

**EGE UNIVERSITY GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

(MASTER OF SCIENCE THESIS)

**REMOVAL OF BORON FROM GEOTHERMAL
WATERS BY REVERSE OSMOSIS METHOD**

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Department Code : 405.03.01

Date of Presentation : 22.07.2010

Bornova-İZMİR

2010

Sayın **Emre YAVUZ** tarafından **Yüksek Lisans** tezi olarak sunulan **“Removal of Boron From Geothermal Waters by Reverse Osmosis Method”** başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve **22/07/2010** tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET**JEOTERMAL SULARDAN TERS OZMOS YÖNTEMİ İLE BOR GİDERİMİ**

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Temmuz 2010, 134 sayfa

Artan nüfus ile birlikte endüstriyel ve tarımsal aktivitelerin gelişmesi nedeniyle dünyadaki ülkelerin çoğu su sıkıntısı çekmektedir. Tuzlu suların ters ozmos yöntemi ile tuzsuzlaştırılması bu soruna çözüm oluşturmaktadır. Ters ozmos yöntemi, deniz suyu veya az tuzlu suların tuzsuzlaştırılmasında kullanılan membran prosesler arasında en çok kullanılanıdır. Tuzsuzlaştırma işlemlerini sınırlayan (sulardaki bor içeriği gibi) bazı etkenler vardır. Jeotermal sular 5-100 mg/L derişim aralığında bor içermektedir. Sulama suyunda bor için izin verilen maksimum sınır değeri 0.5 mg/L'dir. Ters ozmos yöntemiyle gerçekleştirilen desalinasyon süreçlerinde bu sınır değere pek ulaşılamamaktadır.

Bu çalışmada, İzmir-Balçova jeotermal sahasında kurulmuş olan küçük ölçekte ters ozmos sisteminin desalinasyon ve bor giderim performansı incelenmiştir. Çalışmalarda işletme basıncı ve membran konfigürasyonunun sistem performansına olan etkisi araştırılmıştır.

Anahtar sözcükler: Bor, jeotermal su, ters ozmos, tuzsuzlaştırma.

ABSTRACT**REMOVAL OF BORON FROM GEOTHERMAL WATERS BY
REVERSE OSMOSIS METHOD**

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July, 2010, 134 pages

Worldwide many countries suffer from shortage of natural fresh water due to the increasing population along with the expansion of industrial and agricultural activities. Desalination by reverse osmosis provides a solution for this problem. Reverse osmosis is the most widely used membrane process for producing fresh water from brackish or seawater. There are some factors limiting desalination such as rejection of boron. Geothermal waters contains boron 5-100 mg/L of concentration levels. Concentration limit of boron for irrigation water is defined as 0.5 mg/L. It is not possible to reach this limit value in desalination processes using only reverse osmosis method.

In this study, desalination and boron removal performances of a small scale reverse osmosis system which was established in Izmir-Balçova geothermal area in Turkey were investigated. In our studies, the effect of such parameters as operating pressure, membrane configuration on system performance was investigated.

Key words: Boron, geothermal water, reverse osmosis, desalination.

TEŞEKKÜR

Bu çalışma Ulusal Bor Araştırma Enstitüsü (BOREN) tarafından (Proje No: 2008-G-0192) ve Ege Üniversitesi Rektörlüğü Bilimsel Araştırma Proje Saymanlığı (Proje No: 2008 FEN 040) tarafından desteklenmiştir.

Tez çalışmalarım süresince bana bütün olanakları sağlayan, değerli yorumları ve tavsiyeleri ile olaylara farklı bakış açısı kazandıran büyük desteğini gördüğüm saygıdeğer hocalarım Sayın Prof. Dr. Ümran Yüksel ve Sayın Prof. Dr. Nalan Kabay'a saygı ve minnettarlığımı belirtmek isterim.

Değerli bilgi, tecrübe ve yorumları ile çalışmalarımda bana yol gösteren, büyük desteğini gördüğüm saygıdeğer hocam Sayın Prof. Dr. Mithat Yüksel'e saygı ve teşekkürlerimi sunmayı bir borç bilirim.

Yüksek lisans tezimin değerlendirilme aşamasındaki katkılarından dolayı Sn. Doç. Dr. Müşerref Arda'ya çok teşekkür ederim.

Yüksek lisans çalışmalarım süresi içinde üç ay süre ile Erasmus Programı öğrencisi olarak gittiğim Polonya'daki Silesian Teknik Üniversitesi'ndeki danışman hocam Sayın Prof. Dr. Marian Turek'e bana gösterdiği ilgi ve yardımlarından dolayı teşekkürlerimi sunarım.

