
NaCl	23.38
Na_2SO_4	3.41
$NaHCO_3$	0.17
$MgCl_2*6H_2O$	9.05
$CaCl_2*2H_2O$	1.91
KCl_2	0.75
XPO_4†	2
Total	40.67
TDS	31.4

† First phosphate salt

All the diluted samples were given a number. Afterwards they were placed in the sampler container according to correlated number, letter and color section. For instance sample number 33 were placed in GE3 i.e. column 3, row E on green section. The position and the allocated number were linked on the software's interface. Figure 3.8 illustrates interface of Chromeleon software where samples name and position are arranged.

Dionex ICS-3000 and Dionex ICS-5000 used eluent (deionized water) to pass the samples through resin column, thus the eluent container had to be full before running the experiment. Figure 3.9 shows eluent containers.



Name	Type	Position
SSW	Unknown	GA1
SSW	Unknown	GA1
SSW	Unknown	GA2
1	Unknown	GA3
2	Unknown	GA4
3	Unknown	GA5
4	Unknown	GA6
5	Unknown	GA7
6	Unknown	GA8
7	Unknown	GB1
8	Unknown	GB2
9	Unknown	GB3
10	Unknown	GB4
11	Unknown	GB5
12	Unknown	GB6
13	Unknown	GB7
SSW	Unknown	GA2

Figure 3.8 *Samples' numbers and positioning in ISC-5000 on Chromeleon software.*

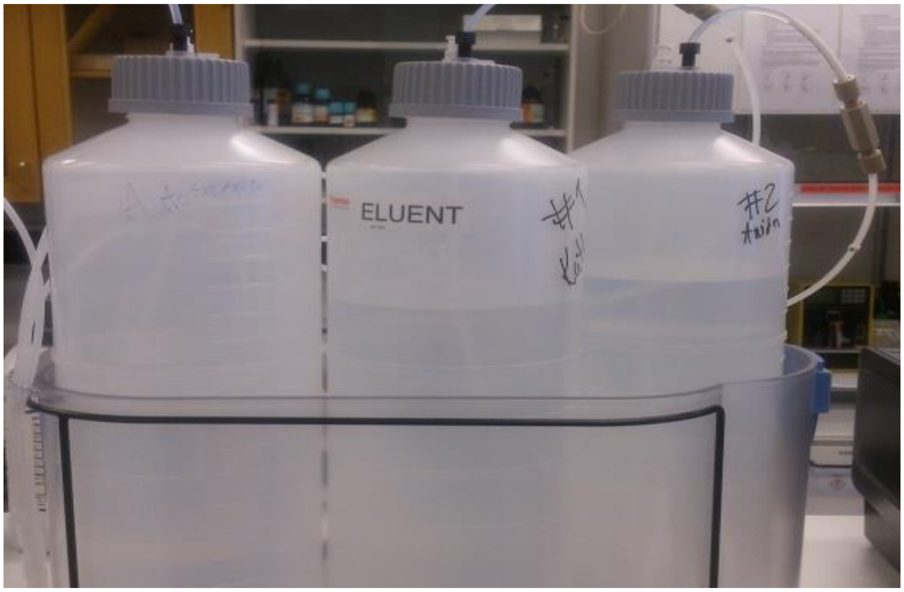
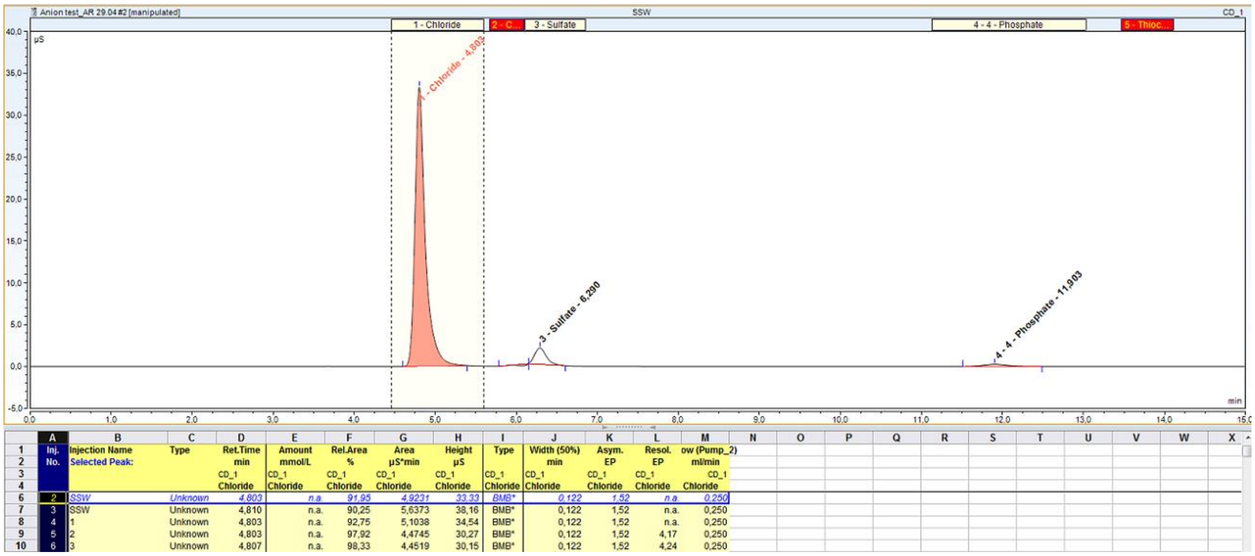


Figure 3.9 *Eluent containers*

Dionex machines were linked to a software called Dionex™ Chromeleon™ 7.2 that facilitated presenting data quantitatively. Combining ionic chromatography and mass spectrometry, the software processed data from chromatography instrument and visualized the identified chromatography it into conductivity peaks. The peak for each ion appeared in different intervals of retention time in the resin column. Figure 3.10 is captured from Chromeleon software interface showing chloride, sulfate and phosphate peaks. More pictures from IC test are available in Appendix II on page 85.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Inj.	Injection Name	Type	Ret.Time	Amount	Rel.Area	Area	Height	Type	Width (50%)	Asym.	Resol.	ow (Pump_2)
2	No.	Selected Peak:		min	mmol/L	%	µS*min	µS		min	EP	EP	ml/min
3				CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1
4				Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride
6	2	SSW	Unknown	4,803	n.a.	91,95	4,9231	33,33	BMB*	0,122	1,52	n.a.	0,250
7	3	SSW	Unknown	4,810	n.a.	90,25	5,6373	38,16	BMB*	0,122	1,52	n.a.	0,250
8	4	1	Unknown	4,803	n.a.	92,75	5,1038	34,54	BMB*	0,122	1,52	n.a.	0,250
9	5	2	Unknown	4,803	n.a.	97,92	4,4745	30,27	BMB*	0,122	1,52	4,17	0,250
10	6	3	Unknown	4,807	n.a.	98,33	4,4519	30,15	BMB*	0,122	1,52	4,24	0,250

Figure 3.10 *Chromeleon software interface showing chloride, sulfate and phosphate peaks.*

These peaks needed to be adjusted to calculate the correct area in μs*min. Finally, the area given by the software were used to calculate the concentration of each ion based on the average area of the reference sample.

Chapter 4: Results and discussion

4 Results and discussion

This chapter presents and explains the results from each step of the experiment in chemical selection, nanofiltration membrane separation and ion chromatography.

4.1 Chemical selection

Low solubility of phosphate compounds results in rapid precipitation by adding a small amount of phosphate anhydrous to water. When seawater is used as solvent, the amount of phosphate salt that is soluble decreases due to effect of common ion of the chemical and seawater. Table 4.1 shows the precipitation observation of three phosphate compounds at different concentration. First estimated concentrations for each chemical was based on their solubility in water at 20 °C and the assumption that the common ion concentration in the water is equal to its concentration in seawater.

Table 4.1 *Precipitation observation of different concentration of phosphate compounds in seawater at room tempreture.*

CONCENTERATION (G/L)	0.1	0.2	0.4	0.5	0.6	1	10
Chemical 1	-	NP*	-	NP	-	NP	P**
Chemical 2	-	NP	NP	-	NP	P	-
Chemical 3	P	-	-	-	-	P	-

* No precipitation observed

** Precipitation observed

It can be seen from the table above that the third chemical showed to be insoluble in seawater while the first two chemicals had low solubility. The different amount of solubility of these chemicals is explainable by their ionic composition and the concentration of common ions in seawater. As the fourth chemical, even in very low amounts, precipitated instantly, it was not considered for further experiments.

NF membrane feed needs to be of high quality in order to prevent membrane fouling. Turbidity of solution as a quality parameter was checked to determine the concentration that is suitable as the membrane feed. Table 4.2 shows the turbidity of each solution for the two first chemicals.

Table 4.2 *Turbidity in NTU for solution of each chemical at different concentration.*

CONCENTRATION (G/L)	0.2	0.4	0.5	0.6
Chemical 1	5.71	-	16.3	-
Chemical 2	6.62	17.7	-	50.2

Table 4.2 confirms that increase in concentration leads to a rise in turbidity of the solution i.e. decrease in solution's clarity. High turbidity of solution with concentration from 0.4 g/l and above together with preventing precipitation resulted in opting 0.23 g/l as higher concentration limit for the membrane separation experiment.

4.2 Membrane performance

The performances of the studied nanofiltration membrane in terms of flux and ion separation were investigated and the results are given in the following sections. The analysis is based on sets of data with 2.5% mass balance error. For instance, Table 4.3 and Table 4.4 below show the flow rate, TDS and mass balance for normal seawater and second dose of second chemical experiment, respectively. Complete and more detailed data are available in Appendix III and Appendix IV from page 88 to page 112.

Table 4.3 *TDS, flow rate and mass balance at different pressures for normal seawater trial.*

Pressure (bar)	**TDS (ppm)**			**Flow rate (L/H)**			**Mass balance (%)**
	Feed	Permeate	Retentate	Feed	Permeate	Retentate	
6	33200	28800	32800	815.3	14.7	800.6	1.42242846
8	33200	27600	32800	763.3	27.6	735.7	1.77214979
10	33200	26800	32900	709.0	38.2	670.8	1.89328744
12	33200	26600	33000	749.8	46.2	703.6	1.79006211
14	33200	25900	33000	716.5	60.0	656.5	2.39224514
16	33200	25700	33200	737.3	71.4	665.8	2.1886015

Table 4.4 *TDS, flow rate and mass balance at different pressures for second dose of second chemical.*

Pressure (bar)	**TDS (ppm)**			**Flow rate (L/H)**			**Mass balance (%)**
	Feed	Permeate	Retentate	Feed	Permeate	Retentate	
6	32100	28800	32400	728.7265	10.64144	718.0851	-0.77081
8	32100	28100	32400	717.4358	14.76822	702.6675	-0.65883
10	32100	27400	32500	704.9228	18.77281	686.1499	-0.823
12	32100	26900	32500	692.6643	22.68908	669.9752	-0.67466
14	32100	26400	32600	686.0535	26.71284	659.3407	-0.80558
16	32100	26100	32600	680.247	29.25244	650.9946	-0.68686

4.2.1 Effect of phosphate on flux and recovery

Experimental data for the permeate flux as a function of the pressure are given in Figure. 4.1 for normal seawater and the three dose of two chemicals as membrane's feed. These graphs compare the flux with normal seawater is the feed to phosphate containing seawater feed.

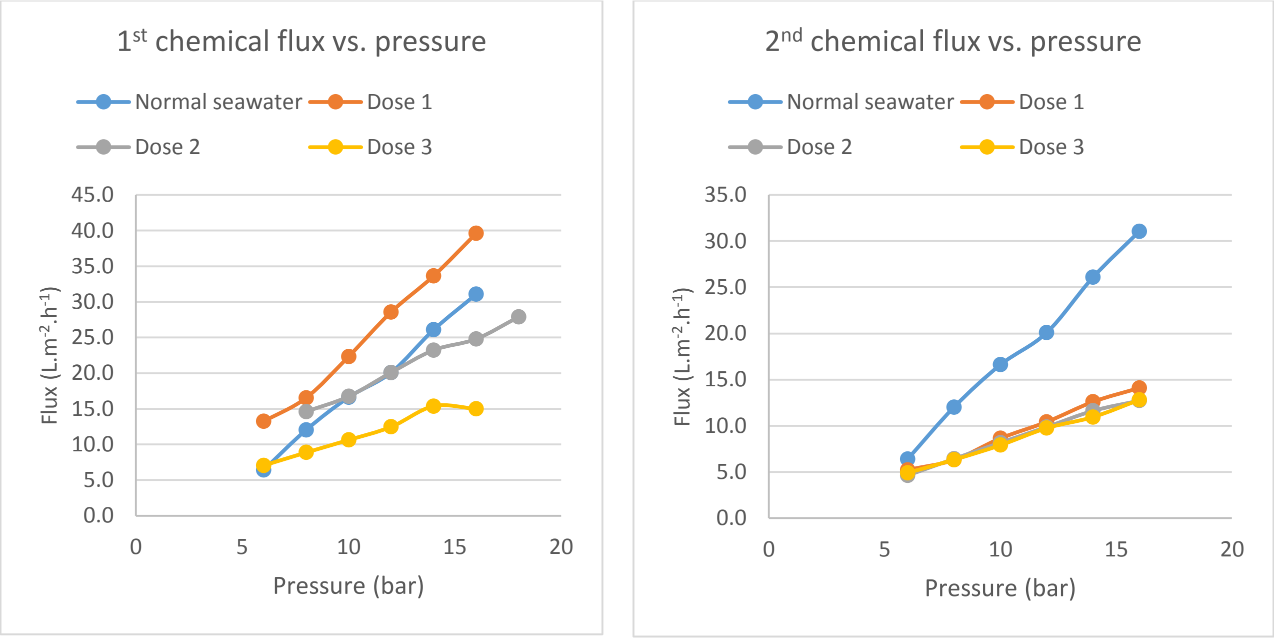


Figure 4.1 *Permeate flux as a function of applied pressure. Seawater and first chemical as feed (left), seawater and second chemical as feed (right).*

For pure water, flux is directly proportional to transmembrane-pressure, with a linear slope, according to Equation 2.3. The experimental data here shows that the permeate flux increases with a rise in applied pressure and the slope seems to be linear here for impure seawater, especially when second chemical is added to seawater. Figure 4.1 also illustrates that, except for first dose of first chemical, permeate flux declines as the feed concentration increases. The flux is virtually half the amount when second chemical is used compared to normal seawater. Concentration polarization and formation of double layer on membrane's surface resulted from increasing salt concentration within feed stream are important factors that contribute to flux decline when chemicals are added to seawater feed. The decline in permeate flux implies that retentate production increases when chemical is added to seawater. In this case, second chemical and more specifically the third dose produces the most volume of retentate. This explanation is also emphasized by recovery rate of membrane. Figure 4.2 depicts the recovery rate as function of pressure, based on experimental data.

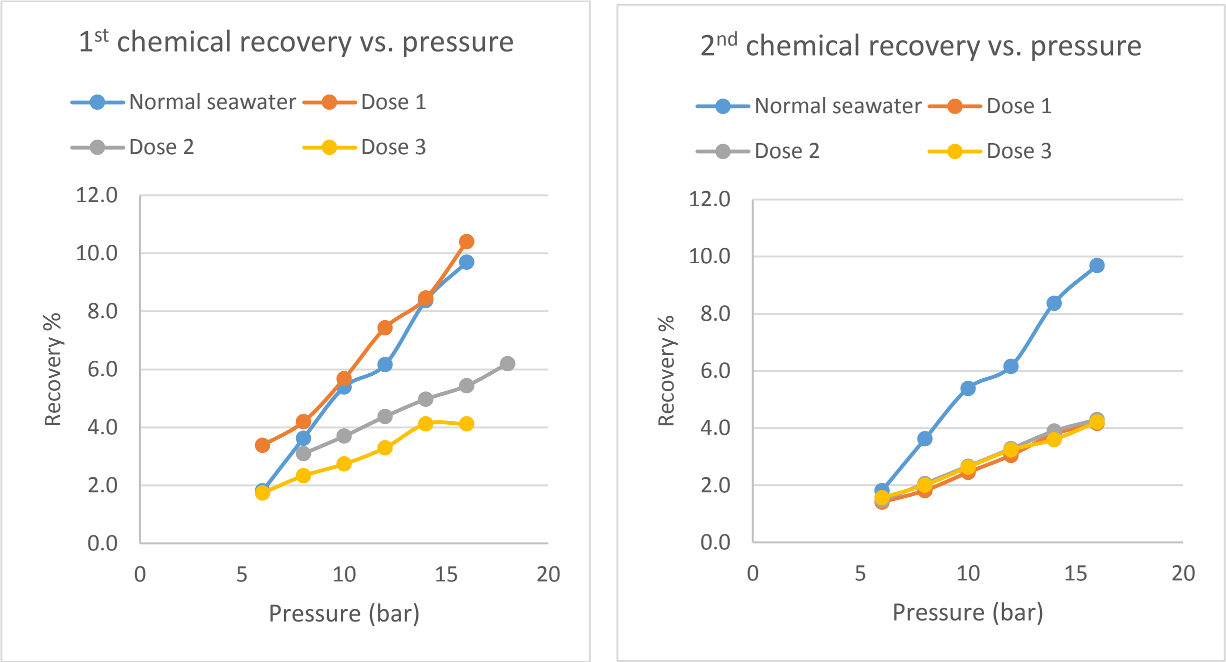


Figure 4.2 *Recovery rate as a function of pressure for seawater and the two chemicals as feed.*

Figure 4.2 illustrates the recovery rate of NANO-SW-2540 NF membrane as a function of pressure. The graph on the left compares the recovery of seawater as feed with seawater containing three different concentration of first chemical as the right graph compares same parameters for seawater feed and seawater containing three different concentration of second chemical as membrane’s feed. Results from recovery comply with flux results, both emphasizing on reduction of permeate flow rate i.e. increase in retentate flow rate. Since the desired product, for water-based oil recovery purposes, according to this study is the retentate, the rise in concentrate production is a positive outcome. In this regard second chemical showed to lead to more satisfactory results.

Membrane's data sheet available in Appendix I on page 84 indicates flux to be 43.5 $L.m^{-2}.h^{-1}$ ($2.4\ m^3.d^{-1}$) which is above 40 $L.m^{-2}.h^{-1}$ that was highest flux achieved during the experiment.

4.2.2 Effect of phosphate on rejection

The ability of a membrane to reject salts which results in fractionation of TDS, salinity, conductivity and separation of ions is a key factor in membrane's performance. This section discusses this ability of Hydranautics' NANO-SW-2540 nanofiltration membrane when seawater and the two chemicals were used as the membrane feed.

4.2.2.1 Salinity and conductivity

As explained in section 2.1.4 salinity and conductivity are two water quality parameter that are directly correlated. Generally, NANO-SW-2540 NF membrane decreased the permeate salinity and conductivity as it retained dissolved salts in feed stream. Figure 4.3 shows the effect of pressure on salinity and conductivity when feed contained the second dose of each chemical separately. It can be seen from Figure 4.3 that by increasing pressure more salts were retained resulting in a decline in both salinity and conductivity of the permeate while these parameter increased slightly on concentrate side. Same behavior was observed when other doses were studied. This is due to permeate flux increase by pressure. As the pressure increases more solvent passes the membrane reducing the concentration of dissolved on permeate side and increasing the dissolved concentration on rejection side.

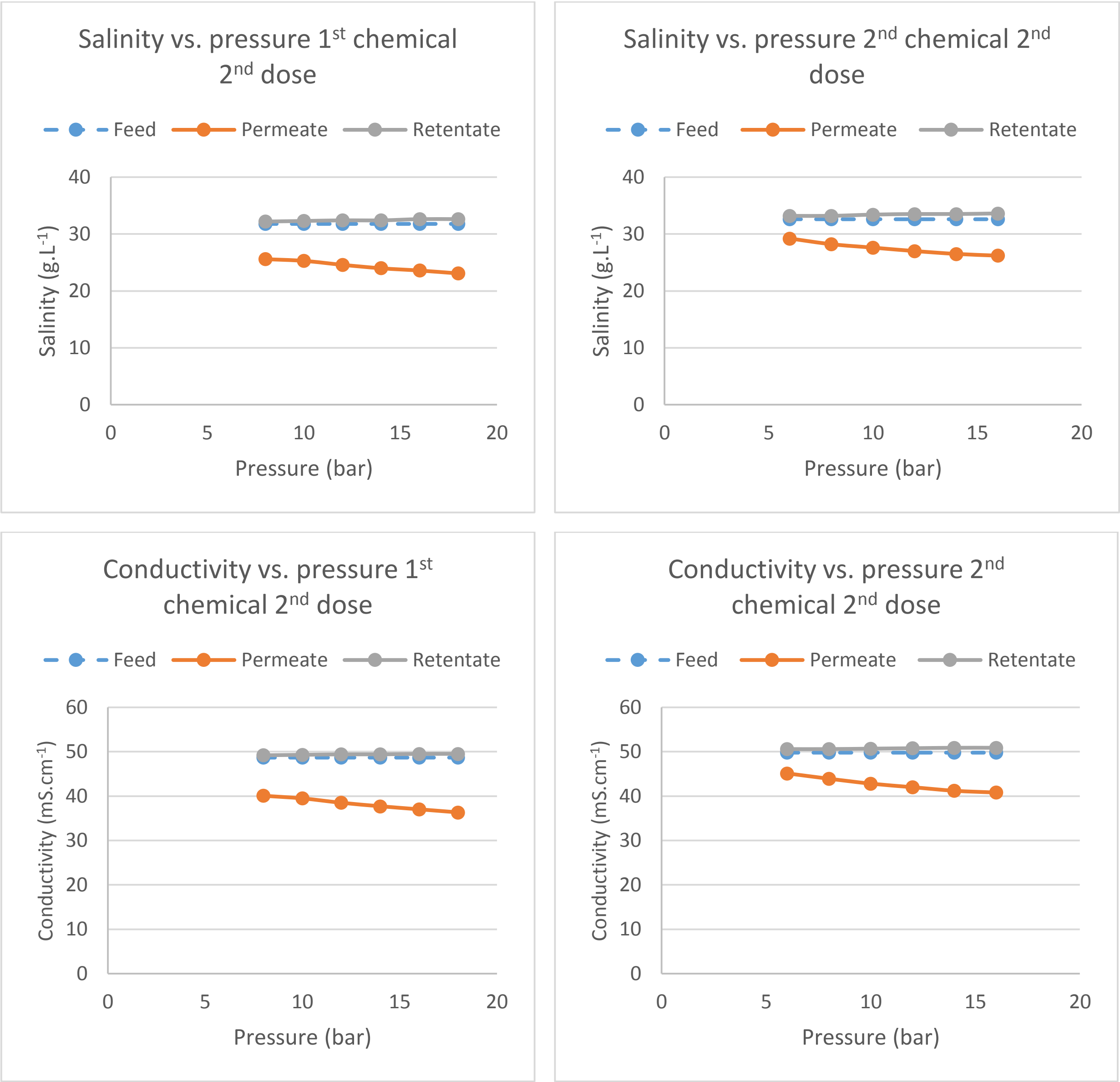


Figure 4.3 *Effect of pressure on salinity (top) and conductivity (bottom) of retentate and permeate stream. Feed containing second dose of first chemical (left), feed containing second dose of second chemical (right).*

Detailed data regarding salinity and conductivity for feed permeate and concentrate stream at different pressure and concentration of chemicals are presented in appendix III from page 88 to page 98.

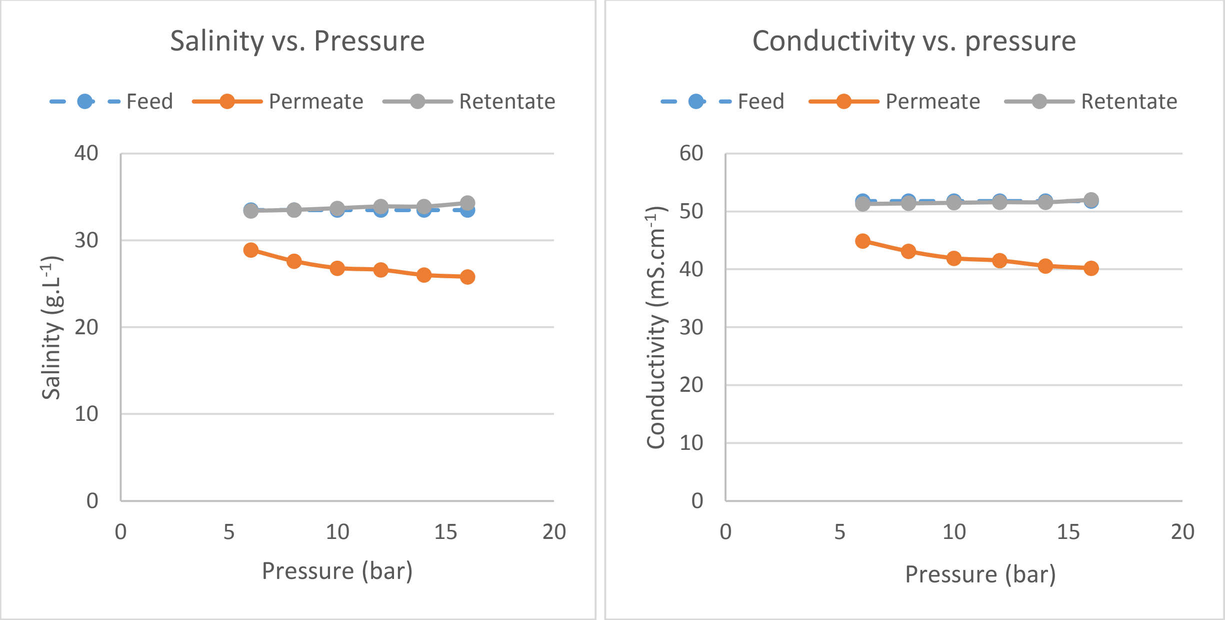


Figure 4.4 *Effect of pressure on salinity and conductivity of normal seawater as membrane feed.*

Figure 4.4 shows the effect of pressure on removal of salinity (left) and conductivity (right) when seawater was used as membrane feed. By comparing Figure 4.3 with Figure 4.4, it can be seen that the NF membrane performance in terms of removing salinity and conductivity is very similar in presence and absence of phosphate in feed stream.