Balçova'daki çalışmalarda verdikleri kolaylık ve desteklerinden ötürü İzmir Jeotermal Enerji Şirketi' ne çok teşekkür ederim.

Çalışmalarımda bana her türlü desteği sağlayan, büyük yardımlarını gördüğüm, Ar.Gör.Özgür Arar'a, laboratuvar çalışmalarımdeki destek ve yardımlarından dolayı, Ar.Gör.Dr. İdil Yılmaz İpek'e, Y.Kimya Mühendisi Enver Güler'e, laboratuvar arkadaşlarım Pelin Köseoğlu, Seyhan Solak, Gökem Öner, Gökhan Sert, Kemal Volkan Özdokur ve Arzu Onaç'a teşekkür ederim.

Bu noktaya gelmemdeki büyük emeklerinden ve özverilerinden dolayı aileme sonsuz teşekkürler.

Emre YAVUZ

ACKNOWLEDGEMENT

This study was supported by National Boron Research Institute (BOREN) (Project No. 2008-G-0192) and Ege University Research Foundation (Project Number: 2007 MUH 040).

I would like to express my gratitude to my supervisors Prof. Dr. Ümran YÜKSEL and Prof. Dr. Nalan KABAY as they encouraged me to support in this study. I wish to thank them for their directions, valuable advices, all kinds of helps during my studies.

I would like to express my gratitude Prof. Dr. Mithat YÜKSEL for encouraging me by his directions valuable advices, knowledges and comments.

I am grateful to Assoc.Prof.Dr.Müşerref ARDA for her support in the evaluation step of my thesis.

I am very thankful to my supervisor Prof. Dr. Marian Turek from Silesian University of Technology for his encouragement and helps during my Erasmus period of education for 3 months in Poland.

I would like to thank Izmir Geothermal Energy Co. for their great support and help for our studies in Balçova geothermal field.

I would like to express my gratitude to Res.Asst. Özgür Arar for his all kinds of helps and encouragements during my studies and also to Res.Ass.Dr. İdil Yılmaz İpek, Chem.Eng. Enver Güler and my friends in the laboratory Pelin Köseoğlu, Seyhan Solak, Görkem Öner, Gökhan Sert, Kemal Volkan Özdokur ve Arzu Onaç’a Kemal Volkan Özdokur, Gökhan Sert for their great support and helps.

Finally, I would like to thank my family for their support and encouragement for my education.

Emre YAVUZ

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NOMENCLATURE

<u>Symbol</u>	<u>Explanation</u>
EC :	electrical conductivity ($\mu\text{S}/\text{cm}$)
P :	pressure (bar)
Q :	flow rate (L/h)
Y :	Permeate recovery (%)
Sal. :	salinity (‰)
t :	temperature ($^{\circ}\text{C}$)
TDS :	total dissolved solids (mg/L)
B :	boron concentration (mg/L)
SAR :	the sodium adsorption ratio
ES :	effective salinity
EC _w :	electrical conductivity of the irrigation water
RO :	reverse osmosis
ED :	electrodialysis
MF :	microfiltration
UF :	ultrafiltration
NF :	nanofiltration
CA :	cellulose acetate
PA :	polyamide
TFC :	thin film composite
PEU :	polyether urea
DMF :	dimethylformamide
NMP :	N-Methylpyrrolidone
SWM:	spiral wound module

NOMENCLATURE (continued)

<u>Symbol</u>	<u>Explanation</u>
SW	: seawater
BSR	: boron selective resin
SWRO	: seawater reverse osmosis
BWRO	: brackish water reverse osmosis
SDI	: silt density index
EDR	: electrodialysis reversal

CHAPTER ONE

1. INTRODUCTION

1.1 Water and the Environment

1.1.1 Water quality standards for irrigation

Water is the most important input required for plant growth in agriculture production. Bulk weight of all living organisms consists of 80 to 90% water. Water need for plant growth is met with soil water storage in plant root zone. Under raided conditions, soil water storage is continuously replenished with natural rainfall; however, irrigation is essential in arid and semi-arid climates so maintain soil water storage at an optimum level to get higher yield (Kirda, 1997).

Nearly all waters contain dissolved salts and trace elements, many of which result from the natural weathering of the earth's surface. In addition, drainage waters from irrigated lands and effluent from city sewage and industrial waste water can impact water quality. In most irrigation situations, the primary water quality concern is salinity levels, since salts can affect both the soil structure and crop yield. However, a number of trace elements are found in water which can limit its use for irrigation (Fipps, 2003).

The suitability of water for irrigation is largely dependent upon the amount and type of dissolved mineral constituents, and the effect these constituents depend upon the particular type of soil and plant species. Whether a particular quality of water is suitable for irrigation, however, also depends to a considerable extent upon such factors as soil type, drainage, climate, and irrigation practices. Several different measurements are used to classify the suitability of water for irrigation, including EC_{iw} , the total dissolved solids, and SAR. The sodium adsorption ratio (SAR) is the sodium concentration divided by the square root of one-half of the combined calcium and magnesium concentrations (meq/L). Some permissible limits for classes of irrigation water were given in Table 1.1. Conversion factors for measurements of salinity of irrigation water were given in Table 1.2.

Table 1.1 Classification of irrigation water (Hopkins et al., 2007).

Water electrical conductivity (EC) (mmhos/cm or dS/m)	Water total dissolved solids, TDS (mg/L)	Salinity hazard and effects on management
below 0.25	below 160	Very low hazard. No detrimental effects on plants, and no soil buildup expected.
0.25–0.75	160–480	Low hazard. Sensitive plants may show stress; moderate leaching prevents salt accumulation in soil.
0.75–2.0	480–1,280	Medium hazard. Salinity may adversely affect plants. Requires selection of salttolerant plants, careful irrigation, good drainage, and leaching.
2.0–3.0	1,280–1,920	Medium-high hazard. Will require careful management to raise most crops.
Above 3.0	Above 1,920	High hazard. Generally unacceptable for irrigation, except for very salt-tolerant plants where there is excellent drainage, frequent leaching, and intensive management.

Table 1.2 Conversion factors for measurements of salinity of irrigation water (Hopkins et al., 2007).

Measurement	Symbol	To convert	Divide by	To obtain
Total dissolved solids	TDS	mg/L or ppm or µg/mL	640	EC (dS/m or mmhos/cm)
Electrical conductivity	EC	dS/m	1	mmhos/cm
Electrical conductivity	EC	µmhos/cm	1,000	mmho/cm

In Table 1.3, the sodium hazard of water was ranked from low to very high based on SAR values.

Table 1.3 The sodium hazard of water based on SAR values (Fipps , 2003).

SAR values	Sodium hazard of water	Comments
1-10	Low	Use on sodium sensitive crops such as avocados must be cautioned.
10 - 18	Medium	Amendments (such as Gypsum) and leaching needed.
18 - 26	High	Generally unsuitable for continuous use.
> 26	Very High	Generally unsuitable for use.

The most commonly used recent method to evaluate the high sodium or in filtration problem has been and probably still is the SAR. The SAR equation is as follows ;

$$SAR = \frac{[Na^+]}{\sqrt{0.5([Ca^{2+}] + [Mg^{2+}])}}$$

Where calcium, magnesium, and sodium concentrations are expressed in units of milliequivalents per liter (meq/L) (Hopkins et al., 2007).

Scofield (1935) is among the first persons putting forward a criteria to assess irrigation water quality. He had recognized toxic effects of Cl^- and SO_4^{2-} in irrigation waters (Table 1.4). Wilcox and Magistad (1943) suggested somewhat simpler classification and neglected potential toxicity of excess chloride ions (Table 1.5). Doneen (1954) modified the classification suggested by Wilcox and Magistad (1943) to include chloride toxicity (Table 1.6). Later, Donen (1958) introduced a new concept called "effective salinity" (ES) to consider relative solubility of different salts likely to occur in irrigation water. ES can simply be calculated by subtracting concentrations of Ca (II) and Mg (II) carbonates from the total salt concentration since it is very likely that they can precipitate out in soil during irrigation. In a new version of water quality criteria, he also gave consideration to soil properties (Table 1.7). (Christiansen et al. (1977). Ayers (1977) gives the guidelines for the irrigation water quality (Table 1.8).

Table 1.4 Concentration limits for irrigation water quality (Scofield, 1935).

Class	EC x 10 ⁶ (25 °C)	Total salt (mg/L)	Na ⁺ (%)	Cl ⁻ (meq/L)	SO ₄ ²⁻ (meq/L)
1. Very good	<250	<175	<20	<4	<4
2. Good	250-750	175-525	20-40	4-7	4-7
3. Can be used	750-2000	525-1400	40-60	7-12	7-12
4. Use with caution	2000-3000	1400-2100	60-80	12-20	12-20
5. Harmful	3000<	2100<	80<	20<	20<

Table 1.5 Irrigation water quality standards (Wilcox et al, 1943).