4.2.2.2 Ion rejection rate

Ionic composition of water is of key importance in water-based oil recovery as discussed in section 2.1.3. This section presents and discusses the performance and ability of NANO-SW-2540 membrane in separation of inlet ions using ionic chromatography analysis.

Results from seawater as membrane feed are demonstrated in Figure 4.5. This figure shows that the rejection rates increases with pressure, which is due the rise in solvent volume in, permeate side. More importantly, the rejection rate of each ion within seawater appeared to be in sequence of R (SO42-) > R (Mg2+) > R (Ca2+) > R (Cl-) > R (Na+).

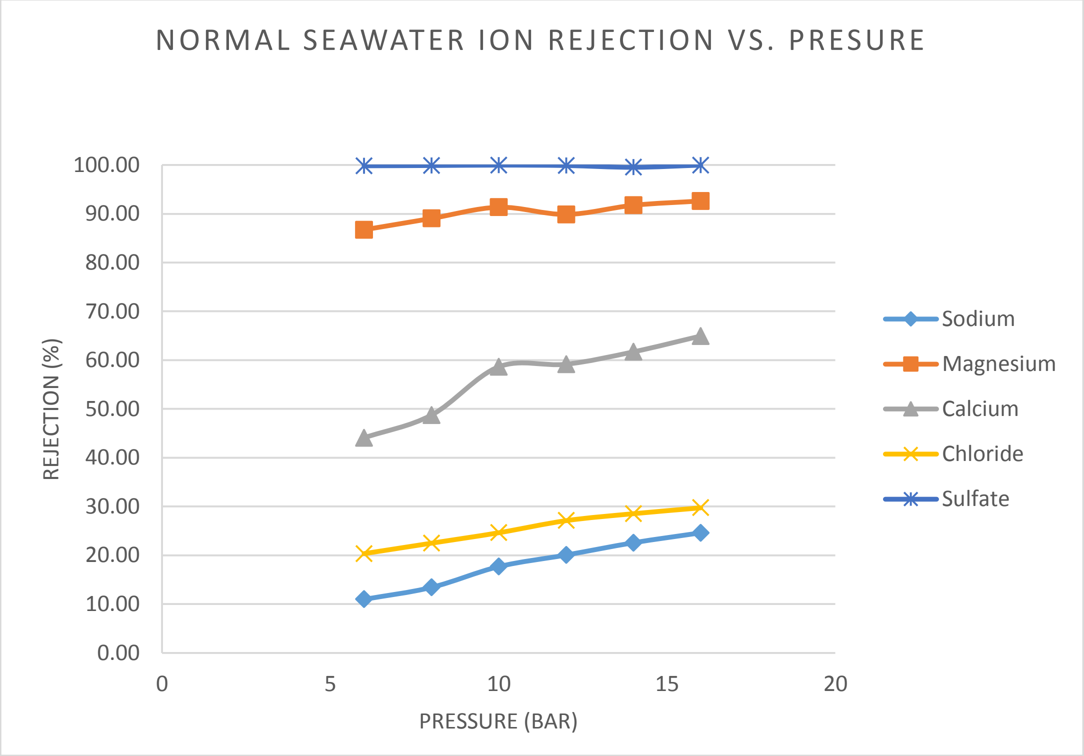


Figure 4.5 *Rejection rate of ions as a function of pressure with seawater as membrane feed.*

The sequence of ion rejection is as expected. Electrostatic repulsion between sulfate and membrane is stronger than repulsion between chloride and membrane surface as defined by Donnan exclusion. Moreover, according to **Table 2.4** between sulfate and chloride co-ions sulfate has both higher hydrated radius and hydrated energy. Higher hydration energy of an ion results in stronger hydration shell i.e. more strictly attached water molecule, which leads to higher likelihood of the ion to be retained. Amongst counter-ions, magnesium has the highest hydration energy resulting in its highest rejection compared to two other positively charged ions. Calcium rejection is placed second in counter-ions, as it is a larger ion compared to sodium.

When phosphate salts were added to seawater feed rejection rates' sequence showed to be in the following order:

Sulfate > Phosphate > Magnesium > Calcium > Chloride > Sodium

In order to be able to discuss this trend attention must be paid to Figure 2.7. All feed, permeate and concentrate solution's pH throughout the overall experiment were between 7.2 to 8.1 meaning the solution was always free of PO_4^{3-} while concertation of HPO_4^{2-} were higher than H_2PO^-. Less rejection of phosphate compare to sulfate could be resulted from size effects, which indicates higher rejection for large size ions. The hydrated radii of these ions are as follows: r_h (SO_4^{2-}) = 0.38 nm, r_h (HPO_4^{2-}) = 0.327 nm and r_h ($H_2PO_4^-$) = 0.302 nm. Sulfate has greatest hydrated radius among the three anion hence the highest rejection.

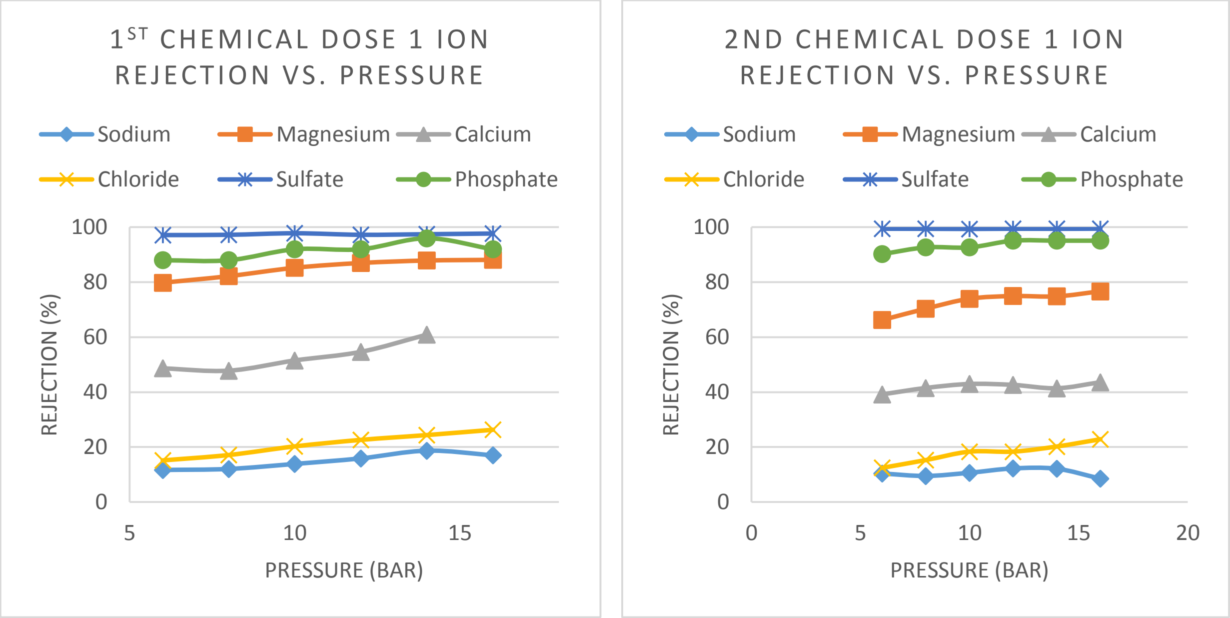


Figure 4.6 *Ion rejection rates as a function pressure at first dose of chemicals*

The graph on the left in Figure 4.6 shows the rejection rates of each ion when first dose of first chemical was spiked to membrane feed while the graph on the right demonstrates the rejection by addition of second chemical at its first dose.

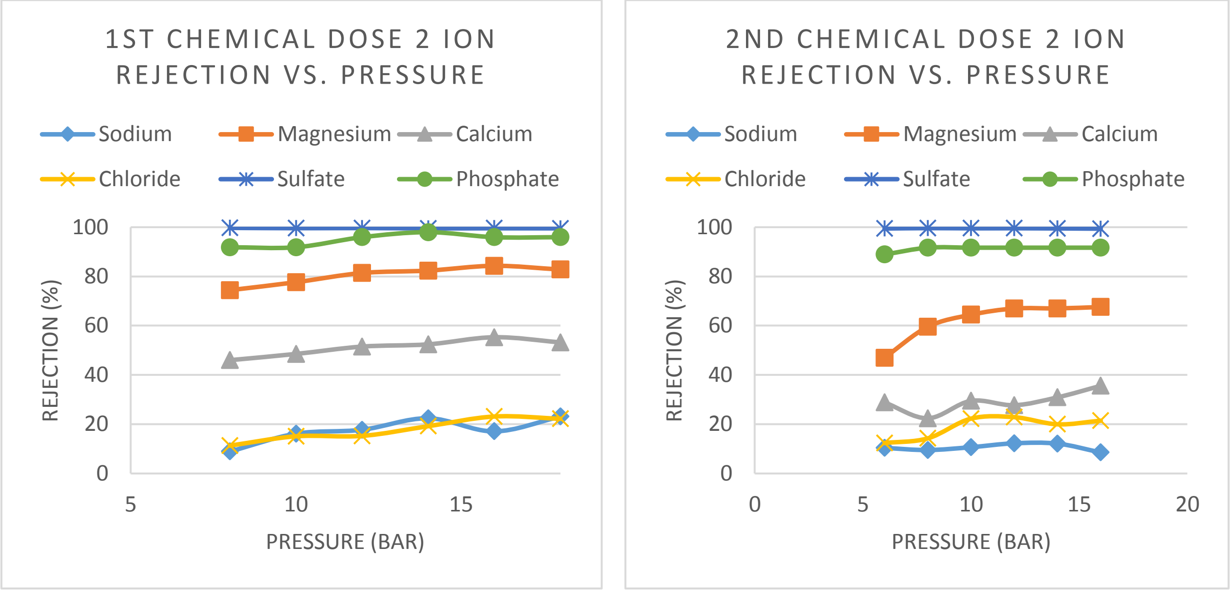


Figure 4.7 *Ion rejection rates as a function pressure at second dose of chemicals*

Figure 4.7 is another demonstration of sequence of rejection when the second dose of chemicals were added to membrane feed. On the left the effects of first chemical is shown while effects of second chemical is illustrated on the right graph. Rejection rates and corresponding mass balance error of the ions for two sets of experiment are given as samples in Appendix V on page 113.

Effects of third dose of the two chemicals is presented in Figure 4.8. As can be seen from Figure 4.6, Figure 4.7 and Figure 4.8 NANO-SW-2540 rejected the inlet ions at the same the sequence.

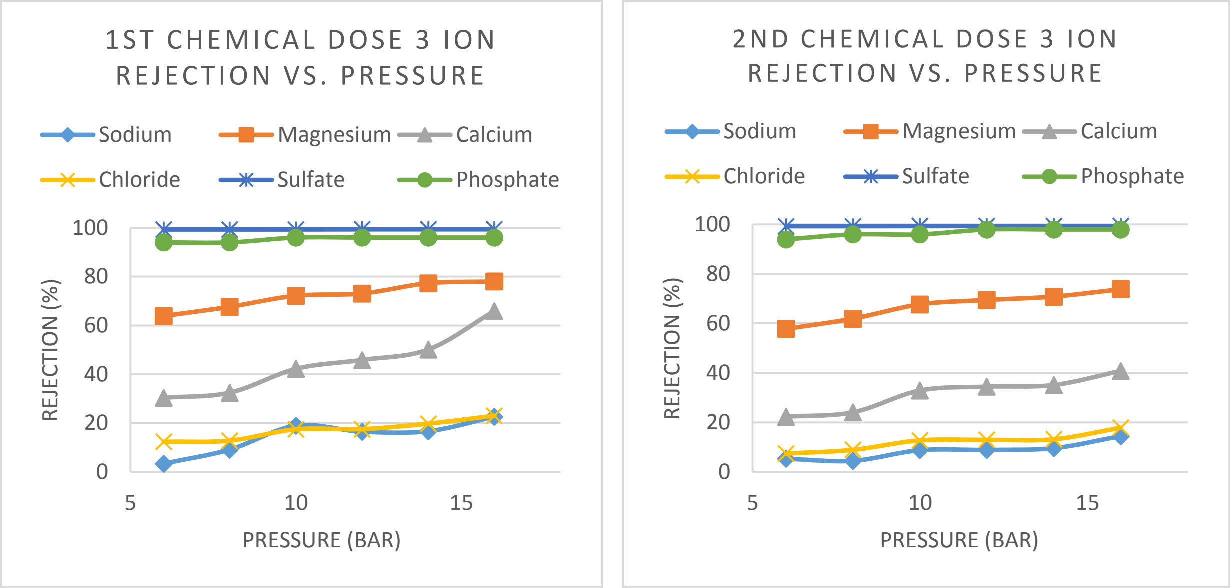


Figure 4.8 *Ion rejection rates as a function pressure at third dose of chemicals*

Rejection rate of phosphate varied from 85% to 98% throughout the experiment depending on operating condition. This rate of rejection is close to what Ballet *et. al* reported in 2007*.* Their study showed that the polyamide NF200 membrane from Dow rejected feed's $H_2PO_2^-$ and HPO_4^{2-} by 85% and 96% respectively (Ballet et al., 2007).

4.2.2.3 First chemical concentration effect on ion separation

Low concentration of monovalent within injection water to carbonate rock discussed to be an important factor for enhanced oil recovery in section 2.1.3. In this section and the following section rejection of different ions are compared according to pressure and concentration difference while rejection rates of normal seawater ions are given as a rejection reference by NANO-SW-2540 membrane.

Figure 4.9 shows the effect of concentration of first chemical on rejection of sodium and chloride. As can be seen from the left graph the rejection of sodium decreases by the increase in concentration of first chemical in seawater feed. Similarly, rejection of chloride on the right graph shows reduction by increasing first chemicals concentration.

Calcium and magnesium as two other crucial ions participating in water-based oil recovery showed to be less retained by membrane as the concentration of first chemical increased.

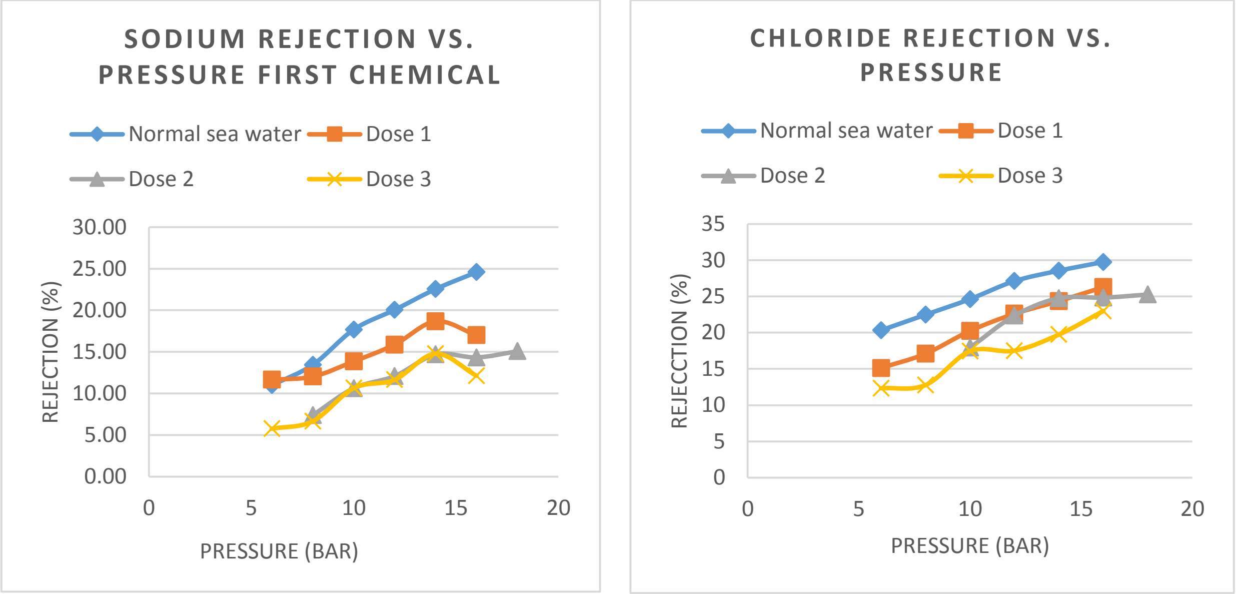


Figure 4.9 *Rejection rate of sodium (left) and chloride (right) as function pressure for first chemical*

Figure 4.10 presents two graph on rejection of calcium on the left and magnesium on the right as a function pressure. It can be seen from the graph that sequence of rejection for magnesium is from lowest feed concentration to highest feed concentration meaning higher concentration of magnesium in concentrate side corresponds to least concentrated feed by first chemical. Calcium, on the other hand, showed to be retained at close rates by adding the three amounts of first chemical to membrane feed. Nevertheless first dose resulted in highest calcium rejection at 14 bar.

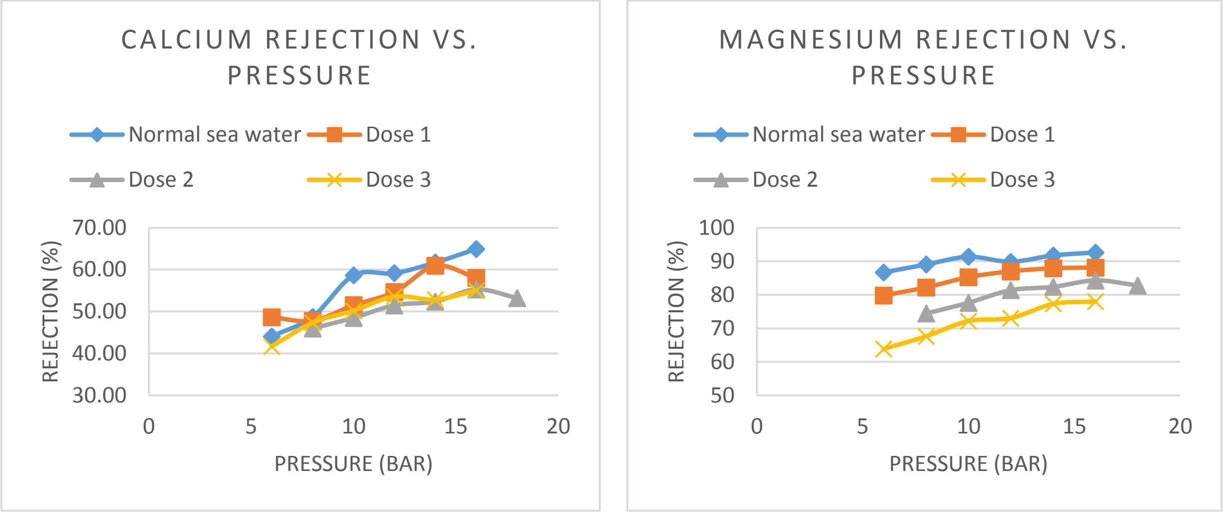


Figure 4.10 *Rejection rate of calcium (left) and magnesium (right) as function pressure for first chemical*

Adding first chemical to seawater as the membrane feed, highest phosphate concentration retained at third dose at which sulfate concentration slightly declined compared to the amount that was rejected with normal seawater as feed. This matter can be observed from figure 4.11. Concentration of sulfate in concentrate side was lowest when first dose of first chemical was introduced into seawater as membrane feed.

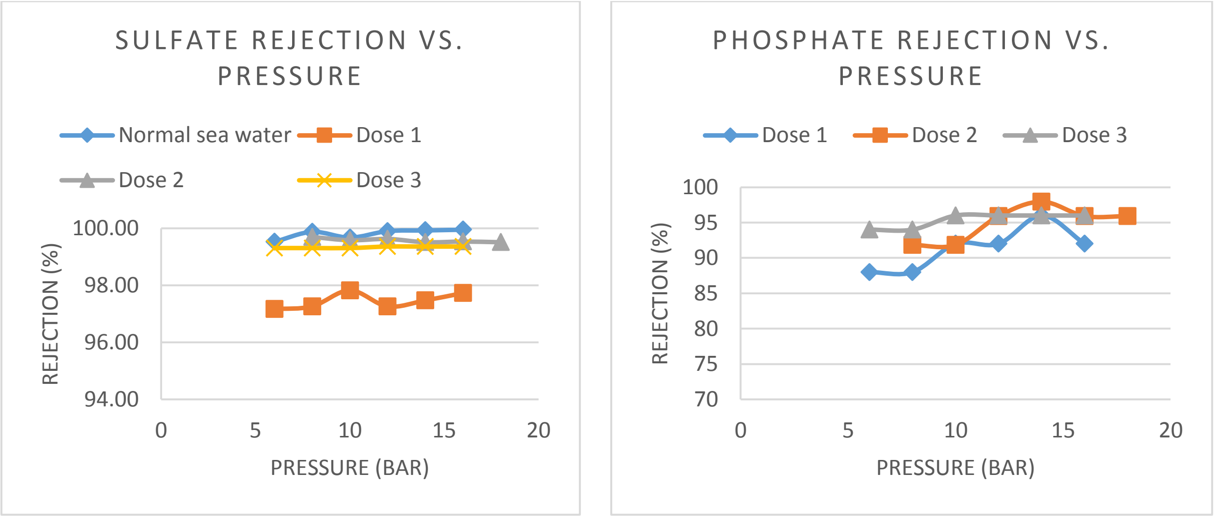


Figure 4.11 *Rejection rate of sulfate (left) and phosphate (right) as function pressure for first chemical*

Generally, all rejection rates increased with a rise in pressure and addition of first chemical resulted higher permeation of ions compared to permeation of ions in normal seawater. More importantly, most desirable results by adding first chemical obtained at its third dose where phosphate rejection rates were highest and monovalent ions' rejection were lowest due to concentration effect and screening phenomenon respectively. However, at this feed concentration magnesium was slightly less retained. Highest rejection of calcium and magnesium were obtained at first dose.

4.2.2.4 Second chemical concentration effect on ion separation

Concentration of monovalent ions declined by spiking the second phosphate salt in to membrane feed. The drop in rejection of sodium and chloride by the membrane was highest at the third dose of the chemical. Figure 4.12 demonstrates rejection of sodium on the right graph and chloride on the left graph as a function of pressure at four different concentration of second chemical while two first dose seemed to decrease both ions by same amount.

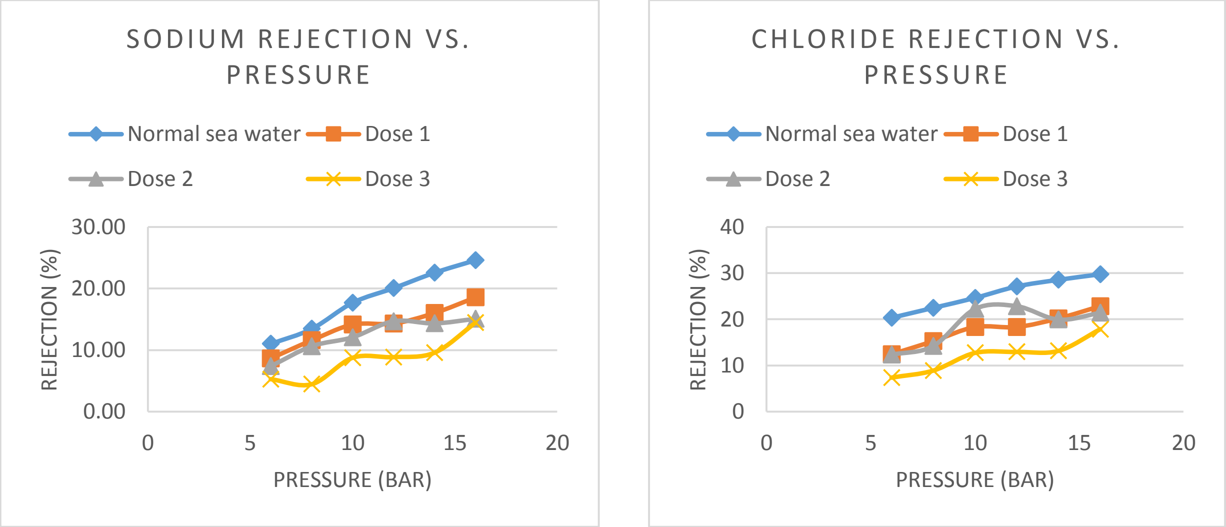


Figure 4.12 *Rejection rate of sodium (left) and chloride (right) as function pressure for second chemical*

Figure 4.13 illustrates rejection of calcium on the left graph and magnesium on the right graph as a function of pressure at different concentration of chemicals. Rejection of both cations declined when second chemical were introduced to normal seawater feed. Concentration of magnesium and calcium within retentate decreased when seawater was spiked with second chemical. The highest rejection of these two ions occurred when normal seawater used as membrane feed. The first dose of second chemical came second in rejection of these two ions while at second dose of the chemical divalent cations had greatest permeation.

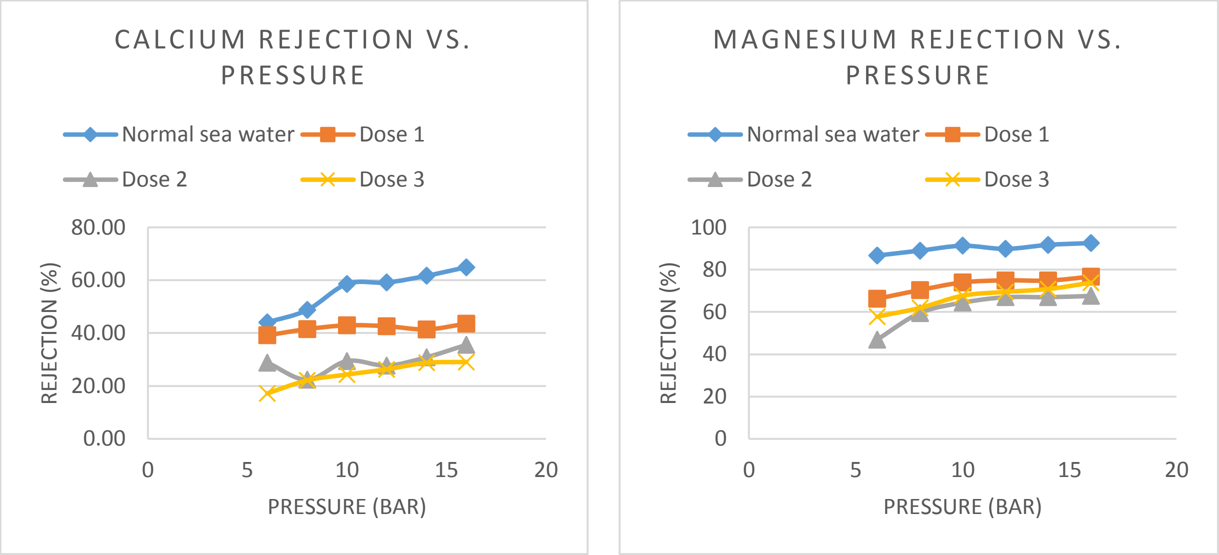


Figure 4.13 *Rejection rate of calcium (left) and magnesium (right) as function pressure for second chemical*

The variation of rejection for sulfate and phosphate ions at different concentration of the second chemical were lower compared to the first chemical. Figure 4.14 presents the rejection rate of sulfate and phosphate at different concentration of second chemical on as a function of pressure left and right graph respectively.

As can be seen from Figure 4.14 sulfate concentration on rejected side has virtually remained the same at different concentration of second chemical as the rejection rates differ by less than 1% compared to normal seawater. Phosphate rejection, on the other hand, increased by spiking higher amount of chemical in membrane feed as third dose resulted in highest rejection rate of 98%.

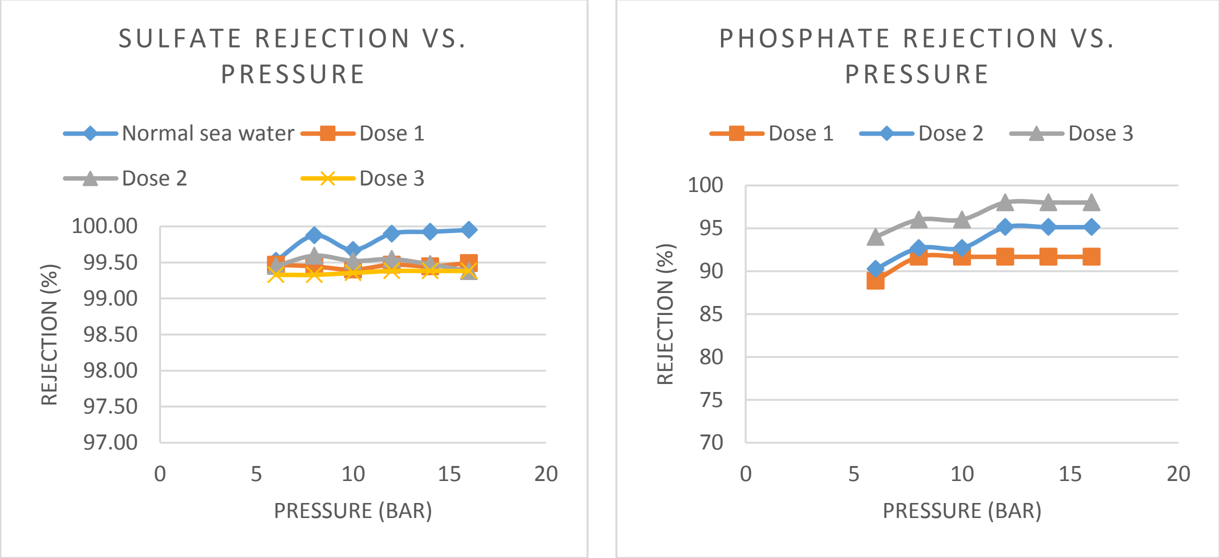


Figure 4.14 *Rejection rate of sulfate (left) and phosphate (right) as function pressure for second chemical*

The results from the experiment regarding second chemical shows that in terms of highest retention of phosphate and high permeation of monovalent ions third dose is the desirable concentration although this concentration within membrane feed decreased rejection of divalent cations.

To sum up the effect of ionic strength for both chemicals it can be said that rejection of seawater ions mostly decreased by increasing the concentration of chemicals within seawater as membrane feed. This lower retention due to the increase in ionic strength by charged membrane is a well-known behavior that can be explained by screening phenomenon (Wang et al., 1997; Chaabane et al., 2006; Paugam et al., 2004). When concentration of counter-ions such as Na^+ increase across the membrane, a positively charged shield forms on the surface of membrane decreasing the effect of co-ions repulsion. However, at low concentrations that were spiked to membrane feed (130 ppm, 180 ppm and 200 ppm), the shielding effect for phosphate is very low and the effect of charge and repulsion between anions lead to higher rejection. The phenomenon of screening showed to control rejection of chloride while having a very low effect on sulfate. Results also indicate that cations are unfavorably less retained by rising concentration of either two chemicals in membrane feed. This could be contributed by decrease in membrane's surface charge or increase of dielectric constant as a result of incline in feed concentration. Ultimately, spiking third dose of each chemical led to high desirable permeation of monovalent ions and rejection of phosphate while declining cations rejection unfavorably.

4.2.2.5 Salt composition effect on ion rejection

This section presents and compares rejection results when same concentration of either chemicals was introduced into feed tank. Rejection of ions for normal seawater are also presented in figures below as a reference for rejection rates for each ion in order to observe the deviation of ion separation when either of two chemicals were added to seawater as membrane feed.

First dose

Figure 4.15 compares sodium (left graph) and chloride (right graph) rejection of for two chemicals as a function of pressure. As can be seen from left graph in Figure 4.15 spiking first dose of either chemicals resulted in lower rejection of both sodium and chloride which means concentration of monovalent ions declined in concentrate side. Here, second chemical resulted in lower rejection of monovalent ions compare to first chemical.

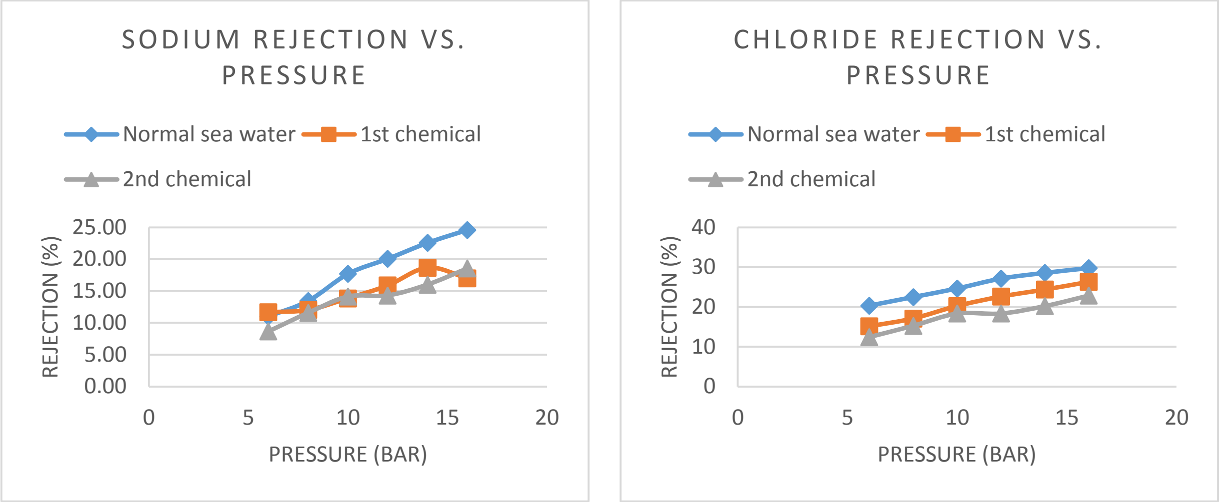


Figure 4.15 *Sodium (left) and chloride (right) rejection as function of pressure for first dose of chemicals*

Rejection of divalent cations are presented in Figure 4.16. Rejection of both calcium and magnesium faced a drop when first dose of either two chemicals were introduced to membrane feed. According to Figure 4.16, this fall was greater for both cations by addition of second chemical while these rejection rates from feed containing first chemical was very close to rejection rates when normal seawater went through NANO-SW-2540 membrane.

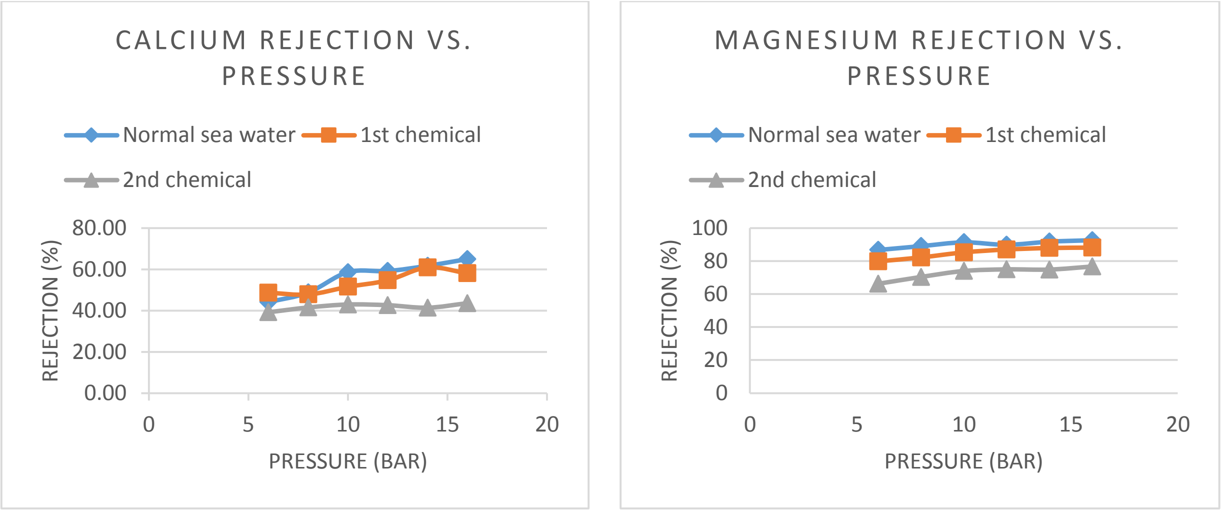


Figure 4.16 *Calcium (left) and magnesium (right) rejection as function of pressure for first dose of chemicals*

Left graph in Figure 4.17 shows sulfate rejection as a function of pressure at first dose of either chemicals. This graph indicates that more sulfate ions are retained when second chemical was added to membrane feed. It can be seen from the graph that rejection rates of sulfate in presence and absence of second chemical are very close.

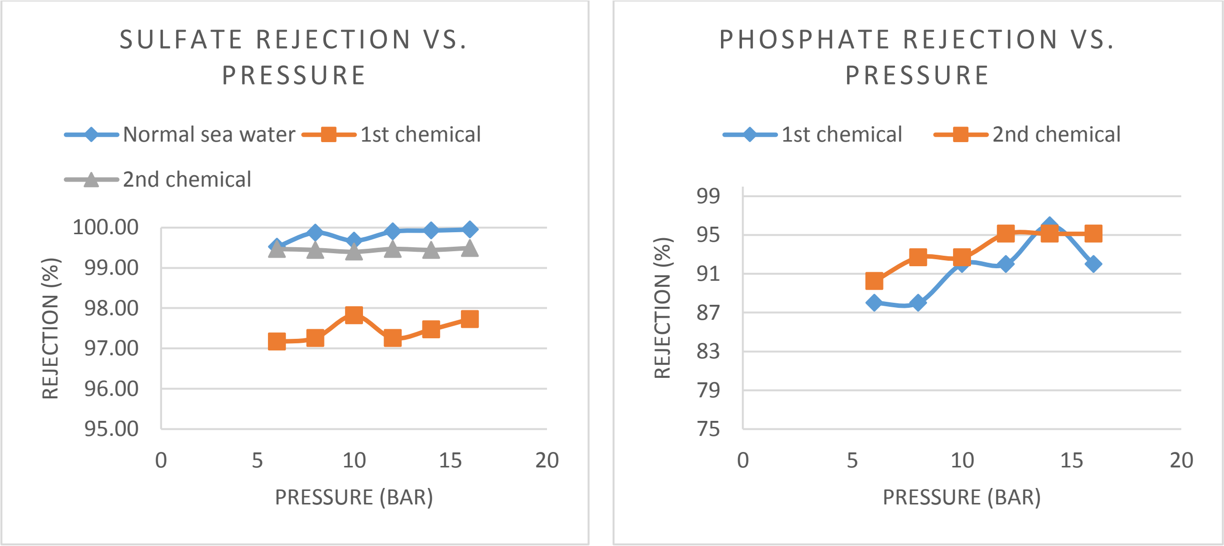


Figure 4.17 *Sulfate (left) and phosphate (right) rejection as function of pressure for first dose of chemicals*

Rejection rate of sulfate decreased by 2% when first chemical was added to membrane feed. The right graph in Figure 4.17 demonstrates rejection rate of phosphate as a function of pressure when feed included either of two chemicals at their first dose. According to this graph, phosphate ions were more retained when seawater included second chemical. Although at 10 bar and 14 bar, the rejection rates of phosphate by NANO-SW-2540 for both chemical were roughly equal.

Second dose

Rejection rate of sodium as a function pressure at the second dose is plotted in Figure 4.18 on the left. The nanofiltration membrane showed to reject sodium at close rates when either of chemical were added to membrane feed. Sodium within feed containing second chemical was more retained at 8, 10 and 12 bar while spiking first chemical to feed resulted in higher rejection at 14 bar. The graph also suggests that sodium rejection rates for two chemicals was approximately equal at 16 bar.

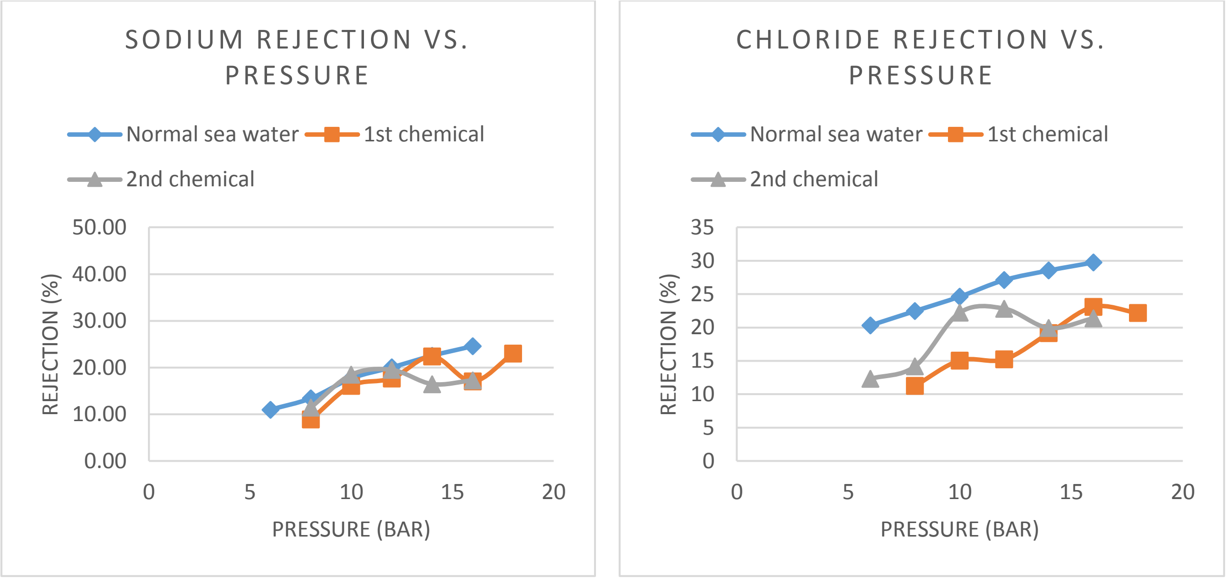


Figure 4.18 *Sodium (left) and chloride (right) rejection as function of pressure for second dose of chemicals*

The right graph in Figure 4.18 shows rejection rates of chloride for two chemicals plotted against pressure when second dose of chemicals were spiked in membrane feed. Adding first chemical to seawater resulted in higher decrease in chloride rejection which means more chloride permeation by adding second dose of first chemical. However, second chemical resulted in slightly lower rejection at 16 bar.

Rates of rejection for calcium (left graph) and magnesium (right graph) is given as a function pressure in Figure 4.19. According to the graph on the left, first chemical contributed to higher rejection of calcium compared to second chemical while second chemical reduced the rejection rate of calcium by around 25% averagely.

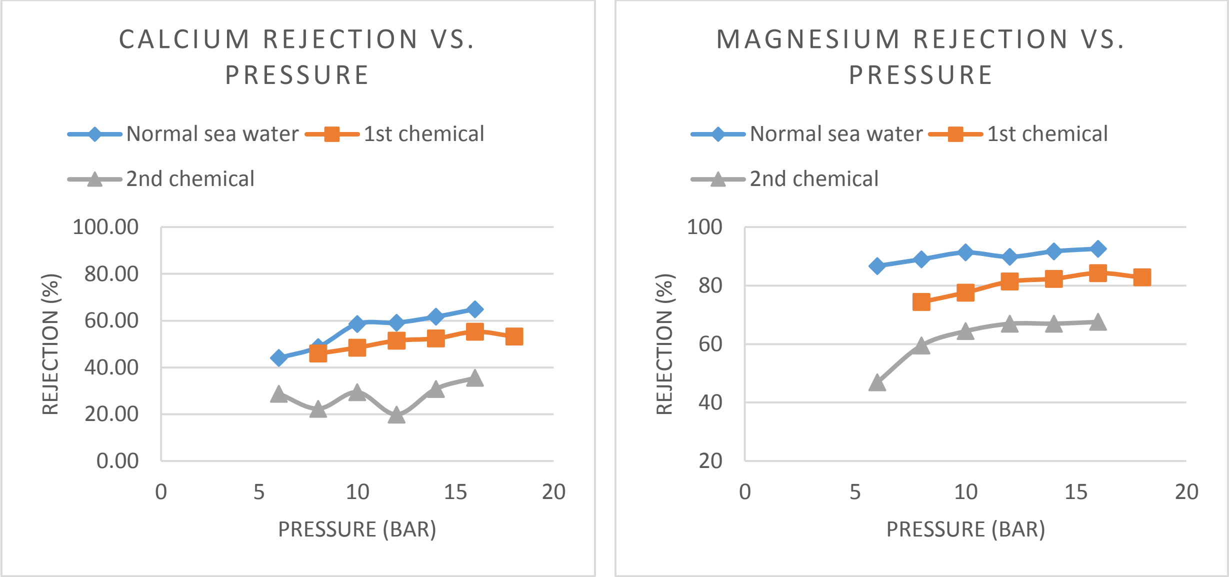


Figure 4.19 *Sodium (left) and chloride (right) rejection as function of pressure for second dose of chemicals*

The graph on the right in Figure 4.19 indicates that addition of first chemical to seawater at its second dose lowered magnesium rejection by 10% while second chemical contributed to around 30% reduction in retention of magnesium ion.

Figure 4.20 illustrates rejection rates of sulfate on the left graph and phosphate on the right graph as functions of pressure when either of two chemical were introduced into seawater. It can be seen from the left graph that both chemical resulted in sulfate rejection rates very close to rejection that was achieved when normal seawater used as membrane feed. Both chemicals contributed to less than 1% reduction in rejection of sulfate compared to membrane feed free of chemicals.

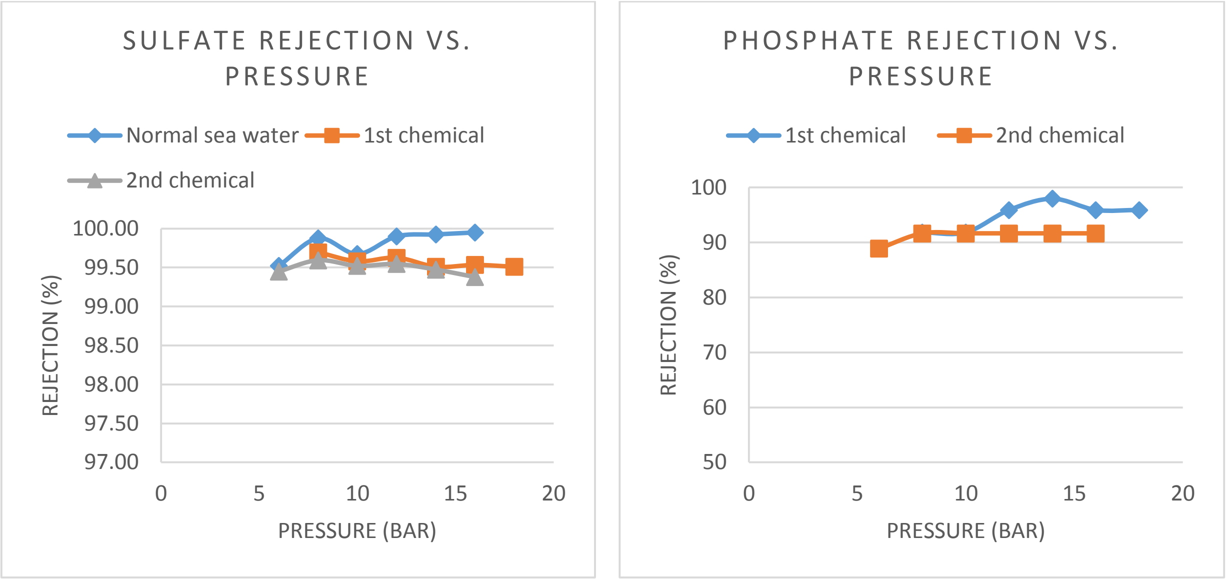


***Figure 4.20** Sodium (left) and chloride (right) rejection as function of pressure for second dose of chemicals*

At the second dose of chemicals, rejection of phosphate was greatest when first chemical was introduced to seawater at pressures higher than 12 bar by about 5% according to the right graph in Figure 4.20. Nevertheless, both chemicals contributed to same rate of rejection at 8 and 10 bar.

Third dose

Figure 4.21 shows the rejection of sodium (left graph) and chloride (right graph) as a function of pressure at third those of either chemicals. Second chemical attributes to highest sodium permeation at third dose as it led to lowest rejection according to the left graph in Figure 4.21. Spiking second chemical decreased the rejection of sodium by 10%.

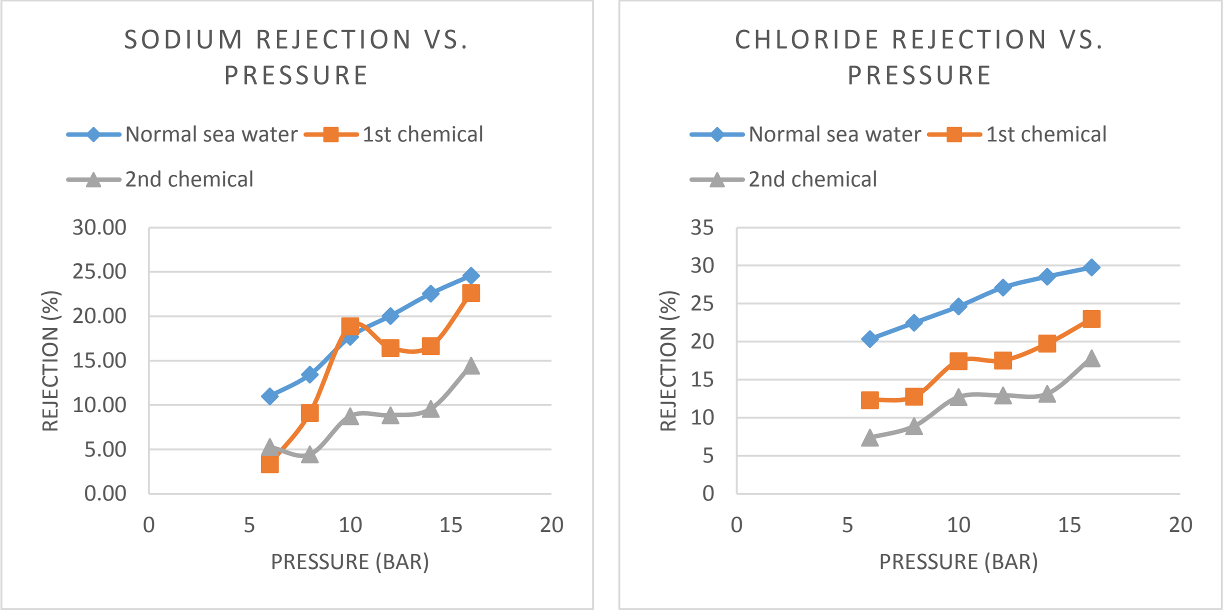


Figure 4.21 *Sodium (left) and chloride (right) rejection as function of pressure for second dose of chemicals*

As can be seen from the right graph in the figure above the addition of first and second chemical to seawater resulted in an approximate 6% and 16% decrease in chloride rejection respectively. Introducing third chemical into membrane feed, second chemical showed to retain less monovalent ions compared to first chemical.