Class	EC x 10 ⁶ (25 °C)	Total salt (mg/L)	Na ⁺ (%)	Cl ⁻ (meq/L)
1.	<1000	<700	<60	<0.5
2.	1000-3000	700-2000	60-75	0.5-2.0
3.	3000<	2000<	75<	2.0<

Table 1.6 Irrigation water classes (Doneen, 1954).

Criteria	Class 1	Class 2	Class 3
	Very good-Good	Good-Hazardous	Hazardous-Very hazardous
EC x 10 ⁶ (25 °C)	<1000	1000-3000	<3000
Boron (mg/L)	<0.5	0.5-2.0	<2
Na (%)	<60	60-75	<75
Cl ⁻ (meq/L)	<5	5-10	<10

Table 1.7 Limit values to assess irrigation water quality (Christiansen et al. (1977).

Quality	EC x 10 ³ (25 °C)	Na ⁺ (%)	SAR	Na ₂ CO ₃ (meq/L)	Cl ⁻ (meq/L)	ES (meq/L)	Boron (mg/L)
1	0.5	40	3	0.5	3	4	0.5
2	1.0	60	6	1.0	6	8	1.0
3	2.0	70	9	2.0	10	16	2.0
4	3.0	80	12	3.0	15	24	3.0
5	4.0	90	15	4.0	20	32	4.0
6*							

* Values are higher than quality 5.

Table 1.8 Guidelines for irrigation water quality (Ayers, 1977).

IRRIGATION PROBLEM	DEGREE OF PROBLEM		
	No Problem	Increasing Problem	Severe Problem
SALINITY (affects crop water availability) EC_w (mS m ⁻¹)	<75	75-300	>300
SPECIFIC ION TOXICITY (affects sensitive crops)			
Sodium 4/5/ (adj. SAR)	<3	3-9	>9
Chloride 4/5/ (meq L⁻¹)	<4	4-10	>10
Boron (mg/L)	<0.75	0.75-2.0	>2.0
MISCELLANEOUS EFFECTS (effects susceptible crops)			
NO₃-N (or) NH₄-N (mg/L)	<5	5-30	>30
HCO₃⁻ (meq L⁻¹) (overhead sprinkling)	<1.5	1.5-8.5	>8.5
pH	Normal Range 6.5 – 8.4		

Many schemes of classification for irrigation water have been proposed. Ayers and Westcot (FAO 1985) classified irrigation water into three groups based on salinity, sodicity, toxicity and miscellaneous hazards, as shown in Table 1.9. These general water quality classification guidelines help to identify potential crop production problems associated with the use of conventional water sources (Pescode, 1992).

Table 1.9 Guidelines for irrigation water quality (Pescode, 1992).

		Degree of restriction on use		
Potential irrigation problem	Units	None	Slight to moderate	Severe
Salinity				
EC _{wb}	dS/m	<0.7	0.7–3.0	>3.0
TDS	mg/L	<450	450–2000	>2000
Sodicity ^c				
SAR ₀₋₃		and EC _w ≥ 0.7	0.7–0.2	<0.2
3-6		≥1.2	1.2–0.3	<0.3
6-12		≥1.9	1.9–0.5	<0.5
12-20		≥2.8	2.9–1.3	<1.3
20-40		≥5.0	5.0–2.9	<2.9
Specific ion toxicity				
Sodium (Na)^{d,e}				
Surface irrigation	SAR	<3	3–9	>9
Sprinkler irrigation	mg/L	<70	>70	
Chloride (Cl)^{d,e}				
Surface irrigation	mg/L	<140	140–350	>350
Sprinkler irrigation	mg/L	<100	>100	
Boron (B)	mg/L	<0.7	0.7–3.0	>3.0
Miscellaneous effects				
Nitrogen (Total N) ^f	mg/L	<5	5–30	>30
Bicarbonate (HCO ₃) mg/L (overhead sprinkling only)	mg/L	<90	90–500	>500
pH	unitless		6.5–8.4	>5.0
Residual Chlorine (overhead sprinkling only)	mg/L	<1.0	1.0–5.0	

^a Adapted from University of California Committee of Consultants (1974); and Ayers and Westcot (1985).

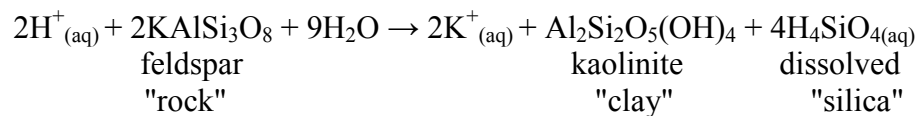
^b EC_w : electrical conductivity of the irrigation water. ; ^c : SAR : sodium adsorption ratio. See this section for details.

^d Most tree crops and woody ornamentals are sensitive to sodium and chloride; use the values shown in this table. Most annual crops are not as sensitive; see the salinity tolerance tables (Table 17-12). ; ^e With overhead sprinkler irrigation and low humidity (<30%), sodium or chloride greater than 70 or 100 mg/L, respectively, have resulted in excessive leaf adsorption and crop damage to sensitive crops.; ^f : Total nitrogen should include nitrate-nitrogen, ammonia-nitrogen, and organic-nitrogen. Although forms of nitrogen in wastewater vary, the plant responds to the total nitrogen.

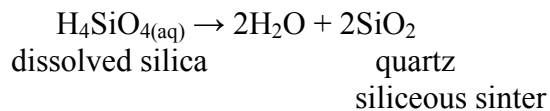
1.1.2 Geothermal water and environmental impacts

Geothermal water is a hot, often salty, mineral-rich liquid withdrawn from a deep underground reservoir. Geothermal water has a temperature appreciably higher than that of the local average annual air temperature. However, in general, a spring is considered hot when its temperature is about 12.2°C higher than mean annual ambient temperature. The relative terms geothermal water, warm springs, and hot springs are common (Lehr et al., 2005).

A variety of chemical reactions occur within geothermal waters. These are mostly associated with interactions between the water and the rock of the chambers in which it is located. Within the waters many other reactions occur, and these typically involve sulfur and/or metal cations. Prolonged water-rock interaction liberates ionic species and produces a saturated silica solution (Hodder, 2005).

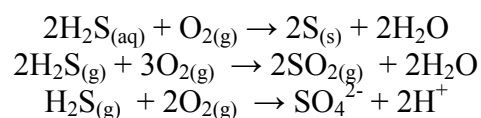


The solubility of silica is also temperature dependent, but this equilibrium is attained rather more rapidly than the dissolution of other silicate minerals.

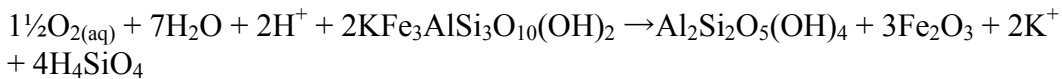


Geothermal waters generally contain sulfur, initially in the form hydrogen sulfide. This, along with other dissolved gases like HCl, is probably derived from the magma. As the water rises to the surface, the sulfide may be oxidised, especially if the path to the surface is tortuous or the rise of water is slow - through rock fractures rather than faults. The water becomes more acidic and sulfur, sulfur dioxide, or sulfate may be produced as shown below

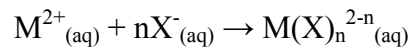
(Hodder, 2005):



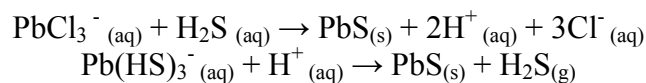
Sulfur or sulfur dioxide are produced under comparatively mild oxidising conditions; Where oxidation is more pervasive and waters are of the "acid sulfate" type the minerals in rocks may be transformed to weaker clay minerals. Also, iron and manganese ions may be liberated from silicate minerals and ultimately precipitate as their highly coloured oxides. The example below shows the oxidative liberation of iron from a silicate mineral under acid conditions. Iron (II) is oxidised to iron (III).



As well as hydrogen sulfide the gases dissolved in geothermal water that originate in the magma include hydrogen chloride. Thus, chloride ion in geothermal waters can be at high concentrations. Both hydrogen sulfide ions (HS^-) and chloride ions (Cl^-) can form complexes with metal cations as given below:



Where X is Cl^- or HS^- and M is any transition metal cation (e.g., Cu, Zn, Fe(II)) or other less common metal cations like those of gold, silver, antimony, arsenic, mercury and lead. These complexes are stable at high temperatures and high concentrations of X. When the temperature falls and/or the fluid boils, the complexes may precipitate metal sulfides, e.g. (Hodder, 2005), as shown below:



From earliest times, hot geothermal water or geothermal springs have been used for bathing and cooking. Today, applications of low and moderate temperature (100°F to 300°F) geothermal waters have expanded enormously to include heating large tracts of homes and buildings (district heating), heating greenhouses for growing vegetables and flowers, fish farming (aquaculture), drying foods and lumber and many other uses (Lehr et al., 2005).