Figure 4.22 demonstrates rejection rates of calcium on the left graph. The graph indicates that both chemicals resulted in a decrease in rejection compared to normal seawater. Both chemicals showed to retain calcium at around 30% at 10 and 12 bar. While at any lower pressure than 10 bar first chemical led to higher permeation and higher pressure than 12 bar second chemical contributed to higher calcium permeation.

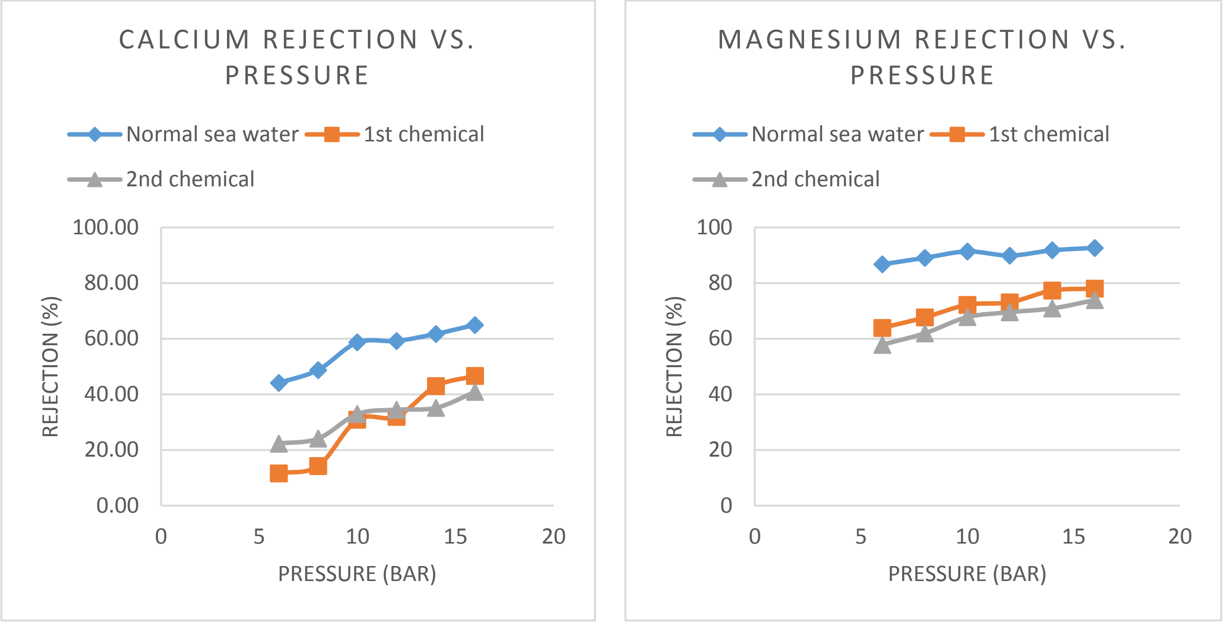


***Figure 4.22** Calcium (left) and magnesium (right) rejection as function of pressure for third dose of chemicals*

Rejection of magnesium is plotted against pressure on the right graph in Figure 4.22. As can be seen from the graph adding first chemical first chemical resulted in higher rejection of magnesium compared to addition of second chemical while both chemicals decreased the rejection from what was achieved when normal seawater was used as membrane feed.

Figure 4.23 includes two graphs illustrating the rejection of sulfate (left) and phosphate (right) plotted against pressure when third dose of chemicals was added to feed tank. Rejection of sulfate decreased by less than 1% for both chemicals showing very low dependency of sulfate rejection on presence of the chemicals by NANO-SW-2540.

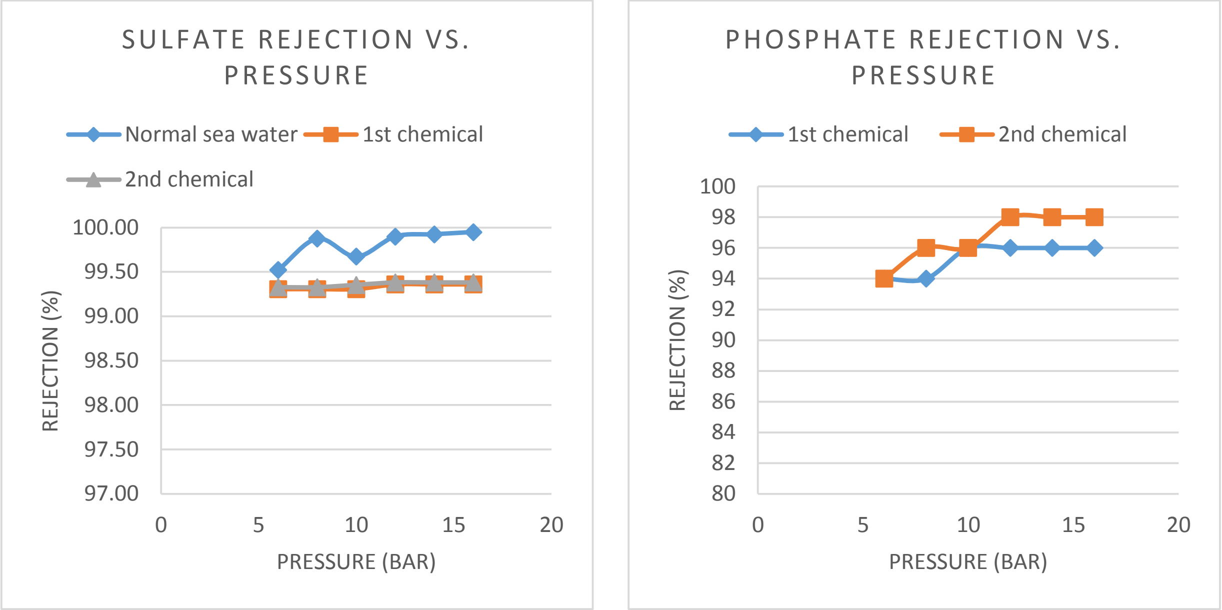


Figure 4.23 *Calcium (left) and magnesium (right) rejection as function of pressure for third dose of chemicals*

Rejection rate of phosphate in presence of either chemical at their third dose, as illustrated on the right graph in figure above, showed to be about 2% higher when second chemical was spiked into seawater at all applied pressure except for 6 and 10 bar at which both chemical led to 94% and 96% of rejection of phosphate respectively.

Generally, second chemical at its first and third dose led to greater phosphate retention and highest monovalent permeation compared with same concentrations of first chemical. This behavior of membrane seems to be due to properties of co-ions within composition of phosphate salt and the concentration of these ions within seawater. One could argue that larger size of first chemical ion could contribute to thicker positive layer on membrane surface leading to less rejection of anions and higher rejection of divalent cations.

However, second chemical resulted in more permeation of divalent cations. Decrease in rejection of magnesium by increasing feed concentration is also reported by *Labbez et. al* (Labbez et al., 2002).

4.2.2.6 pH effect on ion rejection

According to **Figure 2.7** trivalent phosphate anion could be achieved at extremely alkaline conditions alkali (pH>11). In order to investigate effects of PO_4^{3-} pH of solution was increased by adding NaOH to feed at first dose of second chemical. Figure 4.24 compares flux (left graph) and recovery (right graph) at moderate and high pH as functions of pressure when first dose of second chemical was added to membrane feed. As can be seen from flux graph, increasing pH resulted in higher flux and consequently higher recovery about 1.5% that is observable on right graph. This negative outcome as a result of solution's high pH is due to larger effective average pore size and a larger effective membrane thickness.

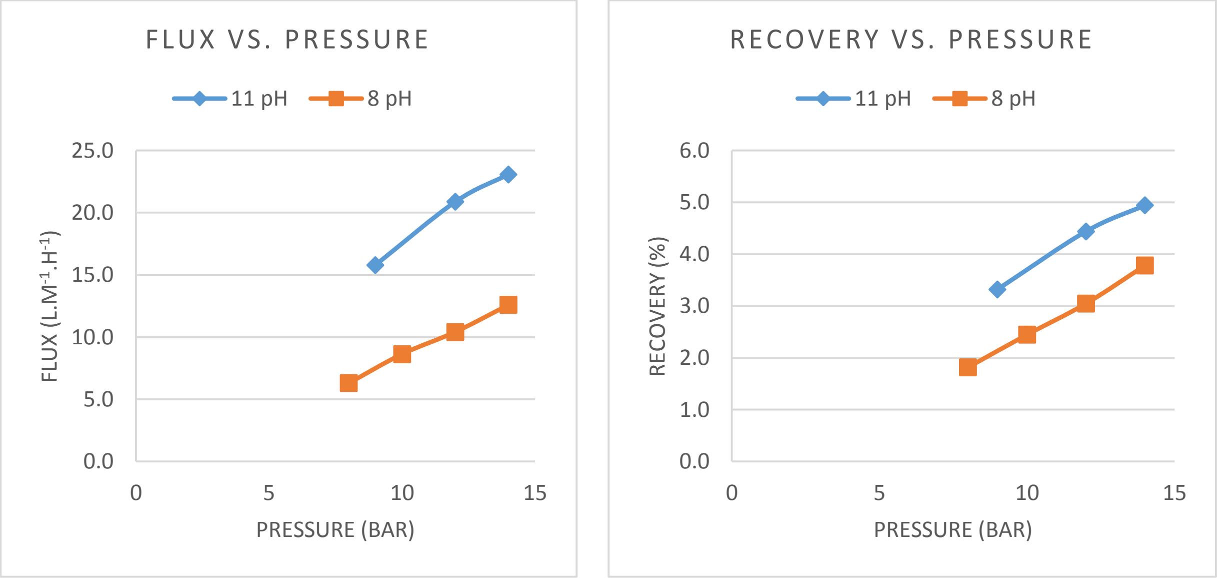


Figure 4.24 *Flux and recovery as functions of pressure at different pH for first dose of second chemical*

This reason also led to higher permeation of different ions as can be seen in Figure 4.25. The decline in rejection was highest for phosphate (about 40% drop) and least for sulfate as sodium showed similar behavior in either conditions.

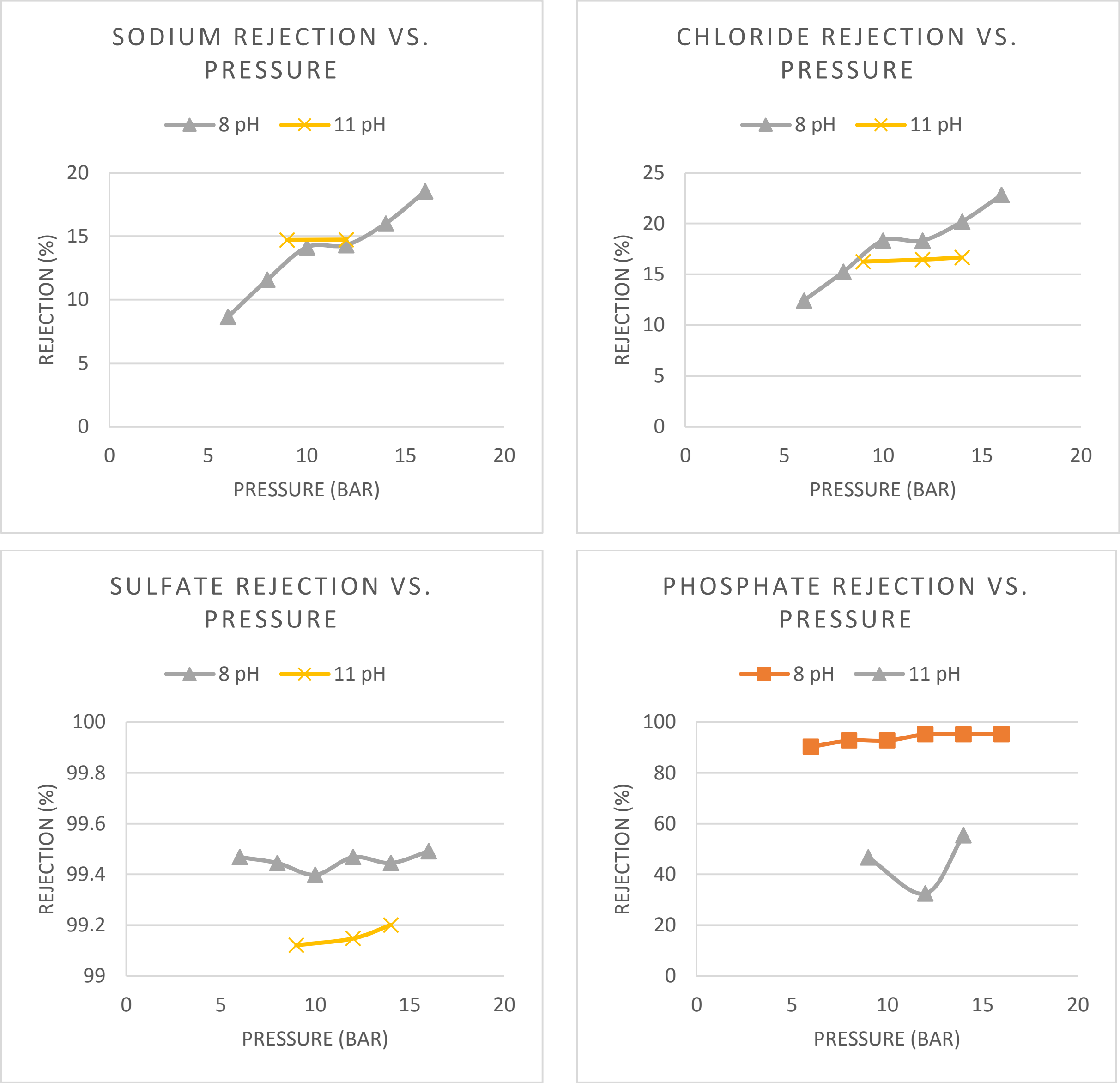


Figure 4.25 *Rejection rates of sodium, chloride, sulfate and phosphate as functions of pressure at to different pH*

Larger effective pore size and probable change in MWCO leading to an increase in permeate flux and decrease in retention of ions in extremely alkaline conditions has been studied previously and reported different authors (Dalwani et al., 2011; Mänttäri et al., 2006; Urase et al., 1998; Xu and Lebrun, 1999). As a result, NANO-SW-2540 nanofiltration membrane was unable to fulfil high phosphate rejection at highly alkaline condition.

Chapter 5: Conclusions and recommendations

5 Conclusions and recommendations

This study investigated effects of introducing phosphate into seawater as NANO-SW-2540 membrane feed on membrane's performance. Production of low salinity seawater that is rich in phosphate, calcium, and sulfate for water-based enhanced oil recovery was discussed. Evaluation of the membrane's performance based on flux and rejection rates carried out by controlling operational parameters such as pressure, feed solution composition and concentration. After finding phosphate salts that are soluble in seawater and determining their solubility limits spiking into the NANO-SW-2540 results suggested that recovery and salt rejection rates increased by rising applied pressure. Increase in phosphate concentration in membrane feed led to a growth in permeation of normal seawater ions and in concentrate flux. More findings from experimental results are as follows:

- Salinity and conductivity remained virtually the same in presence and absence of chemicals.
- Second chemical, regardless of its initial concentration, decreased permeate flux by about half of its value when normal seawater was used as feed.
- Phosphate rejection rates ranged between 87 to 97%.
- Having high rejection of sulfate, phosphate, magnesium and calcium in, NF membrane's concentrate is a favorable product for water-base enhanced oil recovery.
- Except for first dose of first chemical, that decreased sulfate rejection from 99 to 97% the rest of experimental results showed less than 1% drop in sulfate rejection.
- Second chemical showed to result in higher both monovalent permeation and phosphate and sulfate rejection.
- Third dose gave most effective results in terms of both high permeation of monovalent ions and rejection phosphate and sulfate.

- High pH solution unfavorably increased the recovery rate by 1.5% and decreased rejection of phosphate by around 40%.

Recommendations for future research

- Experiments with other nanofiltration membrane, more specifically ceramic membranes with greater pH range, could result in higher retention of phosphate.
- At the third dose, second chemical started to precipitate although first chemical had higher limits before precipitation. As a result, greater concentration of first chemical in sweater feed could be experimented for better understanding of effect of concentration.
- There are other soluble phosphate salts that could be tested in order to find out more on the effect of salt composition.
- Other analytical chemistry techniques such as calorimetric and mass spectrometry analysis could be useful for more precise ionic analysis.
- Sulfate if unfavorable, for any reason such as scale formation, could be removed prior to membrane separation by precipitation as gypsum.

References

AFONSO, M. D., HAGMEYER, G. & GIMBEL, R. 2001. Streaming potential measurements to assess the variation of nanofiltration membranes surface charge with the concentration of salt solutions. *Separation and Purification Technology,* 22**,** 529-541.

AL-GARNI, M. T. & AL-ANAZI, B. D. 2008. Investigation of wettability effects on capillary pressure, and irreducible saturation for Saudi crude oils, using rock centrifuge. *Oil and Gas Business,* 2008.

ANDERSEN, M. A. 1995. *Petroleum research in North Sea chalk*, RF-Rogaland Research.

ANDERSON, W. 1986. Wettability literature survey-part 2: Wettability measurement. *Journal of Petroleum Technology,* 38**,** 1,246-1,262.

AQUACLEARLLC.COM. 2015. *Aqua Clear: Comparison of Reverse Osmosis with Nanofiltration and other Filtration Technologies - Aquaclear LLC* [Online]. Available: http://www.aquaclearllc.com/osmosis-vs-nanofiltration.php [Accessed 20 May 2015].

AUSTAD, T., STRAND, S., HØGNESEN, E. & ZHANG, P. Seawater as IOR fluid in fractured chalk. International Symposium on Oilfield Chemistry, 2005. Society of Petroleum, 2-4.

BALLET, G. T., HAFIANE, A. & DHAHBI, M. 2007. Influence of operating conditions on the retention of phosphate in water by nanofiltration. *Journal of membrane science,* 290**,** 164-172.

BELLONA, C., DREWES, J. E., XU, P. & AMY, G. 2004. Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review. *Water research,* 38**,** 2795-2809.

BEN FARÈS, N. 2006. *Contribution à l'étude de l'élimination des ions zinciques: étude expérimentale et modélisation.* Rennes 1.

CATH, T. Y., CHILDRESS, A. E. & ELIMELECH, M. 2006. Forward osmosis: principles, applications, and recent developments. *Journal of membrane science,* 281**,** 70-87.

CHAABANE, T., TAHA, S., AHMED, M. T., MAACHI, R. & DORANGE, G. 2006. Removal of copper from industrial effluent using a spiral wound module—film theory and hydrodynamic approach. *Desalination,* 200**,** 403-405.

CHELLAM, S. & TAYLOR, J. S. 2001. Simplified analysis of contaminant rejection during ground-and surface water nanofiltration under the information collection rule. *Water research,* 35**,** 2460-2474.

CHERYAN, M. 1986. *Ultrafiltration handbook*, Technomic Publishing Co. Inc.

CHILDRESS, A. E. & ELIMELECH, M. 2000. Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics. *Environmental Science & Technology,* 34**,** 3710-3716.

COSSÉ, R. 1993. *Basics of reservoir engineering: oil and gas field development techniques*, Éditions Technip.

COT, L., AYRAL, A., DURAND, J., GUIZARD, C., HOVNANIAN, N., JULBE, A. & LARBOT, A. 2000. Inorganic membranes and solid state sciences. *Solid State Sciences,* 2**,** 313-334.

CUIEC, L. 1984. Rock/crude-oil interactions and wettability: An attempt to understand their interrelation. *paper SPE,* 13211**,** 16-19.

DALWANI, M., BENES, N. E., BARGEMAN, G., STAMATIALIS, D. & WESSLING, M. 2011. Effect of pH on the performance of polyamide/polyacrylonitrile based thin film composite membranes. *Journal of Membrane Science,* 372**,** 228-238.

DICKSON, A. G. & GOYET, C. 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. Version 2. Oak Ridge National Lab., TN (United States).

ELIMELECH, M., JIA, X., GREGORY, J. & WILLIAMS, R. 1998. *Particle deposition & aggregation: measurement, modelling and simulation*, Butterworth-Heinemann.

EPGEOLOGY. 2015. *Wettability in Oil and Gas Reservoirs : Reservoir Engineering - Exploration & Production Geology.* [Online]. Available: http://www.epgeology.com/reservoir-engineering-f10/wettability-oil-and-gas-reservoirs-t5978.html [Accessed 14 May 2015].

FANE, A., AWANG, A., BOLKO, M., MACOUN, R., SCHOFIELD, R., SHEN, Y. & ZHA, F. 1992. Metal recovery from wastewater using membranes. *Water Science & Technology,* 25**,** 5-18.

FATHI, S. J., AUSTAD, T. & STRAND, S. 2010. "Smart Water" as a Wettability Modifier in Chalk: The Effect of Salinity and Ionic Composition. *Energy & fuels,* 24**,** 2514-2519.

FRAPPART, M., AKOUM, O., DING, L. H. & JAFFRIN, M. Y. 2006. Treatment of dairy process waters modelled by diluted milk using dynamic nanofiltration with a rotating disk module. *Journal of membrane science,* 282**,** 465-472.

GLUYAS, J. & SWARBRICK, R. 2013. *Petroleum geoscience*, John Wiley & Sons.

GREEN, D. W. & WILLHITE, G. P. 1998. *Enhanced oil recovery*, Richardson, Tex.: Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers.

GUPTA, R., GRIFFIN, P., HU, L., WILLINGHAM, T. W., CASCIO, M. L., SHYEH, J. J. & HARRIES, C. 2011. Enhanced waterflood for Middle East carbonate cores–impact of injection water composition. *paper SPE,* 142668.

HANRAHAN, G., SALMASSI, T. M., KHACHIKIAN, C. S. & FOSTER, K. L. 2005. Reduced inorganic phosphorus in the natural environment: significance, speciation and determination. *Talanta,* 66**,** 435-444.

HOBERG, K. 2015. *Conductivity* [Online]. Germany. Available: http://www.kuntze.com/en/parameter/conductivity.html [Accessed 17 May 2015].

HOFFER, L., SCHWINN, H., BIESERT, L. & JOSIC, D. 1995. Improved virus safety and purity of a chromatographically produced Factor IX concentrate by nanofiltration. *Journal of Chromatography B: Biomedical Sciences and Applications,* 669**,** 187-196.

HØGNESEN, E. J., STRAND, S., & AUSTAD, T. 2005. Water flooding of Preferential Oil-Wet Carbonates: Oil recovery Related to Reservoir Temperature and Brine Composition. *SPE Europrec/EAGE Annual*

HUNTER, R. J. 2013. *Zeta potential in colloid science: principles and applications*, Academic press.

JITSUHARA, I. & KIMURA, S. 1983. Rejection of inorganic salts by charged ultrafiltration membranes made of sulfonated polysulfone. *Journal of chemical engineering of Japan,* 16**,** 394-399.

KARAGEORGIOU, K., PASCHALIS, M. & ANASTASSAKIS, G. N. 2007. Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent. *Journal of Hazardous Materials,* 139**,** 447-452.

KIRIUKHIN, M. Y. & COLLINS, K. D. 2002. Dynamic hydration numbers for biologically important ions. *Biophysical Chemistry,* 99**,** 155-168.

KOKAL, S. & AL-KAABI, A. 2010. Enhanced oil recovery: challenges & opportunities. *World Petroleum Council: Official Publication***,** 64-68.

KOŠUTIĆ, K., DOLAR, D. & KUNST, B. 2006. On experimental parameters characterizing the reverse osmosis and nanofiltration membranes' active layer. *Journal of membrane science,* 282**,** 109-114.

KOŠUTIĆ, K. & KUNST, B. 2002. Removal of organics from aqueous solutions by commercial RO and NF membranes of characterized porosities. *Desalination,* 142**,** 47-56.

KOYUNCU, I. 2002. Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity. *Desalination,* 143**,** 243-253.

LABBEZ, C., FIEVET, P., SZYMCZYK, A., VIDONNE, A., FOISSY, A. & PAGETTI, J. 2002. Analysis of the salt retention of a titania membrane using the "DSPM" model: Effect of pH, salt concentration and nature. *Journal of Membrane Science,* 208**,** 315-329.

LHASSANI, A., RUMEAU, M., BENJELLOUN, D. & PONTIE, M. 2001. Selective demineralization of water by nanofiltration application to the defluorination of brackish water. *Water research,* 35**,** 3260-3264.

LV, J., WANG, K. Y. & CHUNG, T.-S. 2008. Investigation of amphoteric polybenzimidazole (PBI) nanofiltration hollow fiber membrane for both cation and anions removal. *Journal of Membrane Science,* 310**,** 557-566.

MA, S., ZHANG, X., MORROW, N. & ZHOU, X. 1999. Characterization of wettability from spontaneous imbibition measurements. *Journal of Canadian Petroleum Technology,* 38**,** 1-8.

MANRIQUE, E. J., MUCI, V. E. & GURFINKEL, M. E. 2007. EOR field experiences in carbonate reservoirs in the United States. *SPE Reservoir Evaluation & Engineering,* 10**,** 667-686.

MÄNTTÄRI, M., PIHLAJAMÄKI, A. & NYSTRÖM, M. 2006. Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH. *Journal of Membrane Science,* 280**,** 311-320.

MARCUS, Y. 1997. *Ion properties,* New York, Marcel Dekker.

MASTERS, G. M. & ELA, W. 2008. *Introduction to environmental engineering and science*, Prentice Hall Englewood Cliffs, NJ.

MULDER, M. 2003. *Basic Principles of Membrane Technology Second Edition,* Boston, Kluwer Academic Pub.

PAUGAM, L., TAHA, S., DORANGE, G., JAOUEN, P. & QUÉMÉNEUR, F. 2004. Mechanism of nitrate ions transfer in nanofiltration depending on pressure, pH, concentration and medium composition. *Journal of Membrane Science,* 231**,** 37-46.