Geothermal groundwater is often regarded as an environmentally friendly energy resource compared to fossil fuels. However, this argument may not be valid if this resource is not used properly. In the liquid-dominated geothermal systems, the geothermal fluid is rich in dissolved constituents with concentrations that are usually above the environmental limits (Dogdu et al., 2005).

Most geothermal systems have water qualities significantly below drinking water standards. Total dissolved solids are in the range 1,000-250,000 parts per million. Because of natural fluid circulation within geothermal systems, it is common for non-thermal waters in the immediate area to also be well below drinking water standards. Excessive concentration of certain dissolved minerals in geothermal water poses water quality problems. The most common of these minerals are dissolved fluoride, arsenic, and iron (Lehr et al., 2005).

Release of geothermal fluids in surface environment will apparently lead to damages whose cost may far exceed the benefits gained from the heat energy. For this reason, geothermal fluids brought to surface for any purpose have to be removed from the surface environment by using the most economically feasible way. The cost of removal of these fluids has to be included in any project that aims to utilize this resource. It should be kept in mind that a feasible-looking project aiming to use geothermal heat energy could be unfeasible if the cost of removal is considered (Dogdu et al., 2004).

1.2 Desalination by membrane filtration methods

Many countries in the world suffer from a shortage of natural fresh water. Increasing amounts of fresh water will be required in the future as a result of the rise in population rates and enhanced living standards, together with the expansion of industrial and agricultural activities. Today, some countries depend on desalination technologies for the purpose of meeting their fresh water requirements (Khawaji et al., 2008).

Desalination is a water treatment process that removes salts or other dissolved minerals and contaminants such as dissolved metals, radionuclides, bacterial and organic matter from high salinity water to produce fresh water. The most widely used technologies for desalination are thermal processes and membrane processes (Alghoul et al., 2009).

Membrane processes are modern physicochemical separation techniques that use differences in permeability (of water constituents) as a separation mechanism. During membrane treatment, water is pumped against the surface of a membrane, resulting in the production of product water (permeate) and waste streams (retentate), as shown on Figure 1.1. The membrane, typically a synthetic material less than 1 mm thickness, is semipermeable meaning that it is highly permeable to some components in the feed stream and less permeable (or

impermeable) to others. During operation, permeable components pass through the membrane and impermeable components are retained on the feed side. As a result, the product stream is relatively free of impermeable constituents and the waste stream is concentrated in impermeable constituents (Crittenden et al, 2005).

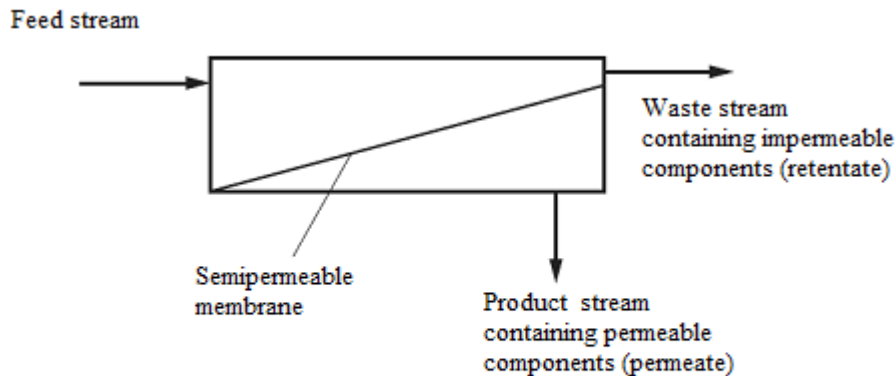


Figure 1.1 Simple illustration of filtration process (Crittenden et al, 2005).

The membrane processes are classified into two groups depending on the driven forces: pressure driven membrane processes and electrically driven membrane processes. Four types of pressure-driven membrane processes are currently used in desalination : microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Electrodialysis (ED) which is an electrically driven process is generally used for desalination.

The hierarchy of membrane processes is shown in Figure 1.2. The distinction between the types of membranes is somewhat arbitrary and subject to differing interpretations, but the membranes are loosely identified by the types of materials rejected (Crittenden et al., 2005).