PEARCE, G. 2007. Introduction to membranes: Membrane selection. *Filtration & Separation,* 44**,** 35-37.

PIDWIRNY, M. 2010. *Ocean* [Online]. Available: http://www.eoearth.org/view/article/154984/ [Accessed 17 May 2015].

PONTALIER, P.-Y., ISMAIL, A. & GHOUL, M. 1997. Mechanisms for the selective rejection of solutes in nanofiltration membranes. *Separation and purification technology,* 12**,** 175-181.

RAUTENBACH, R. & GRÖSCHL, A. 1990. Separation potential of nanofiltration membranes. *Desalination,* 77**,** 73-84.

SADAR, M. J. 1998. *Turbidity science*, Hach Company.

SCHAEP, J. & VANDECASTEELE, C. 2001. Evaluating the charge of nanofiltration membranes. *Journal of membrane science,* 188**,** 129-136.

SCHAEP, J., VANDECASTEELE, C., MOHAMMAD, A. W. & BOWEN, W. R. 1999. Analysis of the salt retention of nanofiltration membranes using the Donnan–Steric partitioning pore model. *Separation science and Technology,* 34**,** 3009-3030.

SCHMELING, N., KONIETZNY, R., SIEFFERT, D., RÖLLING, P. & STAUDT, C. 2010. Functionalized copolyimide membranes for the separation of gaseous and liquid mixtures. *Beilstein journal of organic chemistry,* 6**,** 789-800.

SFORCA, M., YOSHIDA, I. & NUNES, S. 1999. Organic–inorganic membranes prepared from polyether diamine and epoxy silane. *Journal of membrane science,* 159**,** 197-207.

SHARMA, R. R. & CHELLAM, S. 2005. Temperature Effects on the Morphology of Porous Thin Film Composite Nanofiltration Membranes. *Environmental Science & Technology,* 39**,** 5022-5030.

SHIH, M.-C. 2005. An overview of arsenic removal by pressure-drivenmembrane processes. *Desalination,* 172**,** 85-97.

SIDNEY, L. & SRINIVASA, S. 1963. *Sea water demineralization by means of an osmotic membrane*.

STEWART, R. H. 2008. Introduction to Physical Oceanography. Department of Oceanography, Texas A&M University.

STRAND, S. 2005. *Wettability alteration in chalk : a study of surface chemistry.* no. 21, University of Stavanger.

STRAND, S., HØGNESEN, E. J. & AUSTAD, T. 2006a. Wettability alteration of carbonates—Effects of potential determining ions (Ca 2+ and SO 4 2−) and temperature. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 275**,** 1-10.

STRAND, S., STANDNES, D. & AUSTAD, T. 2006b. New wettability test for chalk based on chromatographic separation of SCN− and SO 4 2−. *Journal of Petroleum Science and Engineering,* 52**,** 187-197.

SZYMCZYK, A., FIEVET, P. & RAMSEYER, C. 2006. Dielectric constant of electrolyte solutions confined in a charged nanofiltration membrane. *Desalination,* 200**,** 125-126.

TANNINEN, J., MÄNTTÄRI, M. & NYSTRÖM, M. 2006. Effect of salt mixture concentration on fractionation with NF membranes. *Journal of Membrane Science,* 283**,** 57-64.

TEIXEIRA, M. R., ROSA, M. J. & NYSTRÖM, M. 2005. The role of membrane charge on nanofiltration performance. *Journal of Membrane Science,* 265**,** 160-166.

TREIBER, L. & OWENS, W. 1972. A laboratory evaluation of the wettability of fifty oil-producing reservoirs. *Society of petroleum engineers journal,* 12**,** 531-540.

TZIMAS, E., GEORGAKAKI, A., CORTES, C. G. & PETEVES, S. 2005. Enhanced oil recovery using carbon dioxide in the European energy system. *Report EUR,* 21895**,** 6.

ULBRICHT, M. 2006. Advanced functional polymer membranes. *Polymer,* 47**,** 2217-2262.

URASE, T., OH, J.-I. & YAMAMOTO, K. 1998. Effect of pH on rejection of different species of arsenic by nanofiltration. *Desalination,* 117**,** 11-18.

VAN DER BRUGGEN, B., KONINCKX, A. & VANDECASTEELE, C. 2004. Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration. *Water research,* 38**,** 1347-1353.

VAN DER BRUGGEN, B., SCHAEP, J., WILMS, D. & VANDECASTEELE, C. 1999. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *Journal of Membrane Science,* 156**,** 29-41.

VAN DER BRUGGEN, B. & VANDECASTEELE, C. 2003. Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environmental pollution,* 122**,** 435-445.

VAN DER BRUGGEN, B., VANDECASTEELE, C., VAN GESTEL, T., DOYEN, W. & LEYSEN, R. 2003. A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environmental progress,* 22**,** 46-56.

WANG, X.-L., TSURU, T., NAKAO, S.-I. & KIMURA, S. 1997. The electrostatic and steric-hindrance model for the transport of charged solutes through nanofiltration membranes. *Journal of Membrane Science,* 135**,** 19-32.

WATER.EPA.GOV. 2015a. *5.5 Turbidity | Monitoring & Assessment | US EPA* [Online]. Available: http://water.epa.gov/type/rsl/monitoring/vms55.cfm [Accessed 17 May 2015].

WATER.EPA.GOV. 2015b. *Drinking Water Contaminants | Drinking Water Contaminants | US EPA* [Online]. Available: http://water.epa.gov/drink/contaminants/index.cfm#3 [Accessed 17 May 2015].

WU, A., CONNER, G. & PRABHAKAR, V. 2007. Asymmetrical pore membrane optimizes copper plating filtration. *Solid State Technology,* 50**,** 46-48.

XU, Y. & LEBRUN, R. E. 1999. Investigation of the solute separation by charged nanofiltration membrane: effect of pH, ionic strength and solute type. *Journal of Membrane Science,* 158**,** 93-104.

YANG, F., ZHANG, S., YANG, D. & JIAN, X. 2007. Preparation and characterization of polypiperazine amide/PPESK hollow fiber composite nanofiltration membrane. *Journal of Membrane Science,* 301**,** 85-92.

YAROSHCHUK, A. E. 2001. Non-steric mechanisms of nanofiltration: superposition of Donnan and dielectric exclusion. *Separation and purification Technology,* 22**,** 143.

YOON, Y., WESTERHOFF, P., SNYDER, S. A., WERT, E. C. & YOON, J. 2007. Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes. *Desalination,* 202**,** 16-23.

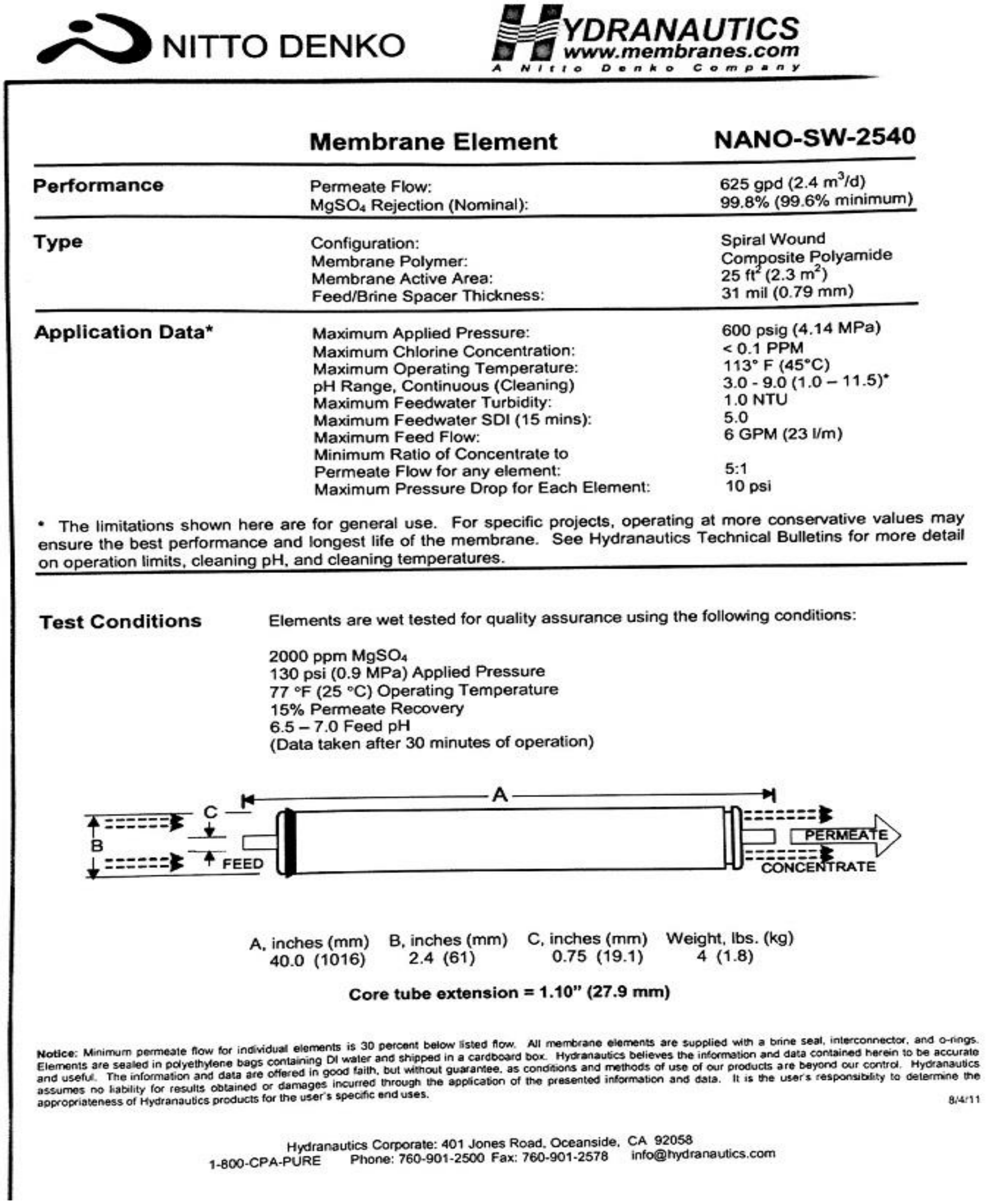
ZHANG, P. & AUSTAD, T. Waterflooding in Chalk–Relationship between Oil Recovery, New Wettability Index, Brine Composition and Cationic Wettability Modifier (SPE94209). 67th EAGE Conference & Exhibition, 2005.

ZHANG, P. & AUSTAD, T. 2006. Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions. *Colloid Surf. A-Physicochem. Eng. Asp.,* 279**,** 179-187.

ZHANG, P., TWEHEYO, M. T. & AUSTAD, T. 2006. Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate. *Energy & fuels,* 20**,** 2056-2062.

ZHANG, P., TWEHEYO, M. T. & AUSTAD, T. 2007. Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca 2+, Mg 2+, and SO 4 2−. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 301**,** 199-208.

Appendix I Membrane specification sheet



NITTO DENKO

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Membrane Element NANO-SW-2540

Performance	Permeate Flow: $MgSO_4$ Rejection (Nominal):	625 gpd (2.4 m^3/d) 99.8% (99.6% minimum)
Type	Configuration: Membrane Polymer: Membrane Active Area: Feed/Brine Spacer Thickness:	Spiral Wound Composite Polyamide 25 ft^2 (2.3 m^2) 31 mil (0.79 mm)
Application Data*	Maximum Applied Pressure: Maximum Chlorine Concentration: Maximum Operating Temperature: pH Range, Continuous (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 (4.14 MPa) < 0.1 PPM 113° F (45°C) 3.0 - 9.0 (1.0 – 11.5)* 1.0 NTU 5.0 6 GPM (23 l/m) 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 membrane. See Hydranautics Technical Bulletins for more detail on operation limits, cleaning pH, and cleaning temperatures.

Test Conditions Elements are wet tested for quality assurance using the following conditions:

2000 ppm $MgSO_4$
130 psi (0.9 MPa) Applied Pressure
77 °F (25 °C) Operating Temperature
15% Permeate Recovery
6.5 – 7.0 Feed pH
(Data taken after 30 minutes of operation)

A, inches (mm)	B, inches (mm)	C, inches (mm)	Weight, lbs. (kg)
40.0 (1016)	2.4 (61)	0.75 (19.1)	4 (1.8)

Core tube extension = 1.10" (27.9 mm)

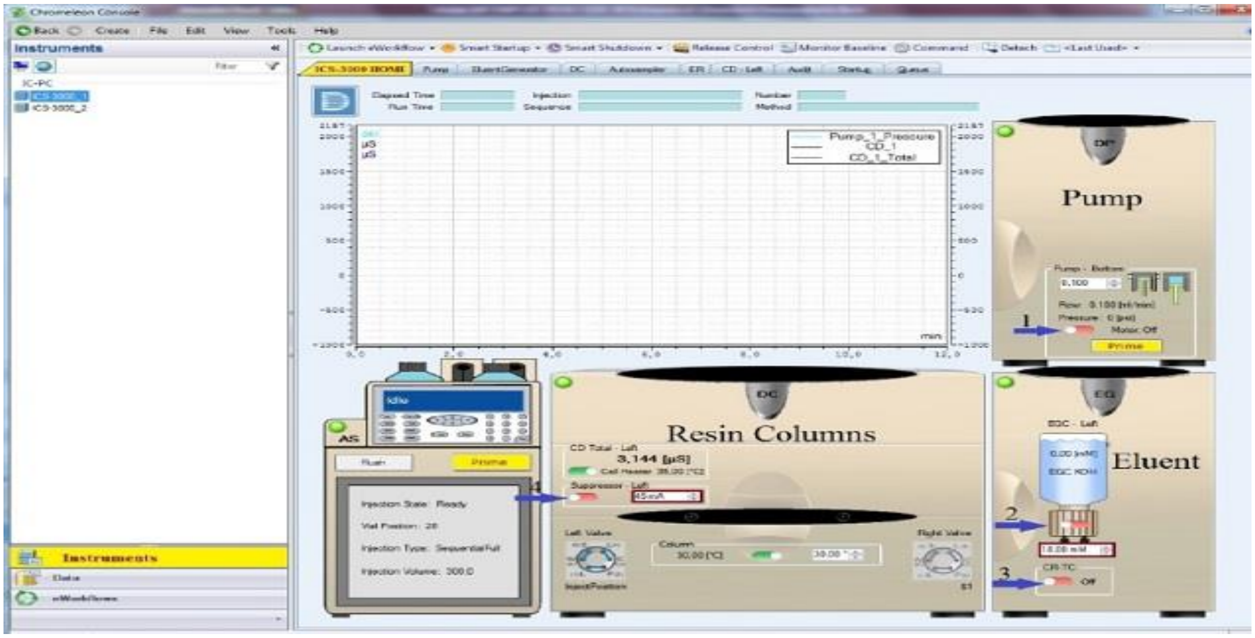
Notice: Minimum permeate flow for individual elements is 30 percent below listed flow. All membrane elements are supplied with a brine seal, interconnector, and o-rings. Elements are sealed in polyethylene bags containing DI water and shipped in a cardboard box. Hydranautics believes the information 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.

8/4/11

Hydranautics Corporate: 401 Jones Road, Oceanside, CA 92058
1-800-CPA-PURE Phone: 760-901-2500 Fax: 760-901-2578 info@hydranautics.com

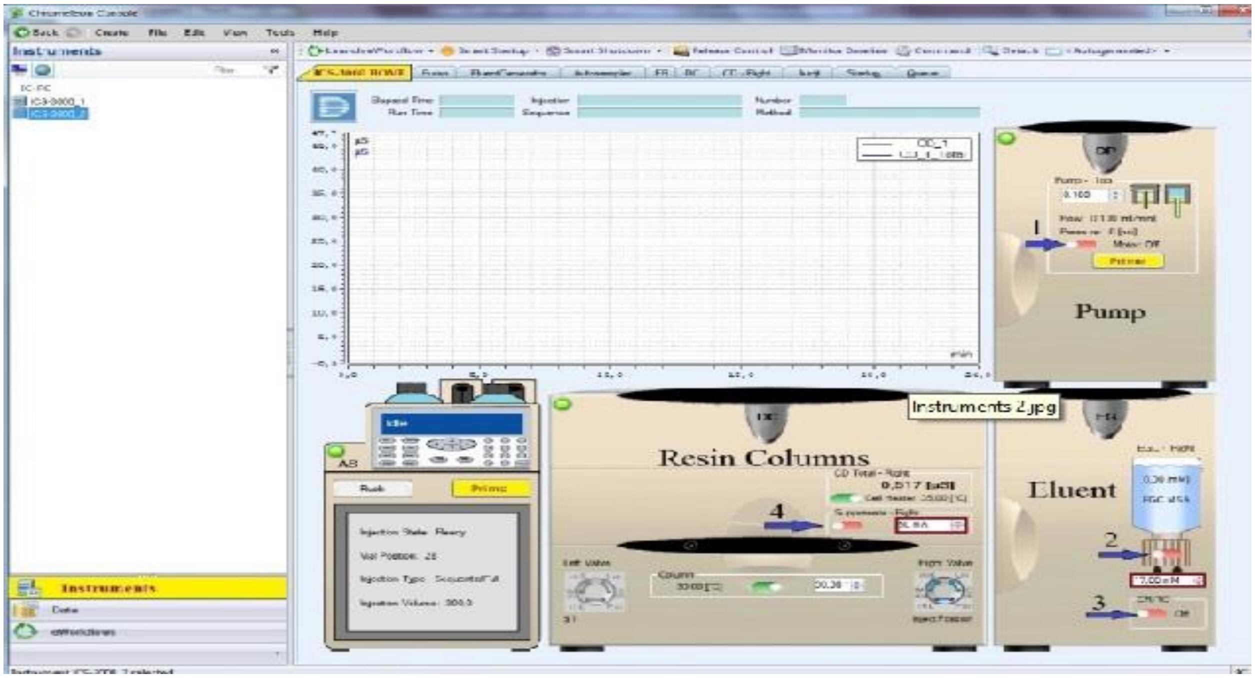
Figure I.1 *Specification sheet of NANO-SW-2540 by Hydranautics used for all separation experiments*

Appendix II Ionic chromatography chromeleon software interface



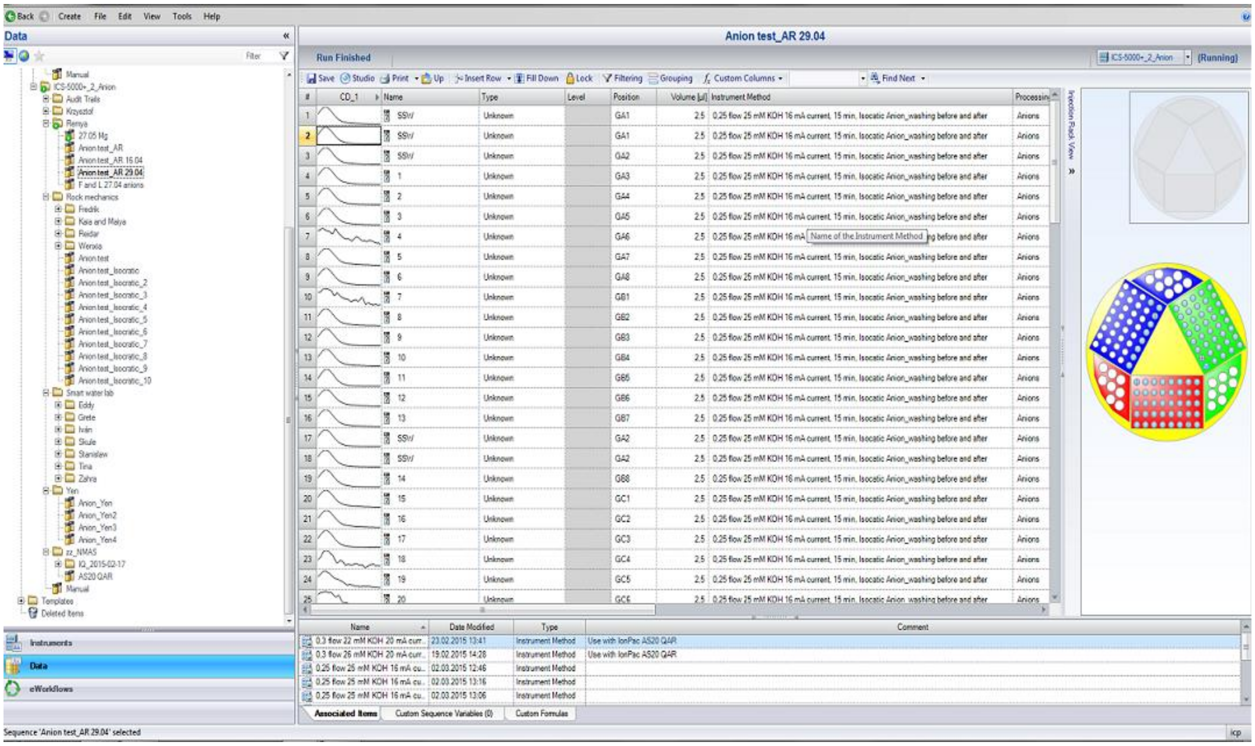
Injection State: Ready
Vial Position: 28
Injection Type: SequentialFull
Injection Volume: 300.0
CD Total - Left 3,144 [µS]

Figure II.1 *Preparing the instruments in the program of the IC software for anions*



Injection State: Ready
Vial Position: 28
CD Total - Right 0,517 [µS]

Figure II.2 *Preparing the instruments in the program of the IC software for cations.*



Anion test_AR 29.04

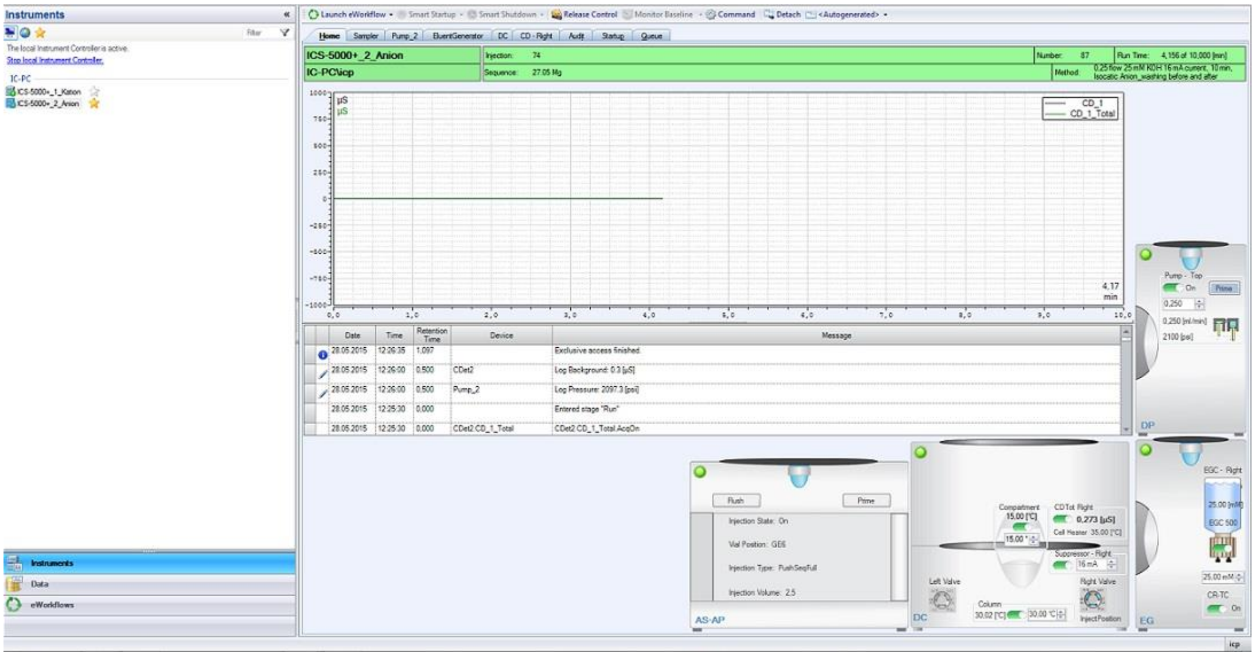
Run Finished

#	CD_1	Name	Type	Level	Position	Volume [µl]	Instrument Method	Processing
1		SSW	Unknown		GA1	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
2		SSW	Unknown		GA1	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
3		SSW	Unknown		GA2	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
4		1	Unknown		GA3	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
5		2	Unknown		GA4	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
6		3	Unknown		GA5	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
7		4	Unknown		GA6	2,5	0,25 flow 25 mM KOH 16 mA Name of the Instrument Method ng before and after	Anions
8		5	Unknown		GA7	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
9		6	Unknown		GA8	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
10		7	Unknown		GB1	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
11		8	Unknown		GB2	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
12		9	Unknown		GB3	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
13		10	Unknown		GB4	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
14		11	Unknown		GB5	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
15		12	Unknown		GB6	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
16		13	Unknown		GB7	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
17		SSW	Unknown		GA2	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
18		SSW	Unknown		GA2	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
19		14	Unknown		GB8	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
20		15	Unknown		GC1	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
21		16	Unknown		GC2	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
22		17	Unknown		GC3	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
23		18	Unknown		GC4	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
24		19	Unknown		GC5	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions
25		20	Unknown		GC6	2,5	0,25 flow 25 mM KOH 16 mA current, 15 min, Isocatic Anion_washing before and after	Anions

Name	Date Modified	Type	Comment
0.3 flow 22 mM KOH 20 mA curr...	23.02.2015 13:41	Instrument Method	Use with IonPac AS20 QAR
0.3 flow 26 mM KOH 20 mA curr...	19.02.2015 14:28	Instrument Method	Use with IonPac AS20 QAR
0.25 flow 25 mM KOH 16 mA cu...	02.03.2015 12:46	Instrument Method	
0.25 flow 25 mM KOH 16 mA cu...	02.03.2015 13:16	Instrument Method	
0.25 flow 25 mM KOH 16 mA cu...	02.03.2015 13:06	Instrument Method	

Sequence 'Anion test_AR 29.04' selected

Figure II.3 *An example of the list of sample data with the specified numbers and positions in the sampler.*



The local Instrument Controller is active.
Stop local Instrument Controller.