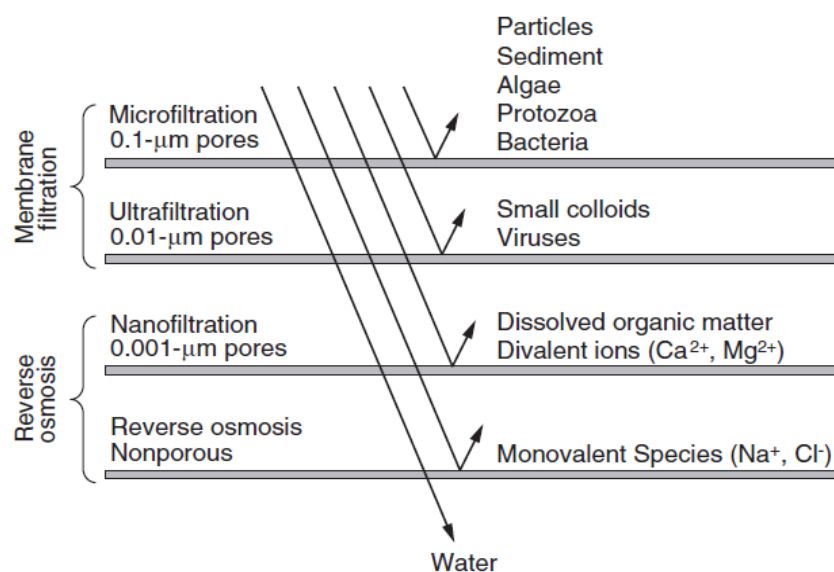


Figure 1.2 Comparison of rejection properties of membrane processes (Crittenden et al, 2005).

In Table 1.10 the most important parameters affecting the performance of membrane processes were illustrated.

Table 1.10 Factors impacting on the performance of membrane processes (Nicholas, 2002).

Membrane Processes	Driving Force	Influencing Factors			
		Size	Diffusivity	Ionic Charge	Solubility
Microfiltration	Pressure	+++	-	-	-
Ultrafiltration	Pressure	+++	-	+	-
Nanofiltration	Pressure	+++	+	+	-
Reverse Osmosis	Pressure	+	+++	+	+++
Electrodialysis	Electrically	+	+	+++	-

1.2.1. Microfiltration (MF)

Microfiltration membranes are typically used to remove particles in the range 0.1–10 μm from a suspension. Crossflow microfiltration is a pressure driven separation process, which is widely used in concentrating, purifying or

separating macromolecules, colloids and suspended particles from a solution. In the case of microfiltration, a more porous membrane is used than in the other membrane separation technologies, thus yielding a relatively higher flux (Nicholas, 2002).

The most widely used process design, illustrated in Figure 1.3 (a), is dead-end or in-line filtration, in which the entire fluid flow is forced through the membrane under pressure. In cross-flow systems, the feed solution is circulated across the surface of the filter, producing two streams: a clean particle-free permeate and a concentrated retentate containing the particles. The equipment required for cross-flow filtration is more complex, but the membrane lifetime is longer than with in-line filtration (Baker, 2004).

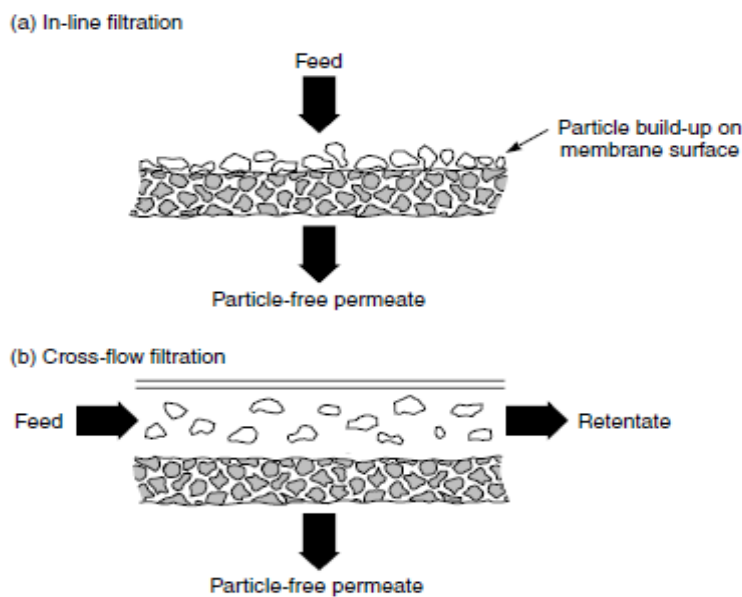


Figure 1.3 Schematic representation of (a) in-line and (b) cross-flow filtration with microfiltration membranes (Baker, 2004).