IC-PC
ICS-5000+_1_Kation
ICS-5000+_2_Anion

ICS-5000+_2_Anion
IC-PC\icp
Injection: 74
Sequence: 27.05 Mg
Number: 87
Run Time: 4,156 of 10,000 [min]
Method: 0.25 flow 25 mM KOH 16 mA current, 10 min, Isocatic Anion_washing before and after

Date	Time	Retention Time	Device	Message
28.05.2015	12:26:35	1,097		Exclusive access finished.
28.05.2015	12:26:00	0,500	CDet2	Log Background: 0.3 [µS]
28.05.2015	12:26:00	0,500	Pump_2	Log Pressure: 2097.3 [psi]
28.05.2015	12:25:30	0,000		Entered stage "Run"
28.05.2015	12:25:30	0,000	CDet2.CD_1_Total	CDet2.CD_1_Total.AcqOn

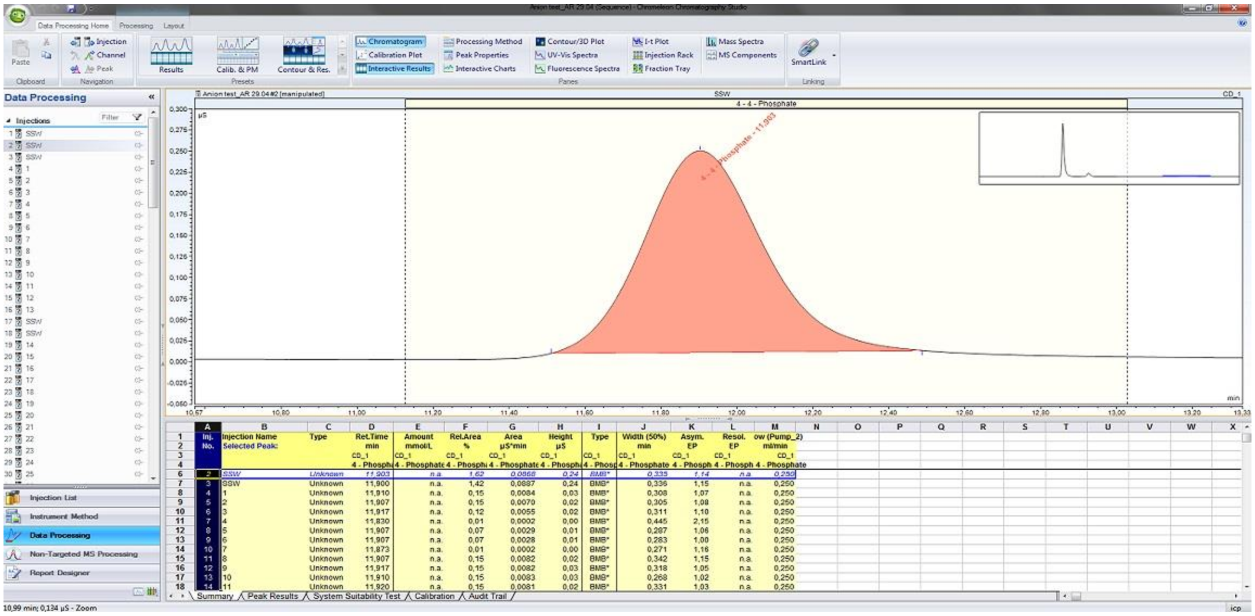
Injection State: On
Vial Position: GE6
Injection Type: PushSeqFull
Injection Volume: 2.5

Compartment 15,00 [°C]
15,00 °
CDTot Right 0,273 [µS]
Cell Heater 35,00 [°C]
Suppressor - Right 16 mA
Column 30,02 [°C] 30,00 °C

0,250
0,250 [ml/min]
2100 [psi]

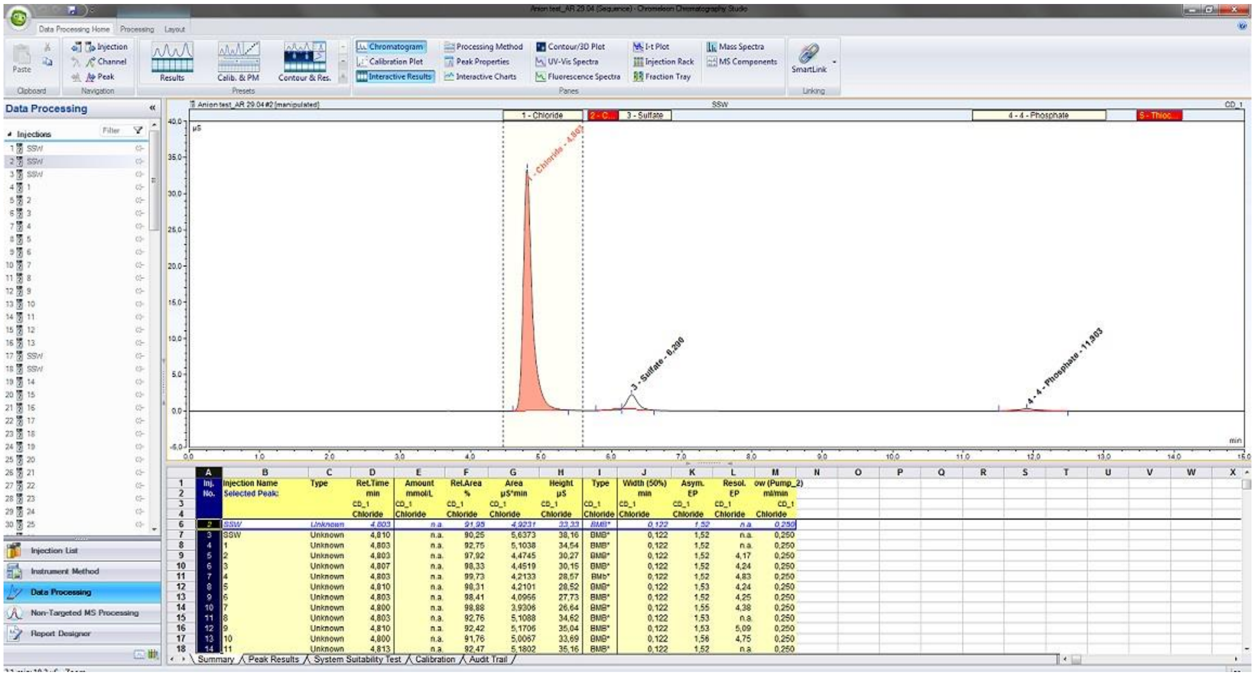
25,00 [mM]
25,00 mM

Figure II.4 *Signals of detection be IC machine as the program is being run*



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Inj.	Injection Name	Type	Ret.Time	Amount	Rel.Area	Area	Height	Type	Width (50%)	Asym.	Resol.	ow (Pump_2)
2	No.	Selected Peak:		min	mmol/L	%	µS*min	µS		min	EP	EP	ml/min
3				CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1
4				4 - Phosph	4 - Phosphate	4 - Phosph	4 - Phosphate	4 - Phosph	4 - Phosp	4 - Phosphate	4 - Phosph	4 - Phosph	4 - Phosphate
6	2	SSW	Unknown	11,903	n.a.	1,62	0,0868	0,24	BMB*	0,335	1,14	n.a.	0,250
7	3	SSW	Unknown	11,900	n.a.	1,42	0,0887	0,24	BMB*	0,336	1,15	n.a.	0,250
8	4	1	Unknown	11,910	n.a.	0,15	0,0084	0,03	BMB*	0,308	1,07	n.a.	0,250
9	5	2	Unknown	11,907	n.a.	0,15	0,0070	0,02	BMB*	0,305	1,08	n.a.	0,250
10	6	3	Unknown	11,917	n.a.	0,12	0,0055	0,02	BMB*	0,311	1,10	n.a.	0,250
11	7	4	Unknown	11,830	n.a.	0,01	0,0002	0,00	BMB*	0,445	2,15	n.a.	0,250
12	8	5	Unknown	11,907	n.a.	0,07	0,0029	0,01	BMB*	0,287	1,06	n.a.	0,250
13	9	6	Unknown	11,907	n.a.	0,07	0,0028	0,01	BMB*	0,283	1,00	n.a.	0,250
14	10	7	Unknown	11,873	n.a.	0,01	0,0002	0,00	BMB*	0,271	1,16	n.a.	0,250
15	11	8	Unknown	11,907	n.a.	0,15	0,0082	0,02	BMB*	0,342	1,15	n.a.	0,250
16	12	9	Unknown	11,917	n.a.	0,15	0,0082	0,03	BMB*	0,318	1,05	n.a.	0,250
17	13	10	Unknown	11,910	n.a.	0,15	0,0083	0,03	BMB*	0,268	1,02	n.a.	0,250
18	14	11	Unknown	11,920	n.a.	0,15	0,0081	0,02	BMB*	0,331	1,03	n.a.	0,250

Figure II.5 *An example of detected phosphate peak by IC machine illustrated by Choromeleon software.*



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Inj.	Injection Name	Type	Ret.Time	Amount	Rel.Area	Area	Height	Type	Width (50%)	Asym.	Resol.	ow (Pump_2)
2	No.	Selected Peak:		min	mmol/L	%	µS*min	µS		min	EP	EP	ml/min
3				CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1	CD_1
4				Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride	Chloride
6	2	SSW	Unknown	4,803	n.a.	91,95	4,9231	33,33	BMB*	0,122	1,52	n.a.	0,250
7	3	SSW	Unknown	4,810	n.a.	90,25	5,6373	38,16	BMB*	0,122	1,52	n.a.	0,250
8	4	1	Unknown	4,803	n.a.	92,75	5,1038	34,54	BMB*	0,122	1,52	n.a.	0,250
9	5	2	Unknown	4,803	n.a.	97,92	4,4745	30,27	BMB*	0,122	1,52	4,17	0,250
10	6	3	Unknown	4,807	n.a.	98,33	4,4519	30,15	BMB*	0,122	1,52	4,24	0,250
11	7	4	Unknown	4,803	n.a.	99,73	4,2133	28,57	BMb*	0,122	1,52	4,83	0,250
12	8	5	Unknown	4,810	n.a.	98,31	4,2101	28,52	BMB*	0,122	1,53	4,24	0,250
13	9	6	Unknown	4,803	n.a.	98,41	4,0966	27,73	BMB*	0,122	1,52	4,25	0,250
14	10	7	Unknown	4,800	n.a.	98,88	3,9306	26,64	BMB*	0,122	1,55	4,38	0,250
15	11	8	Unknown	4,803	n.a.	92,76	5,1088	34,62	BMB*	0,122	1,53	n.a.	0,250
16	12	9	Unknown	4,810	n.a.	92,42	5,1706	35,04	BMB*	0,122	1,53	5,09	0,250
17	13	10	Unknown	4,800	n.a.	91,76	5,0067	33,69	BMB*	0,122	1,56	4,75	0,250
18	14	11	Unknown	4,813	n.a.	92,47	5,1802	35,16	BMB*	0,122	1,52	n.a.	0,250

Figure II.6 *An example of detected chloride peak by IC machine illustrated by Choromeleon software.*

Appendix III Membrane separation results

Per.: Permeate

Ret.: Retentate

Table III. 1 *Normal seawater first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error (%)
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	8.129			13.7			32700			51.3			33.1								
6		7.64	7.885		17.6	17		23300	29200		36.5	45.8		22.8	29.3	26.4	836.6	862.9	11.5	3.1	11.25493201
8		7.668	7.846		19	19.2		23000	29100		36	45.5		22.5	29.2	30.5	825.1	855.5	13.3	3.6	11.6740074
10		7.6	7.834		20.4	20.4		21900	29300		34.3	45.6		21.4	29.5	45.0	809.0	854.0	19.5	5.3	11.58907429
12		7.589	7.822		22.1	21.6		21500	29400		33.4	45.9		20.7	29.6	59.2	789.5	848.7	25.7	7.0	11.77725624
14		7.558	7.829		22.9	22.5		20900	29500		32.6	46		20.2	29.8	75.2	758.4	833.6	32.7	9.0	12.15713473
16		7.546	7.815		24	25.3		20400	29700		32	46.4		19.9	30.1	93.6	779.2	872.8	40.7	10.7	12.22385151

Table III. 2 *Normal seawater second trial temperature, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/L)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error (%)
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	14.7			33200			51.8			33.5								
6		19.6	18.6		28800	32800		44.9	51.3		28.9	33.4	14.7	800.6	815.3	6.4	1.8	1.422428457
8		21.3	21.1		27600	32800		43.1	51.4		27.6	33.5	27.6	735.7	763.3	12.0	3.6	1.772149791
10		22.9	22.8		26800	32900		41.9	51.5		26.8	33.7	38.2	670.8	709.0	16.6	5.4	1.893287435
12		23.7	24.4		26600	33000		41.5	51.6		26.6	33.9	46.2	703.6	749.8	20.1	6.2	1.790062115
14		25.7	26.1		25900	33000		40.6	51.6		26	33.9	60.0	656.5	716.5	26.1	8.4	2.392245144
16		27.3	27.4		25700	33200		40.2	52		25.8	34.3	71.4	665.8	737.3	31.1	9.7	2.188601497

Table III. 3 *First chemical first dose first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m²h)	Recovery (%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	8.02			14.3			32500			50.8			32.7								
6		7.815	7.988		19.7	18.5		26100	31600		40.6	49.6		25.9	32.1	25.0	818.8	843.8	10.9	3.0	3.271075201
8		7.801	7.961		20.2	19.9		25600	31800		39.9	49.7		25.3	32.3	32.6	824.4	857.0	14.2	3.8	2.878846712
10		7.749	7.998		21.3	20.9		24600	31900		38.4	49.8		24.3	32.5	44.8	828.2	873.0	19.5	5.1	2.999115827
12		7.683	7.953		22.4	22.3		23900	32000		37.2	50.1		23.6	32.7	56.4	780.3	836.8	24.5	6.7	3.219105587
14		7.676	7.927		23.5	23.5		23600	32200		36.8	50.4		23.3	33	69.1	752.1	821.2	30.1	8.4	3.150959734
16		7.673	7.92		24	24.9		23200	32400		36.1	50.6		22.8	33.3	82.9	774.2	857.1	36.0	9.7	3.0452473

Table III. 4 *First chemical first dose second trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m²h)	Recovery (%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	8.017			21.7			31800			49.6			32.3								
6		7.803	7.95		23	23.2		26500	31800		41.4	49.7		26.5	32.4	30.4	868.9	899.3	13.2	3.4	0.563672807
8		7.77	7.917		23.9	24		25900	31700		40.4	49.9		25.7	32.4	38.0	868.9	906.9	16.5	4.2	1.079010958
10		7.756	7.908		24.5	24.9		25100	31900		39.1	49.9		25	32.7	51.3	853.1	904.4	22.3	5.7	0.899185542
12		7.69	7.91		25.8	26.1		24400	32000		38.1	50		24.2	32.8	65.7	818.8	884.5	28.6	7.4	1.146128051
14		7.67	7.901		26.8	27		24100	32100		37.6	50.1		24	33	77.4	837.9	915.2	33.6	8.5	1.183148003
16		7.646	7.884		27.6	28.1		23500	32200		36.7	50.3		23.3	33.1	91.1	784.9	875.9	39.6	10.4	1.586296949

Table III. 5 *First chemical first dose third trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature(°C)			TDS(ppm)			Conductivity(mS/cm)			Salinity			Flow Rate (L/h)			Flux (L/m^2h)	Recovery%	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.88			26.9			31500			49.3			32.3								
6		7.767	7.914		26.8	27.1		26500	31700		41.5	49.6		26.7	32.5	36.0	856.5	892.5	15.6	4.0	0.030760281
8		7.759	7.899		26.9	27.7		25700	31800		40.1	49.8		25.8	32.7	46.2	847.1	893.3	20.1	5.2	0.049057952
10		7.731	7.89		27.7	28.2		24900	31900		39	49.8		24.9	32.8	58.3	817.6	875.9	25.4	6.7	0.209698852
12		7.688	7.889		28.6	28.8		24400	31800		38	49.7		24.3	32.8	69.9	837.2	907.1	30.4	7.7	0.857939353
14		7.677	7.894		29.3	29.2		23900	32100		37.4	50.1		23.9	33.1	80.1	824.4	904.5	34.8	8.9	0.399399399
16		7.636	7.846		30	30.6		23500	32200		36.7	50.2		23.4	33.3	90.2	793.5	883.8	39.2	10.2	0.597485512

Table III. 6 *First chemical second dose first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^2h)	Recovery (%)	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	8.049			14.8			31800			49.7			32								
8		7.854	8.064		18.6	17.5		24900	31800		38.9	49.6		24.6	32.1	29.7	1076.8	1106.4	12.9	2.7	0.58154631
10		7.84	8.005		19.8	19.6		24900	31700		39	49.6		24.6	32.2	34.8	1044.5	1079.3	15.1	3.2	1.004260499
12		7.788	7.974		21.2	20.8		24200	31800		37.8	49.7		23.9	32.3	43.6	1001.9	1045.5	19.0	4.2	0.99673174
14		7.854	7.944		22.5	22.1		23900	31800		37.3	49.8		23.6	32.4	54.4	995.4	1049.8	23.6	5.2	1.286913465
16		7.679	7.916		23.8	23.8		23200	31900		36.2	49.8		22.9	32.6	61.7	1019.8	1081.5	26.8	5.7	1.245803938
18		7.744	7.89		25.4	25.4		22800	31900		35.7	49.8		22.5	32.7	68.8	982.7	1051.5	29.9	6.5	1.558747473

Table III. 7 *First chemical second dose second trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.91			24.6			31200			48.7			31.8								
8		7.803	7.875		25.8	25.3		25600	31500		40.1	49.2		25.6	32.2	33.6	1052.6	1086.2	14.6	3.1	-0.376896652
10		7.786	7.865		26.2	25.8		25300	31500		39.5	49.3		25.3	32.3	38.5	1002.8	1041.3	16.7	3.7	-0.22726313
12		7.769	7.844		27.1	26.9		24600	31600		38.5	49.4		24.6	32.4	46.2	1010.3	1056.5	20.1	4.4	-0.301071514
14		7.759	7.842		27.9	27.3		24100	31600		37.7	49.4		24	32.4	53.4	1020.8	1074.2	23.2	5.0	-0.086793631
16		7.591	7.798		28.5	29.1		23700	31700		37	49.5		23.6	32.6	57.0	992.6	1049.7	24.8	5.4	-0.209642398
18		7.6	7.813		28.9	29.8		23200	31700		36.3	49.5		23.1	32.6	64.1	971.2	1035.4	27.9	6.2	0.08498446

Table III. 8 *First chemical second dose third trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.82			28.3			31300			48.8			32.1								
8		7.681	7.828		28.7	28.5		26100	31300		40.7	48.8		26.2	32.1	31.1	1023.7	1054.8	13.5	2.9	0.48951701
10		7.697	7.814		29	29.6		25500	31400		39.8	49.2		25.6	32.2	34.8	977.4	1012.1	15.1	3.4	0.327879433
12		7.661	7.784		29.5	29.4		24800	31400		38.8	49.2		24.8	32.3	38.8	981.8	1020.6	16.9	3.8	0.481716301
14		7.654	7.824		29.9	29.8		24300	31400		37.8	49.1		24.3	32.3	48.8	946.5	995.3	21.2	4.9	0.792237853
16		7.625	7.792		30.5	30.7		24000	31500		37.4	49.1		24	32.4	51.9	931.0	982.9	22.6	5.3	0.626180633
18		7.586	7.748		30.6	31.8		23400	31700		36.5	49.5		23.3	32.7	55.8	938.3	994.1	24.3	5.6	0.21083675

Table III. 9 *First chemical third dose first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^2h)	Recovery (%)	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	8.035			14.5			32400			50.6			32.6								
8		7.855	7.939		18.9	18.8		26500	32300		41.4	50.5		26.3	32.8	20.4	992.6	1013.0	8.9	2.0	0.669131781
10		7.829	7.912		20.6	20.7		26300	32200		41	50.4		26.1	32.8	23.9	1011.2	1035.2	10.4	2.3	1.038440089
12		7.825	7.88		22.4	22.2		25500	32300		39.9	50.4		25.4	32.9	29.7	944.9	974.6	12.9	3.1	0.949148447
14		7.696	7.849		23.6	23.7		25000	32200		39.1	50.4		24.8	33	35.4	949.9	985.2	15.4	3.6	1.414918407
16		7.718	7.834		25.1	25		24500	32200		38.2	50.4		24.3	33	41.1	962.6	1003.7	17.9	4.1	1.590736594
18		7..709	7.844		26	25.7		24900	32300		38.8	50.5		24.8	33.1	44.1	980.9	1025.1	19.2	4.3	1.292225496

Table III. 10 *First chemical third dose second trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^2h)	Recovery (%)	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.81			25.5			32000			49.9			32.7								
6		7.731	7.838		26.1	25.4		27800	32100		43.4	50.1		28	32.8	16.2	916.0	932.2	7.0	1.7	-0.079067763
8		7.714	7.836		26.4	26.6		27300	32100		42.6	50.2		27.5	33	20.4	854.4	874.8	8.9	2.3	0.037031745
10		7.676	7.812		27.3	27.3		26700	32100		41.7	50.2		26.9	33	24.4	868.2	892.6	10.6	2.7	0.149137419
12		7.673	7.79		27.8	28.4		26000	32100		40.7	50.2		26.1	33	28.6	841.1	869.8	12.5	3.3	0.315353735
14		7.629	7.768		28.6	29.4		25400	32100		40	50.2		25.5	33.1	35.4	822.5	857.9	15.4	4.1	0.550285598
16		7.67	7.757		29.5	29.3		25300	32200		39.6	50.3		25.4	33.2	34.5	804.2	838.7	15.0	4.1	0.261853811

Table III. 11 *First chemical third dose third trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity(mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error (
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.76			29			31900			49.8			32.8								
8		7.738	7.77		28.8	28.8		28200	31900		44.1	49.9		28.6	32.9	14.2	851.7	865.9	6.2	1.6	0.19018026
10		7.737	7.756		28.4	28.9		27500	32000		43	50		27.8	32.9	18.4	855.8	874.2	8.0	2.1	-0.016484064
12		7.655	7.764		28.8	29.5		26900	32000		42	50		27.1	33	23.9	836.6	860.5	10.4	2.8	0.130568738
14		7.706	7.754		29.7	29.9		26300	32000		41	50.1		26.5	33	28.6	810.8	839.4	12.4	3.4	0.295824225
16		7.669	7.75		30.1	30.1		25800	32100		40.4	50.1		26	33.1	32.0	804.8	836.8	13.9	3.8	0.129374531
18		7.61	7.746		30.2	31.6		25400	32100		39.6	50.3		25.5	33.2	36.2	764.9	801.1	15.7	4.5	0.322593337

Table III. 12 *Second chemical first dose first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	8.103			12.2			32900			51.5			33.1								
6		7.942	8.006		18.8	17.9		28400	32600		44.3	50.9		28.4	33.1	9.1	852.4	861.5	4.0	1.1	1.046903558
8		7.868	7.979		19.8	19.3		28400	32700		43.4	50.9		27.8	33.2	12.3	825.1	837.4	5.4	1.5	0.800351589
10		7.92	7.975		20.6	20.5		27100	32600		42.3	50.9		27	33.2	16.8	806.0	822.8	7.3	2.0	1.253648669
12		7.865	7.96		21.4	21.7		26400	32600		41.3	51		26.3	33.3	20.5	791.2	811.7	8.9	2.5	1.387728754
14		7.946	7.8		22.4	22.6		25800	32600		40.3	51		25.7	33.4	24.3	758.4	782.8	10.6	3.1	1.554282593
16		7.794	7.942		23.4	23.7		25300	32600		39.6	51.1		25.2	33.4	29.2	731.2	760.4	12.7	3.8	1.762928984

Table III. 13 *Second chemical first dose second trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery(%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.936			22.7			32400			50.7			33.1								
6		7.815	7.913		23.9	23.1		28400	32500		44.4	50.7		28.6	32.2	12.0	839.2	851.2	5.2	1.4	-0.130158177
8		7.818	7.916		24.7	24.1		27900	32500		43.5	50.7		28	33.3	14.5	783.7	798.2	6.3	1.8	-0.050719447
10		7.8	7.9		25.1	25.4		27200	32500		42.5	50.7		27.3	33.4	19.9	791.8	811.6	8.6	2.4	0.09162255
12		7.79	7.89		25.8	26.3		26600	32500		41.6	50.7		26.7	33.4	24.0	762.2	786.1	10.4	3.0	0.24630555
14		7.744	7.884		26.8	27.2		26000	32400		40.7	50.7		26.1	33.4	29.0	736.7	765.7	12.6	3.8	0.747188169
16		7.733	7.813		26.9	28.1		25600	32600		40	50.9		25.6	33.5	32.4	745.9	778.3	14.1	4.2	0.282507542

Table III. 14 *Second chemical first dose third trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.86			27.4			32400			50.6			33.3								
6		7.804	7.869		27.2	27.5		29000	32300		45.3	50.5		29.4	33.2	9.7	684.0	693.7	4.2	1.4	0.450965424
8		7.777	7.847		27.6	27.9		28200	32300		44	50.6		28.5	33.4	14.9	633.8	648.7	6.5	2.3	0.598880258
10		7.756	7.846		27.8	28.2		27400	32400		42.9	50.7		27.7	33.4	19.5	617.1	636.6	8.5	3.1	0.472218444
12		7.749	7.805		27.8	28.7		27000	32400		42.1	50.7		27.2	33.4	23.3	605.7	629.0	10.1	3.7	0.618028548
14		7.778	7.8		28	28.7		26400	32500		41.2	50.8		26.5	33.5	28.0	575.4	603.4	12.2	4.6	0.564195732
16		7.696	7.795		28.2	29.3		25800	32600		40.4	51		25.9	33.7	31.0	559.0	590.0	13.5	5.2	0.484508021

Table III. 15 *Second chemical second dose first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature(°C)			TDS(ppm)			Conductivity(mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance erro
	Feed	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Per.**	**Ret.**	**Feed**			
Atmospheric pressure	7.914			18.1			32500			50.8			33								
6		7.791	7.836		21	20.2	32500	28500	32600	50.8	44.5	50.8	33	28.6	33.4	10.1	742.3	752.3	4.4	1.3	-0.138821756
8		7.766	7.857		22.1	21.9	32500	27900	32500	50.8	43.7	50.8	33	28	33.1	13.5	741.8	755.2	5.9	1.8	0.252314021
10		7.725	7.818		22.7	23.1	32500	27300	32600	50.8	42.6	50.9	33	27.3	33.3	17.6	689.2	706.9	7.7	2.5	0.099434906
12		7.695	7.83		23.6	24	32500	26700	32600	50.8	41.7	50.9	33	26.7	33.3	21.8	677.1	698.9	9.5	3.1	0.258561425
14		7.679	7.777		24.3	24.9	32500	26200	32600	50.8	40.9	50.9	33	26.2	33.4	25.1	672.9	698.0	10.9	3.6	0.400410164
16		7.666	7.8		24.5	25.2	32500	25800	32600	50.8	40.3	50.9	33	25.7	33.5	29.3	637.5	666.9	12.7	4.4	0.612349544

Table III. 16 *Second chemical second dose second trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature(°C)			TDS(ppm)			Conductivity(mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance erro
	Feed	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Per.**	**Ret.**	**Feed**			
Atmospheric pressure	7.795			24.8			32100			49.8			32.6								
6		7.74	7.792		24.9	25.2	32100	28800	32400	49.8	45.1	50.6	32.6	29.2	33.2	10.6	718.1	728.7	4.6	1.5	-0.770809805
8		7.758	7.78		25.4	25.5	32100	28100	32400	49.8	43.9	50.6	32.6	28.2	33.2	14.8	702.7	717.4	6.4	2.1	-0.658833841
10		7.667	7.762		25.9	26.6	32100	27400	32500	49.8	42.8	50.7	32.6	27.6	33.4	18.8	686.1	704.9	8.2	2.7	-0.822996203
12		7.665	7.753		25.8	27	32100	26900	32500	49.8	42	50.8	32.6	27	33.5	22.7	670.0	692.7	9.9	3.3	-0.674657525
14		7.635	7.745		27	27.8	32100	26400	32600	49.8	41.2	50.9	32.6	26.5	33.5	26.7	659.3	686.1	11.6	3.9	-0.805578981
16		7.597	7.747		27.5	28.7	32100	26100	32600	49.8	40.8	50.9	32.6	26.2	33.6	29.3	651.0	680.2	12.7	4.3	-0.686861826

Table III. 17 *Second chemical second dose third trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	**pH**			**Temparature (°C)**			**TDS (ppm)**			**Conductivity (mS/cm)**			**Salinity (g/l)**			**Flow Rate (L/h)**			Flux (L/m^2h)	Recovery (%)	Mass balance erro
	Feed	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Per.**	**Ret.**	**Feed**			
Atmospheric pressure	7.725			27.6			32300			50.5			33.2								
6		7.701	7.742		27	27.7	32300	29000	32300		45.5	50.4		29.5	33.2	10.0	705.4	715.4	4.4	1.4	0.143146815
8		7.655	7.745		27.4	28.5	32300	28200	32400		44	50.6		28.5	33.4	14.7	665.8	680.6	6.4	2.2	-0.028503834
10		7.637	7.704		27.6	28.8	32300	27700	32400		43.2	50.7		28	33.4	18.3	664.2	682.5	8.0	2.7	0.081116228
12		7.628	7.703		27.4	29.1	32300	27000	32500		42.2	50.8		27.2	33.5	23.7	661.8	685.4	10.3	3.5	-0.031456083
14		7.63	7.702		27.5	29.3	32300	26700	32600		41.6	50.8		26.9	33.6	25.8	655.7	681.6	11.2	3.8	-0.236191328
16		7.572	7.692		27.6	29.7	32300	26300	32600		41	51		26.4	33.7	27.6	653.0	680.6	12.0	4.1	-0.137585401

Table III. 18 *Second chemical third dose first trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	**pH**			**Temparature (°C)**			**TDS(ppm)**			**Conductivity (mS/cm)**			**Salinity (g/l0**			**Flow Rate (L/h)**			Flux (L/m^2h)	Recovery (%)	Mass balance error (%
	Feed	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Feed**	**Per.**	**Ret.**	**Per.**	**Ret.**	**Feed**			
Atmospheric pressure	7.9			18.4			32600			51			33.1								
6		7.75	7.856		20.7	20.5		29000	32600		45.2	50.9		29.1	33.3	9.0	689.7	698.6	3.9	1.3	0.141474292
8		7.749	7.828		21.5	21.4		28100	32600		43.9	50.9		28.2	33.3	12.2	686.6	698.7	5.3	1.7	0.24004942
10		7.709	7.81		22.3	22.4		27300	32600		42.7	50.9		27.3	33.3	16.9	664.2	681.1	7.3	2.5	0.402567072
12		7.68	7.8		23	23.2		26800	32600		41.9	50.9		26.9	33.4	19.8	648.3	668.1	8.6	3.0	0.527166983
14		7.707	7.785		23.8	24		26500	32600		41.4	51		26.5	33.4	22.5	618.6	641.1	9.8	3.5	0.657275825
16		7.642	7.775		24.1	24.8		26000	32700		40.6	51		25.9	33.5	27.0	616.8	643.8	11.7	4.2	0.554365406

Table III. 19 *Second chemical third dose second trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m²h)	Recovery (%)	Mass balance error (%
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.762			24.3			32400			50.7			33.2								
6		7.701	7.76		24.5	24.8		28900	32400		45.1	50.6		29.2	33.2	9.8	715.2	725.0	4.3	1.4	0.146227955
8		7.704	7.755		24.9	25.5		28300	32400		44.2	50.6		28.5	33.3	13.1	685.7	698.8	5.7	1.9	0.236775237
10		7.674	7.776		25.5	26		27500	32400		43	50.6		27.7	33.3	18.0	678.4	696.4	7.8	2.6	0.390396666
12		7.628	7.741		26	26.7		27000	32500		42.2	50.8		27.2	33.4	21.4	661.0	682.3	9.3	3.1	0.22330138
14		7.625	7.74		26.4	27.1		26500	32600		41.4	50.9		26.6	33.5	25.4	660.1	685.5	11.0	3.7	0.080113019
16		7.615	7.739		26.5	27.2		26100	32600		40.8	50.9		26.2	33.5	27.8	653.0	680.7	12.1	4.1	0.2015419

Table III. 20 *Second chemical third dose third trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m²h)	Recovery (%)	Mass balance error (%
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	7.725			26.7			32400			50.6			33.3								
6		7.677	7.733		26.4	27.1		28900	32400		45.1	50.6		29.3	33.3	11.3	711.9	723.2	4.9	1.6	0.168738178
8		7.642	7.729		26.7	27.5		28200	32400		44.1	50.6		28.5	33.3	14.5	710.5	725.1	6.3	2.0	0.260080566
10		7.62	7.717		27.7	27.9		27600	32400		43.1	50.7		27.9	33.4	18.2	672.5	690.6	7.9	2.6	0.389620944
12		7.591	7.714		27.6	28.3		26600	32500		41.6	50.8		26.8	33.5	22.4	670.8	693.2	9.8	3.2	0.280425761
14		7.588	7.714		27.8	28.9		26600	32500		41.6	50.8		26.8	33.5	25.2	674.6	699.7	10.9	3.6	0.346342463
16		7.588	7.588		27.9	29.1		26200	32600		40.9	50.9		26.2	33.6	29.5	669.6	699.0	12.8	4.2	0.214984377

Table III. 21 *Second chemical first dose first high pH trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	10.544			20.3			29800			46.6			29.8								
9		10.422	10.444		21.6	21.5		25400	28100		40	44.5		25.3	28.4	36.4	1069.3	1105.7	15.8	3.3	6.002776381
12		10.385	10.405		22.8	22.6		25100	28700		39.5	44.8		25.1	29	48.7	1026.6	1075.3	21.2	4.5	4.238546067
14		10.324	10.364		23.8	24.2		25100	28800		39.1	45.1		25	29.1	58.7	1000.0	1058.7	25.5	5.5	4.043718858

Table III. 22 *Second chemical first dose second high pH trial temperature, pH, salinity, TDS, conductivity, flow rate, flux, recovery and mass balance error.*

Pressure (bar)	pH			Temparature (°C)			TDS (ppm)			Conductivity (mS/cm)			Salinity (g/l)			Flow Rate (L/h)			Flux (L/m^{2}h)	Recovery (%)	Mass balance error
	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Feed	Per.	Ret.	Per.	Ret.	Feed			
Atmospheric pressure	11.237			20.2			30800			48.3			31								
9		11.143	11.147		21.7	21.6		28000	30800		44	48		28.2	31.1	36.3	1057.8	1094.1	15.8	3.3	0.301936117
12		11.048	11.042		23.3	23.3		28000	32500		43.6	50.8		28.2	33.3	48.0	1033.5	1081.5	20.9	4.4	-4.870750664
14		10.992	10.977		24.5	24.4		28000	32500		43.8	50.8		28.2	33.3	53.1	1020.8	1073.9	23.1	4.9	-4.797086267

Appendix IV Ionic chromatography results

Table IV. 1 *Concentration of sodium, calcium, magnesium, chloride and sulfate at different pressures regarding normal seawater first trial.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	9318.549	8293.9015	9393.7011	1129.889	186.83674	1131.46594	308.7796	172.656779	315.815769	16730.88	13423.061	16782.0227	2392.411	4.17940608	2468.83488
8	9318.549	8066.3568	9302.1961	1129.889	188.01925	1188.62064	308.7796	158.313817	306.07338	16730.88	13105.2474	16878.4627	2392.411	2.98529006	2533.9142
10	9318.549	7671.1108	9413.533	1129.889	136.97419	1196.50405	308.7796	127.733542	316.357013	16730.88	12443.6835	17042.4838	2392.411	1.19411602	2582.2759
12	9318.549	7450.1767	9435.8003	1129.889	135.59459	1215.22714	308.7796	126.10981	301.472808	16730.88	12282.9502	17089.2426	2392.411	2.98529006	2623.4729
14	9318.549	7217.0651	9509.561	1129.889	104.84931	1223.89889	308.7796	118.261775	313.650794	16730.88	11788.3298	17260.5697	2392.411	10.7470442	2705.86691
16	9318.549	7027.7924	9653.951	1129.889	102.48429	1285.19237	308.7796	108.248764	340.712985	16730.88	11522.3892	17499.1126	2392.411	1.19411602	2796.02267

Table IV. 2 *Concentration of sodium, calcium, magnesium, chloride and sulfate at different pressures regarding normal seawater second trial.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	9261.141	8292.5098	9290.0186	1099.341	232.36341	1166.5471	302.0141	178.339839	314.462659	16581.47	13737.587	16729.0538	9261.141	8292.50978	9290.01862
8	9261.141	8011.0362	9372.4775	1099.341	194.12889	1173.44508	302.0141	151.007026	310.403331	16581.47	13275.1133	16808.3245	9261.141	8011.03624	9372.47749
10	9261.141	7645.3642	9447.9778	1099.341	171.85827	1220.15427	302.0141	136.393443	320.416341	16581.47	12746.8851	16911.34	9261.141	7645.36419	9447.97781
12	9261.141	7324.2269	9721.7969	1099.341	139.93047	1233.95023	302.0141	114.202446	361.009628	16581.47	12157.6512	17404.8644	9261.141	7324.22688	9721.79694
14	9261.141	7491.5801	9624.7251	1099.341	139.33921	1280.65941	302.0141	145.323966	340.171741	16581.47	11818.65	17355.1832	9261.141	7491.58012	9624.72511
16	9261.141	7188.1871	9548.181	1099.341	124.952	1262.33049	302.0141	110.413739	326.911267	16581.47	11682.392	17300.7531	9261.141	7188.18713	9548.181

Table IV. 3 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with first dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10529.13	9436.6366	10377.137	1298.045	212.0169	1282.5215	363.4375	193.1957	376.18964	19527.46	15558.896	19164.778	2781.059	78.863973	2793.6774	61.79846	3.635203	56.345654
8	10529.13	9334.8494	10635.731	1298.045	199.04496	1289.1138	363.4375	200.2094	386.7102	19527.46	15139.193	19301.317	2781.059	78.863973	2846.67399	61.79846	5.452805	56.345654
10	10529.13	9038.4285	10805.95	1298.045	158.42788	1360.5658	363.4375	181.08112	429.43004	19527.46	14719.489	19134.134	2781.059	71.293032	2853.61402	61.79846	5.452805	61.7984593
12	10529.13	8275.0245	10553.889	1298.045	160.34177	1353.3356	363.4375	162.90924	394.68032	19527.46	14233.844	19353.683	2781.059	66.876649	2895.25419	61.79846	7.270407	43.6224418
14	10529.13	8647.098	10651.893	1298.045	119.72469	1351.6343	363.4375	137.40486	386.39139	19527.46	13953.395	19411.867	2781.059	66.876649	2979.79637	61.79846	3.635203	50.8928488
16	10529.13	8575.9157	10913.239	1298.045	134.18522	1413.0916	363.4375	163.86566	424.64797	19527.46	13718.718	19473.543	2781.059	57.412973	3026.48385	61.79846	1.817602	54.5280523

Table IV. 4 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with first dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10573.83	9341.7269	10519.157	1231.91	248.59354	1263.1699	376.8273	193.5145	373.6392	18871.53	16017.002	19032.117	2693.993	76.340326	2815.75931	45.44004	5.452805	45.4400436
8	10573.83	9302.525	10589.308	1231.91	219.24717	1263.3826	376.8273	196.70255	382.24693	18871.53	15645.785	19096.508	2693.993	73.816679	2842.88852	45.44004	5.452805	50.8928488
10	10573.83	9109.2669	10651.549	1231.91	181.60726	1310.1666	376.8273	182.67514	397.23076	18871.53	15052.304	19164.778	2693.993	58.674796	2895.88511	45.44004	3.635203	47.2576453
12	10573.83	8896.064	10271.911	1231.91	160.12912	1260.1927	376.8273	170.87936	376.50845	18871.53	14607.388	18587.588	2693.993	73.816679	2823.96116	45.44004	3.635203	49.0752471
14	10573.83	8599.6431	10581.055	1231.91	149.07106	1352.9103	376.8273	147.28781	415.40263	18871.53	14274.961	19390.145	2693.993	68.138473	2991.7837	45.44004	1.817602	52.7104506
16	10573.83	8775.7075	10886.76	1231.91	146.09389	1336.3232	376.8273	158.12717	398.82478	18871.53	13912.278	19531.727	2693.993	61.198443	3056.1367	45.44004	3.635203	49.0752471

Table IV. 5 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with first dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10309.63	9475.4945	10727.202	1190.415	283.46894	1281.8835	363.4375	167.1531	392.6521	18859.12	15974.333	19065.864	2690.839	80.125797	2812.60475	52.71045	14.54081	49.0752471
8	10309.63	9234.4377	10633.324	1190.415	228.81664	1290.3897	363.4375	172.83	356.69842	18859.12	15581.006	19110.084	2690.839	75.709415	2862.44678	52.71045	1.817602	54.5280523
10	10309.63	9103.0771	10358.223	1190.415	202.87274	1328.8803	363.4375	134.66863	354.49073	18859.12	15090.706	19165.165	2690.839	72.554856	2903.45605	52.71045	1.817602	50.8928488
12	10309.63	8853.4234	10669.431	1190.415	163.74425	1306.7642	363.4375	185.12995	348.81384	18859.12	14583.338	19321.1	2690.839	87.065827	2924.27614	52.71045	3.635203	52.7104506
14	10309.63	8909.4751	10750.586	1190.415	155.87602	1316.3336	363.4375	140.34553	368.99836	18859.12	15327.322	19372.302	2690.839	88.958562	3075.69497	52.71045	3.635203	47.2576453
16	10309.63	8680.7978	10878.851	1190.415	159.2785	1364.3936	363.4375	147.91473	355.75227	18859.12	14011.967	19545.691	2690.839	76.340326	3072.54041	52.71045	3.635203	50.8928488

Table IV. 6 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with second dose of first chemical.*

Pressure	Na^+			Mg^{2+}			Ca^{2+}			Cl^-			SO_4^{2-}			PO_4^{3-}		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10204.59	7526.2663	8848.2903	1179.603	150.68337	1027.7956	452.4724	205.58677	388.93569	17909.28	11703.378	15238.725	2536.772	11.310849	2235.77774	97.51216	21.66937	72.7471652
8	10204.59	8449.8134	10272.758	1179.603	199.03699	1209.1216	452.4724	234.63215	466.54129	17909.28	14345.902	17958.167	2536.772	13.19599	2631.02906	97.51216	27.86062	100.607782
10	10204.59	8726.7607	9970.8811	1179.603	193.69561	1215.3064	452.4724	226.0093	442.94192	17909.28	14071.658	12384.856	2536.772	13.824371	1422.02502	97.51216	12.3825	55.7212329
12	10204.59	8349.7073	10052.29	1179.603	163.05291	1215.5875	452.4724	184.71041	436.13441	17909.28	13719.058	13709.712	2536.772	14.452751	1577.235	97.51216	6.191248	52.6256089
14	10204.59	8349.3178	10363.515	1179.603	169.23767	1247.6359	452.4724	201.04843	539.15472	17909.28	13341.297	18353.539	2536.772	13.824371	2732.8267	97.51216	13.93031	85.1296614
16	10204.59	9666.6676	10345.597	1179.603	293.49523	1268.158	452.4724	247.3395	453.3801	17909.28	12352.507	18386.607	2536.772	7.5405657	2784.98228	97.51216	12.3825	89.7730975
18	10204.59	9490.9949	10149.28	1179.603	269.03729	1262.5355	452.4724	253.23934	433.41141	17909.28	15898.637	18230.974	2536.772	8.7973267	2825.19863	97.51216	12.3825	82.0340374

Table IV. 7 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with second dose of first chemical (second IC trial).*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10796.98	8350.8198	9586.3922	1226.939	279.71828	1231.5511	399.316	242.73969	393.75713	19844.46	14137.293	17262.494	2786.388	9.8038272	2385.13111	74.2123	6.058147	66.6396171
8	10796.98	9568.9451	10814.431	1226.939	279.71828	1273.0641	399.316	241.8132	395.6101	19844.46	16289.12	19655.968	2786.388	14.705741	2855.01454	74.2123	6.058147	72.6977641
10	10796.98	9179.5574	11096.757	1226.939	252.04297	1312.6002	399.316	236.25428	411.36038	19844.46	15411.877	20100.433	2786.388	14.705741	2894.22985	74.2123	3.029074	72.6977641
12	10796.98	9012.2238	10946.474	1226.939	208.22373	1296.1269	399.316	217.72453	418.77228	19844.46	14932.353	19870.849	2786.388	14.705741	2937.6468	74.2123	1.514537	75.7268376
14	10796.98	9004.2933	11166.942	1226.939	208.22373	1335.3335	399.316	214.01858	420.62526	19844.46	14917.651	20218.052	2786.388	14.705741	2951.65227	74.2123	3.029074	75.7268376
16	10796.98	8925.7813	11526.193	1226.939	195.04502	1338.6282	399.316	208.45965	422.47823	19844.46	14832.829	20834.421	2786.388	14.705741	2997.87031	74.2123	3.029074	75.7268376
18	10796.98	8898.8176	11038.864	1226.939	203.61118	1346.206	399.316	201.97424	424.33121	19844.46	14777.413	20144.163	2786.388	14.705741	3013.27633	74.2123	1.514537	75.7268376

Table IV. 8 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with second dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
8	11100.87	10113.445	10970.384	1253.258	320.76442	1282.2143	501.4865	270.93886	491.04832	19875.72	12255.461	19931.074	2690.097	8.1689462	2846.56356	80.48623	13.93031	83.5818494
10	11100.87	9312.2062	11312.381	1253.258	280.28232	1352.4957	501.4865	258.23151	478.7948	19875.72	15654.584	20300.927	2690.097	11.310849	2954.01663	80.48623	9.286872	83.5818494
12	11100.87	9135.7546	11289.789	1253.258	233.33433	1338.1583	501.4865	243.25499	501.4865	19875.72	11482.688	19957.672	2690.097	10.054088	2932.02331	80.48623	9.286872	82.0340374
14	11100.87	8616.1376	11231.751	1253.258	221.24592	1364.0219	501.4865	238.71665	468.35662	19875.72	14551.855	20076.643	2690.097	13.19599	3042.61827	80.48623	10.83468	83.5818494
16	11100.87	9207.4259	10845.349	1253.258	196.78799	1331.9736	501.4865	224.19397	476.52564	19875.72	14144.262	19492.211	2690.097	12.56761	2927.62465	80.48623	17.02593	83.5818494
18	11100.87	8543.2977	10959.088	1253.258	215.62341	1309.4835	501.4865	234.63215	501.4865	19875.72	14277.611	19596.446	2690.097	13.19599	3028.16552	80.48623	23.21718	88.2252855

Table IV. 9 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with second dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
8	10686.04	9897.2622	10515.427	1211.09	396.94949	1212.7763	445.6649	278.65404	444.75726	18987.57	16848.249	18516.361	2649.252	9.4257072	2676.90084	77.3906	17.02593	80.4862253
10	10686.04	9550.9807	2066.0033	1211.09	336.22634	1307.5156	445.6649	263.67752	471.53346	18987.57	16127.593	19507.307	2649.252	10.054088	2889.29344	77.3906	15.47812	80.4862253
12	10686.04	9395.563	12699.454	1211.09	299.67999	1312.857	445.6649	247.79333	484.24081	18987.57	16097.032	16305.511	2649.252	9.4257072	1727.41793	77.3906	9.286872	54.1734209
14	10686.04	9117.0577	10948.571	1211.09	280.84457	1317.355	445.6649	240.07815	506.93251	18987.57	15349.788	19414.934	2649.252	12.56761	2915.05704	77.3906	12.3825	83.5818494
16	10686.04	9154.4514	7223.6108	1211.09	280.84457	782.37282	445.6649	223.74013	292.72289	18987.57	14601.816	19450.517	2649.252	11.939229	2949.61796	77.3906	12.3825	82.0340374
18	10686.04	9075.7688	11093.472	1211.09	246.54724	1364.303	445.6649	216.47879	466.99512	18987.57	14778.655	19762.862	2649.252	13.19599	3008.68573	77.3906	20.12156	82.0340374

Table IV. 10 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with third dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10725.77	10162.913	11022.19	1232.736	385.14221	1247.0736	442.9419	258.23151	477.4333	19109.78	17125.01	19415.653	2580.13	8.7973267	2694.49549	77.3906	4.643436	78.9384133
8	10725.77	9838.8345	10131.362	1232.736	362.37103	1252.9772	442.9419	233.27064	392.11252	19109.78	16866.58	18447.71	2580.13	10.682468	2712.71852	77.3906	4.643436	77.3906013
10	10725.77	9749.2454	10369.358	1232.736	303.33463	1274.905	442.9419	220.56329	415.25805	19109.78	16468.332	18565.243	2580.13	11.310849	2746.02269	77.3906	3.095624	78.9384133
12	10725.77	9435.6834	10154.344	1232.736	275.50318	1275.7484	442.9419	205.58677	389.84335	19109.78	15917.327	18531.097	2580.13	12.56761	2750.42135	77.3906	3.095624	78.9384133
14	10725.77	9549.0331	10666.95	1232.736	269.59955	1293.1782	442.9419	208.76361	423.42706	19109.78	15791.527	18890.886	2580.13	13.19599	2784.3539	77.3906	3.095624	78.9384133
16	10725.77	9273.2544	10857.424	1232.736	267.06941	1294.0216	442.9419	199.2331	402.5507	19109.78	15697.716	19038.611	2580.13	15.081131	2816.4013	77.3906	3.095624	80.4862253

Table IV. 11 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with third dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10897.93	10270.81	11276.545	1247.636	506.58851	1321.853	413.8966	266.85436	429.32691	19407.75	17828.413	20039.622	2637.941	9.4257072	2854.73251	72.74717	6.191248	74.2949772
8	10897.93	10172.651	11482.6	1247.636	423.09418	1349.6845	413.8966	261.40835	428.87307	19407.75	17750.776	20395.098	2637.941	11.939229	2882.38125	72.74717	9.286872	75.8427893
10	10897.93	9738.7284	11295.632	1247.636	393.29485	1364.0219	413.8966	225.10163	473.80263	19407.75	16840.342	20117.259	2637.941	13.824371	2895.57724	72.74717	1.547812	78.9384133
12	10897.93	9628.8843	11324.456	1247.636	340.72435	1387.9176	413.8966	233.72448	466.08745	19407.75	16346.845	20296.255	2637.941	14.452751	2958.41529	72.74717	3.095624	80.4862253
14	10897.93	9287.6666	11407.034	1247.636	309.51939	1401.1305	413.8966	205.13294	452.92627	19407.75	15905.107	20314.586	2637.941	15.081131	2998.00326	72.74717	1.547812	80.4862253
16	10897.93	9576.6889	11294.853	1247.636	312.04953	1403.3795	413.8966	228.27847	480.61014	19407.75	16237.219	20472.734	2637.941	14.452751	3085.34815	72.74717	4.643436	85.1296614

Table IV. 12 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with third dose of first chemical (second IC trial).*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11356.88	10976.213	11145.529	1216.725	439.83969	1217.384	423.4047	374.30089	399.31605	19240.53	16868.168	19259.38	2623.224	18.207108	2689.75003	127.2211	106.0176	124.192014
8	11356.88	10321.55	11555.536	1216.725	394.04365	1236.4932	423.4047	363.18304	400.24254	19240.53	16782.97	19492.357	2623.224	18.207108	2780.78557	127.2211	83.29952	124.192014
10	11356.88	9211.2794	11609.86	1216.725	338.69304	1243.0825	423.4047	292.77	427.11067	19240.53	15883.485	18874.479	2623.224	18.207108	2787.7883	127.2211	3.029074	125.70655
12	11356.88	9490.0366	11553.95	1216.725	327.82059	1250.0013	423.4047	288.13757	429.89013	19240.53	15871.421	19528.547	2623.224	16.806561	2820.00087	127.2211	57.5524	122.677477
14	11356.88	9466.6416	11312.07	1216.725	276.4236	1266.1453	423.4047	241.8132	432.66959	19240.53	15443.544	19537.972	2623.224	16.806561	2891.42876	127.2211	49.97971	125.70655
16	11356.88	8788.5836	11371.152	1216.725	267.85743	1282.2892	423.4047	226.06291	435.44906	19240.53	14817.75	19550.412	2623.224	16.806561	2892.12903	127.2211	3.029074	127.221087

Table IV. 13 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with third dose of first chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10991.42	10552.431	7608.4546	1290.648	597.67324	762.41289	436.5882	304.06874	258.68534	15058.29	18470.354	19799.523	1585.404	7.5405657	2788.12418	58.81686	9.286872	83.5818494
8	10991.42	10064.755	11187.735	1290.648	453.73688	1340.6885	436.5882	294.99206	436.58825	15058.29	17454.966	19909.868	1585.404	11.939229	2877.35421	58.81686	35.59968	85.1296614
10	10991.42	9709.5145	11718.648	1290.648	373.61605	1351.3712	436.5882	252.33167	498.7635	15058.29	16582.631	21250.18	1585.404	12.56761	2911.28675	58.81686	4.643436	82.0340374
12	10991.42	9542.8008	11076.723	1290.648	354.21838	1365.7086	436.5882	236.44748	450.6571	15058.29	16340.735	19817.135	1585.404	12.56761	2931.39493	58.81686	4.643436	86.6774734
14	10991.42	9534.2314	11201.758	1290.648	316.26641	1366.8331	436.5882	217.84029	441.58042	15058.29	16127.593	19845.171	1585.404	13.824371	2932.65169	58.81686	1.547812	82.0340374
16	10991.42	6393.9375	2196.4919	1290.648	184.98071	1394.6646	436.5882	148.85753	460.64145	15058.29	15859.819	20093.177	1585.404	14.452751	2942.70578	58.81686	51.0778	82.0340374

Table IV. 14 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with third dose of first chemical (second IC trial).*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11272.42	10628.064	10709.748	1226.28	512.32264	1222.326	401.169	355.77114	378.93333	19167.02	17720.153	18680.709	2663.14	17.506834	2749.27326	81.78498	80.27045	69.6686906
8	11272.42	10345.341	10639.96	1226.28	427.64938	1241.7646	401.169	349.28573	379.85981	19167.02	16817.652	18755.729	2663.14	17.506834	2758.37682	81.78498	65.12508	77.2413743
10	11272.42	10131.614	10788.26	1226.28	367.02728	1260.2148	401.169	267.75485	382.63928	19167.02	16601.64	19133.845	2663.14	17.506834	2789.18885	81.78498	56.03786	81.7849846
12	11272.42	9351.6493	10719.265	1226.28	324.85538	1293.8206	401.169	249.2251	386.34523	19167.02	16186.203	19063.726	2663.14	17.506834	2817.90005	81.78498	127.2211	81.7849846
14	11272.42	9151.4041	11871.17	1226.28	303.1105	1324.4611	401.169	239.96022	390.97766	19167.02	15815.628	20278.746	2663.14	17.506834	2841.70935	81.78498	6.058147	81.7849846
16	11272.42	9076.4609	11904.478	1226.28	281.03615	1340.9345	401.169	217.72453	391.90415	19167.02	15558.147	20397.119	2663.14	17.506834	2932.04461	81.78498	4.54361	84.8140581

Table IV. 15 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with first dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11035.43	9834.1603	11348.606	1260.287	379.23857	1334.7848	440.6728	255.50851	452.47244	19533.91	16599.524	20189.864	2664.962	15.081131	2817.02968	66.55592	1.547812	68.1037291
8	11035.43	9904.2735	11364.966	1260.287	358.71639	1340.1262	440.6728	255.50851	442.48809	19533.91	12988.338	20316.023	2664.962	10.682468	2908.14485	66.55592	4.643436	65.0081051
10	11035.43	9787.0286	11223.571	1260.287	351.68825	1357.2749	440.6728	290.45372	439.76509	19533.91	16452.158	19946.17	2664.962	13.19599	2871.69878	66.55592	69.65154	68.1037291
12	11035.43	9128.7432	11331.078	1260.287	282.53133	1383.4196	440.6728	218.74796	489.68682	19533.91	11848.587	20064.423	2664.962	11.310849	2886.77992	66.55592	18.57374	83.5818494
14	11035.43	9082.7801	11524.279	1260.287	293.77636	1406.753	440.6728	216.02495	498.30966	19533.91	15230.098	20542.464	2664.962	13.19599	3019.3682	66.55592	23.21718	86.6774734
16	11035.43	8343.475	12348.888	1260.287	278.03332	1463.5404	440.6728	169.28006	428.87307	19533.91	13902.726	22226.39	2664.962	13.19599	3110.48337	66.55592	1.547812	71.1993532

Table IV. 16 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with first dose of second chemical (second IC trial).*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11585.28	10583.256	11945.32	1330.392	495.1903	1363.6678	392.8306	294.62298	389.12469	21113.01	18489.578	21771.982	2988.066	14.005467	2986.66594	62.09601	6.058147	63.6105436
8	11585.28	10244.227	12156.272	1330.392	433.90927	1392.3315	392.8306	289.06405	391.90415	21113.01	17891.304	21996.664	2988.066	15.406014	2987.36621	62.09601	4.54361	65.1250803
10	11585.28	9947.6267	11557.519	1330.392	362.41473	1399.2503	392.8306	266.82836	397.46307	21113.01	17245.153	20868.727	2988.066	15.406014	3015.37715	62.09601	4.54361	65.1250803
12	11585.28	9927.8004	11599.55	1330.392	334.73942	1421.9836	392.8306	250.15159	402.09551	21113.01	17244.399	21037.239	2988.066	15.406014	3028.68234	62.09601	3.029074	65.1250803
14	11585.28	9730.3309	11592.016	1330.392	325.51432	1439.1159	392.8306	244.59266	403.94849	21113.01	16850.073	21048.172	2988.066	15.406014	3106.41268	62.09601	3.029074	65.1250803
16	11585.28	9437.6953	88337.478	1330.392	291.24965	13142.805	392.8306	230.69535	1662.1183	21113.01	16293.267	164828.9	2988.066	15.406014	24374.4153	62.09601	3.029074	528.573326

Table IV. 17 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with first dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10672.01	9567.3405	10587.878	1250.728	422.2508	1322.4153	408.9044	248.701	410.26588	19063.41	16505.354	18979.306	2716.489	14.452751	2788.12418	65.00811	1.547812	65.0081051
8	10672.01	9660.8248	10779.131	1250.728	370.52367	1328.0378	408.9044	239.17049	440.21892	19063.41	16319.888	19229.468	2716.489	15.081131	2799.43503	65.00811	1.547812	69.6515412
10	10672.01	9537.3476	10814.967	1250.728	325.26243	1302.7365	408.9044	233.27064	431.59608	19063.41	16218.888	18861.413	2716.489	16.337892	2776.81333	65.00811	3.095624	66.5559171
12	10672.01	9367.9073	10223.289	1250.728	313.17403	1252.6961	408.9044	234.63215	421.15789	19063.41	15466.962	18094.75	2716.489	14.452751	2668.10351	65.00811	3.095624	65.0081051
14	10672.01	9383.0985	10726.156	1250.728	314.57966	1323.5398	408.9044	239.62432	481.06397	19063.41	15592.403	19073.117	2716.489	15.081131	2797.54989	65.00811	6.191248	66.5559171
16	10672.01	9765.2156	10479.202	1250.728	291.52735	1290.9292	408.9044	230.69535	414.80422	19063.41	16586.585	18561.289	2716.489	13.824371	2790.6377	65.00811	4.643436	66.5559171

Table IV. 18 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with first dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11266.42	9713.7482	10896.765	1297.676	603.90321	1326.6322	562.7541	300.69522	454.28777	20039.98	17123.257	17832.367	2807.604	14.797001	2424.29188	66.55592	3.104464	65.0081051
8	11266.42	9667.9303	11720.985	1297.676	534.8857	1399.4437	562.7541	288.04768	486.50998	20039.98	17065.824	20919.146	2807.604	17.487365	2866.04336	66.55592	3.104464	68.1037291
10	11266.42	9180.6611	10517.375	1297.676	419.09975	1296.8328	562.7541	249.78888	408.90438	20039.98	15789.231	18654.022	2807.604	18.159956	2696.38063	66.55592	1.552232	61.912481
12	11266.42	6381.7722	10832.884	1297.676	280.61067	1364.5841	562.7541	250.15159	511.01701	20039.98	15473.866	19192.807	2807.604	18.159956	2758.5903	66.55592	1.552232	198.119939
14	11266.42	8772.6641	8262.0657	1297.676	370.06099	887.23271	562.7541	243.46511	299.07657	20039.98	14863.771	19185.977	2807.604	16.814774	2879.86773	66.55592	1.552232	72.7471652
16	11266.42	9370.4779	10926.758	1297.676	629.55775	1381.4517	562.7541	260.22309	472.89496	20039.98	16703.343	19161.536	2807.604	16.142183	2902.48943	66.55592	3.104464	120.729338

Table IV. 19 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with first dose of second chemical (second IC trial).*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10978.59	67253.443	11440.544	1211.454	8508.8389	1253.296	386.3452	397.46307	390.97766	19875	124391.29	20671.187	2669.442	15122.403	2848.71208	62.09601	325.6254	62.0960068
8	10978.59	10053.102	11392.564	1211.454	497.49658	1290.1964	386.3452	1195.1687	392.83064	19875	17778.586	20702.854	2669.442	15.406014	2877.42329	62.09601	4.54361	63.6105436
10	10978.59	10457.161	11197.87	1211.454	432.92086	1297.4447	386.3452	296.47595	394.68361	19875	17745.788	20273.846	2669.442	15.406014	2910.33614	62.09601	4.54361	63.6105436
12	10978.59	9926.6108	16334.457	1211.454	397.33833	1900.371	386.3452	294.62298	402.09551	19875	17156.184	29778.377	2669.442	15.406014	4464.94303	62.09601	4.54361	99.9594256
14	10978.59	9889.734	11320.397	1211.454	349.89495	1316.2244	386.3452	280.72567	397.46307	19875	17115.847	20618.786	2669.442	15.406014	2963.55692	62.09601	4.54361	68.1541538
16	10978.59	9311.2038	11406.839	1211.454	314.31241	1331.3799	386.3452	274.24026	397.46307	19875	15775.667	20775.235	2669.442	15.406014	2981.06375	62.09601	1.514537	68.1541538

Table IV. 20 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with second dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10020.66	9436.2956	10274.835	1185.33	478.80898	1204.401	354.1311	283.30485	369.30811	18017.77	11274.387	12394.156	2729.374	10.761455	1427.91059	54.32812	4.656696	26.3879421
8	10020.66	9001.3897	9848.2927	1185.33	414.55912	1187.3736	354.1311	259.59072	360.45483	18017.77	15305.007	17720.971	2729.374	16.814774	2662.11498	54.32812	3.104464	55.880348
10	10020.66	8819.5728	10044.291	1185.33	532.16133	1220.5202	354.1311	233.34708	352.86631	18017.77	14657.081	17925.941	2729.374	7.3985005	2775.11026	54.32812	4.656696	54.3281161
12	10020.66	10800.286	10109.018	1185.33	565.98899	1228.6933	354.1311	288.68005	354.76344	18017.77	18820.106	18184.905	2729.374	10.088864	2834.29826	54.32812	9.313391	51.2236523
14	10020.66	10549.379	9951.9283	1185.33	551.23195	1210.3038	354.1311	278.87821	356.34438	18017.77	18236.836	12268.629	2729.374	11.434046	1626.99751	54.32812	3.104464	26.3879421
16	10020.66	10176.29	10234.835	1185.33	475.40351	1473.6601	354.1311	272.23826	368.04336	18017.77	12059.532	19103.832	2729.374	10.088864	2964.10832	54.32812	3.104464	63.6415074

Table IV. 21 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with second dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11504.64	9210.1155	11306.464	1299.754	549.64274	1318.5977	398.3974	283.62104	407.8831	20750.13	16169.939	20193.337	2810.085	15.469592	2903.57513	55.88035	6.208928	58.9848118
8	11504.64	10394.107	11586.098	1299.754	600.27071	1366.5013	398.3974	309.2323	410.41261	20750.13	18236.148	14213.438	2810.085	11.434046	1522.07332	55.88035	4.656696	34.1491016
10	11504.64	9903.2014	10033.019	1299.754	515.36101	1207.8064	398.3974	281.09153	377.21282	20750.13	17174.499	17573.434	2810.085	13.451819	2641.26466	55.88035	4.656696	54.3281161
12	11504.64	10679.559	11623.553	1299.754	788.25261	1408.5021	398.3974	288.12415	435.07531	20750.13	19347.664	20952.689	2810.085	12.779228	3185.39074	55.88035	4.656696	62.0892756
14	11504.64	9191.2065	10698.105	1299.754	452.70038	1309.7435	398.3974	275.40014	383.53659	20750.13	15699.127	18966.612	2810.085	14.797001	2829.59013	55.88035	4.656696	58.9848118
16	11504.64	9215.9336	10991.921	1299.754	421.37006	1369.4527	398.3974	256.74502	389.22798	20750.13	15708.757	19763.45	2810.085	17.487365	2997.06527	55.88035	4.656696	62.0892756

Table IV. 22 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with second dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10655.92	10486.106	11212.646	1249.353	662.70431	1393.518	383.2204	338.95402	394.287	18983.81	16643.681	20674.467	2632.521	14.797001	2739.46294	58.98481	6.208928	58.9848118
8	10655.92	9434.4775	10287.926	1249.353	505.8257	1315.1922	383.2204	280.77534	385.43372	18983.81	16285.837	18462.44	2632.521	20.850319	2735.42739	58.98481	3.104464	60.5370437
10	10655.92	8686.1192	11216.283	1249.353	444.52725	1355.6038	383.2204	287.09911	396.50032	18983.81	14763.349	19962.23	2632.521	19.505138	2979.57791	58.98481	3.104464	63.6415074
12	10655.92	8576.3018	10942.467	1249.353	412.74287	1391.9288	383.2204	262.12022	417.36875	18983.81	14649.515	19804.375	2632.521	18.159956	2901.55736	58.98481	3.104464	65.1937393
14	10655.92	8900.6631	11414.827	1249.353	412.28881	1365.3661	383.2204	264.33354	428.11916	18983.81	15199.77	20272.78	2632.521	21.52291	2987.649	58.98481	3.104464	68.2982031
16	10655.92	8814.1183	11757.006	1249.353	405.02381	1408.7291	383.2204	255.79646	417.05257	18983.81	14923.267	21266.679	2632.521	20.177729	3018.58818	58.98481	3.104464	68.2982031

Table IV. 23 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first trial with third dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10305.38	10592.651	10145.381	1236.412	624.56306	1245.2666	371.2052	360.77102	362.66815	18385.4	18402.6	18104.087	2647.318	11.434046	2717.94003	76.05936	6.208928	69.850435
8	10305.38	10233.017	10221.381	1236.412	550.32383	1261.3858	371.2052	306.07042	379.74233	18385.4	17560.022	18159.456	2647.318	13.451819	2773.76508	76.05936	4.656696	68.2982031
10	10305.38	9631.2033	9987.2008	1236.412	467.68444	1242.9963	371.2052	300.69522	374.36712	18385.4	16462.262	18060.066	2647.318	15.469592	2654.71648	76.05936	6.208928	68.2982031
12	10305.38	9340.2963	9989.7462	1236.412	433.62975	1261.6128	371.2052	326.93886	368.99192	18385.4	15921.637	18048.029	2647.318	17.487365	2666.82312	76.05936	12.41786	68.2982031
14	10305.38	9295.933	10030.837	1236.412	419.55381	1275.2347	371.2052	298.79809	364.56528	18385.4	15736.269	18092.05	2647.318	18.159956	2670.18607	76.05936	1.552232	68.2982031
16	10305.38	9478.4772	11218.828	1236.412	414.55912	1392.8369	371.2052	266.23067	398.71364	18385.4	16101.845	20248.363	2647.318	20.177729	2907.61068	76.05936	3.104464	68.2982031

Table IV. 24 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second trial with third dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	11025.38	10053.382	10841.74	1292.262	645.904	1307.2461	412.6259	310.81325	403.77265	19374.49	17717.188	19418.165	2528.942	11.434046	2680.27494	62.08928	6.208928	68.2982031
8	11025.38	9209.0246	8312.6674	1292.262	496.29038	899.27091	412.6259	319.03415	292.7905	19374.49	16004.863	19585.993	2528.942	19.505138	2851.11304	62.08928	3.104464	68.2982031
10	11025.38	9862.838	10925.012	1292.262	518.76648	1339.0305	412.6259	318.40177	398.39745	19374.49	16875.642	19541.629	2528.942	14.12441	2701.12526	62.08928	7.761159	68.2982031
12	11025.38	9545.0221	10584.287	1292.262	470.86288	1300.6622	412.6259	282.67247	398.08126	19374.49	16319.54	18917.777	2528.942	18.159956	2752.91476	62.08928	3.104464	68.2982031
14	11025.38	9271.2059	11039.193	1292.262	436.58116	1375.1285	412.6259	270.65731	409.78023	19374.49	15841.506	19852.867	2528.942	18.832547	2836.31604	62.08928	3.104464	72.9548988
16	11025.38	9245.0243	10919.194	1292.262	420.46194	1361.2796	412.6259	274.13539	408.19929	19374.49	15664.736	19596.654	2528.942	20.177729	2791.92503	62.08928	3.104464	74.5071307

Table IV. 25 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with third dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10665.01	10154.472	10830.831	1269.105	658.16369	1309.5164	399.0298	330.41693	402.82409	19074.94	17640.153	19331.156	2695.745	8.7436824	2749.5518	77.61159	9.313391	79.1638263
8	10665.01	10262.108	10071.564	1269.105	613.66556	1252.9856	399.0298	310.81325	374.9995	19074.94	17945.2	17950.015	2695.745	12.779228	2783.18135	77.61159	6.208928	74.5071307
10	10665.01	9974.4736	11077.738	1269.105	538.74523	1374.4474	399.0298	301.95997	413.57449	19074.94	17330.634	19994.213	2695.745	15.469592	2921.73509	77.61159	4.656696	91.5816814
12	10665.01	9814.4747	10727.559	1269.105	503.55539	1336.3061	399.0298	294.05526	384.80134	19074.94	16882.52	19089.387	2695.745	18.159956	2920.38991	77.61159	6.208928	72.9548988
14	10665.01	9494.1134	10737.014	1269.105	471.54397	1321.7761	399.0298	284.25342	402.19171	19074.94	16251.79	13275.94	2695.745	18.159956	1686.8581	77.61159	3.104464	37.2535653
16	10665.01	9315.9329	10705.014	1269.105	441.12178	1349.0199	399.0298	282.98866	396.8165	19074.94	15844.601	19263.75	2695.745	18.159956	2968.14386	77.61159	4.656696	74.5071307

Table IV. 26 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding third trial with third dose of second chemical (second IC trial).*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	10620.93	10061.033	11190.337	1257.25	530.44337	1324.4611	419.6988	326.12355	425.2577	19023.39	17621.383	20198.072	2603.616	17.506834	2721.9626	75.72684	4.54361	75.7268376
8	10620.93	10148.665	11074.551	1257.25	478.71691	1326.1084	419.6988	318.71165	429.89013	19023.39	17332.613	20020.512	2603.616	17.506834	2719.86178	75.72684	3.029074	78.7559111
10	10620.93	9691.4714	11299.381	1257.25	405.90449	1332.0389	419.6988	281.65216	431.74311	19023.39	16603.902	20258.389	2603.616	16.806561	2748.57299	75.72684	3.029074	78.7559111
12	10620.93	9680.7652	11226.817	1257.25	383.50067	1343.8997	419.6988	275.16674	428.03716	19023.39	16563.565	20274.6	2603.616	16.106288	2835.40689	75.72684	1.514537	80.2704479
14	10620.93	9604.2359	10867.168	1257.25	366.36834	1354.1132	419.6988	272.38728	432.66959	19023.39	16520.966	19496.881	2603.616	16.106288	2836.10716	75.72684	1.514537	78.7559111
16	10620.93	9087.5636	11240.695	1257.25	328.809	1361.691	419.6988	248.29861	438.22852	19023.39	15629.774	20260.274	2603.616	16.106288	2784.28693	75.72684	1.514537	78.7559111

Table IV. 27 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding first high pH trial with first dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	12472.14	11725.699	9595.843	968.7947	721.0883	72.871438	310.7022	237.32603	227.00751	18203.63	17050.612	15244.588	2417.323	2408.9522	21.2497786	116.9442	82.17698	107.462208
8	12472.14	11883.87	9593.1159	968.7947	759.50115	42.93201	310.7022	242.29421	205.60613	18203.63	17136.718	15209.11	2417.323	2429.558	20.605846	116.9442	82.17698	79.0163292
10	12472.14	11934.516	9465.722	968.7947	780.11981	47.168721	310.7022	247.64456	189.17292	18203.63	17526.601	15168.089	2417.323	2548.6856	19.3179806	116.9442	83.75731	52.1507773

Table IV. 28 *Concentration of sodium, calcium, magnesium, chloride, sulfate and phosphate at different pressures regarding second high pH trial with first dose of second chemical.*

Pressure	Na^+ (ppm)			Mg^{2+} (ppm)			Ca^{2+} (ppm)			Cl^- (ppm)			SO_4^{2-} (ppm)			PO_4^{3-} (ppm)		
(bar)	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate	feed	Permeate	Retentate
6	12644	12756.927	10784.074	941.1148	943.65688	60.161303	306.1162	316.81688	203.69529	18034.74	18034.372	16961.548	2448.876	2458.535	22.537644	94.8196	80.59666	50.5704507
8	12644	12802.509	10781.347	941.1148	945.63401	38.977746	306.1162	317.96338	201.78445	18034.74	18056.176	16938.636	2448.876	2463.0425	21.2497786	94.8196	77.436	77.4360026
10	12644	12933.019	30114.842	941.1148	976.70323	1281.7465	306.1162	349.30112	1011.5974	18034.74	18232.824	51099.727	2448.876	2569.9354	3830.11162	94.8196	99.56057	66.3737165

Appendix V Rejection rates and mass balance error for ions

Table V. 1 *Ion rejection and mass balance error regarding first trial with third dose of first chemical*

Pressure (bar)	Rejection (%)						Mass balance error (%)					
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}
6	5.24768	68.7571	41.7008	10.3861	99.659	94	-2.6023	0.24498	-6.7903	-1.3592	-2.3364	-0.0668
8	8.26917	70.6043	47.3361	11.7385	99.586	94	5.60491	0.02894	12.3048	3.65591	-2.7168	2.17402
10	9.10445	75.3934	50.2049	13.8225	99.5616	96	3.49936	-1.0155	7.59143	3.18439	-3.1949	0.99079
12	12.0279	77.6511	53.5861	16.7059	99.5129	96	5.56807	-0.5768	13.4808	3.51913	-2.7913	1.51757
14	10.9711	78.13	52.8689	17.3642	99.4886	96	0.9753	-1.502	6.39083	1.80978	-3.5159	2.01416
16	13.5423	78.3352	55.0205	17.8551	99.4155	96	-0.5914	-1.3839	11.0956	1.1253	-4.4816	0.3065

Table V. 2 *Ion rejection and mass balance error regarding third trial with third dose of second chemical*

Pressure (bar)	Rejection (%)						Mass balance error (%)					
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}
6	5.271607	57.80922	22.29581	7.369902	99.3276	94	-5.19512	-4.35941	-0.95555	-5.96337	-2.92292	1.468311
8	4.446519	61.92348	24.06181	8.887876	99.3276	96	-4.09614	-4.12466	-1.89678	-4.95808	-2.38234	-1.99366
10	8.751167	67.71488	32.89183	12.71848	99.35449	96	-5.98976	-4.01133	-1.92925	-5.98679	-2.80812	-1.37006
12	8.851969	69.49686	34.43709	12.93052	99.38139	98	-5.2338	-4.42094	-0.80849	-5.94617	-5.39978	-2.63572
14	9.572522	70.85954	35.09934	13.15445	99.38139	98	-1.89076	-4.87856	-1.71687	-1.92633	-5.03374	-0.3312
16	14.43718	73.84696	40.83885	17.83917	99.38139	98	-4.9812	-4.84568	-2.5083	-5.47634	-2.45955	0.297626