Microfiltration (MF) has increasingly been accepted as promising technology in a wide range of applications including water and wastewater treatments, dairy, biotechnological and pharmaceutical industries, food and beverage processing, and medical applications (Susanto et al, 2009). The primary limitation of microfiltration systems is usually the service life of the filter and its associated change-out costs (Starbard, 2008).

1.2.2. Ultrafiltration (UF)

Ultrafiltration uses a finely porous membrane to separate water and microsolute from macromolecules and colloids. The average pore diameter of the membrane is in the 1–100 nm range. Ultrafiltration membranes are usually anisotropic structures made by the Loeb–Sourirajan process. They have a finely porous surface layer or skin supported on a much more open microporous substrate. The finely porous surface layer performs the separation; the microporous substrate provides mechanical strength. The membranes discriminate between dissolved macromolecules of different sizes and are usually characterized by their molecular weight cut-off, a loosely defined term generally taken to mean the molecular weight of the globular protein molecule that is 90% rejected by the membrane (Baker, 2004).

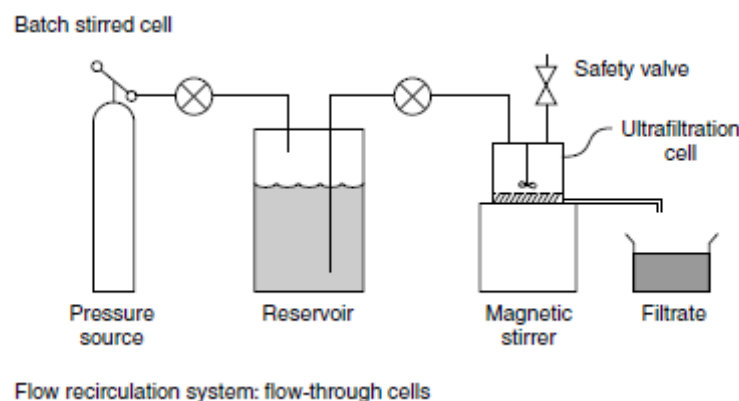


Figure 1.4 Laboratory ultrafiltration test system (Baker, 2004).

Ultrafiltration and microfiltration are related processes. The distinction between the two lies in the pore size of the membranes. Microfiltration membranes have larger pores and are used to separate particles in the 0.1–10 μm range, whereas ultrafiltration is generally considered to be limited to membranes with pore diameters from 1 nm–100 nm (Baker, 2004).

In the 1960s and early 1970s, it was thought that ultrafiltration would be widely used to treat industrial wastewater. This application did not materialize. Ultrafiltration is far too expensive to be generally used for this application, however, it is used to treat small, concentrated waste streams from particular point

sources before they are mixed with the general sewer stream. Ultrafiltration is also used if the value of the components to be separated is sufficient to offset the cost of the process. Examples exist in food processing, in which the ultrafiltered concentrate is used to produce a high-value product, or in the production of ultrapure water in the electronics industry (Baker, 2004).

1.2.3. Nanofiltration (NF)

The nanofiltration (NF) membrane is a type of pressure-driven membrane with properties in between reverse osmosis (RO) and ultrafiltration (UF) membranes. In addition to having the capability to reduce the ionic strength of the solution, NF membranes can remove hardness, organics and particulate contaminants (Hilal et al, 2004). The rejection of salts by nanofiltration membranes is more complicated and depends on both molecular size and Donnan exclusion effects caused by the acid groups attached to the polymer backbone (Baker, 2004). NF offers several advantages such as low operation pressure, high flux, high retention of multivalent anion salts and an organic molecular above 300, relatively low investment and low operation and maintenance costs. Because of these advantages, the applications of NF worldwide have increased (Hilal et al, 2004).

1.2.4. Electrodialysis (ED)

In an electrodialysis system, anionic and cationic membranes are formed into a multicell arrangement built on the plate-and-frame principle to form up to 100 cell pairs in a stack. The cation and anion exchange membranes are arranged in an alternating pattern between the anode and cathode. Each set of anion and cation membranes forms a cell pair. Salt solution is pumped through the cells while an electrical potential is maintained across the electrodes. The positively charged cations in the solution migrate toward the cathode and the negatively charged anions migrate toward the anode. Cations easily pass through the negatively charged cation exchange membrane but are retained by the positively charged anion exchange membrane. Similarly, anions pass through the anion exchange membrane but are retained by the cation exchange membrane. The overall result of the process is that one cell of the pair becomes depleted of ions

while the adjacent cell becomes enriched in ions. The process, which is widely used to remove dissolved ions from water, was illustrated in Figure 1.5 (Baker, 2004).

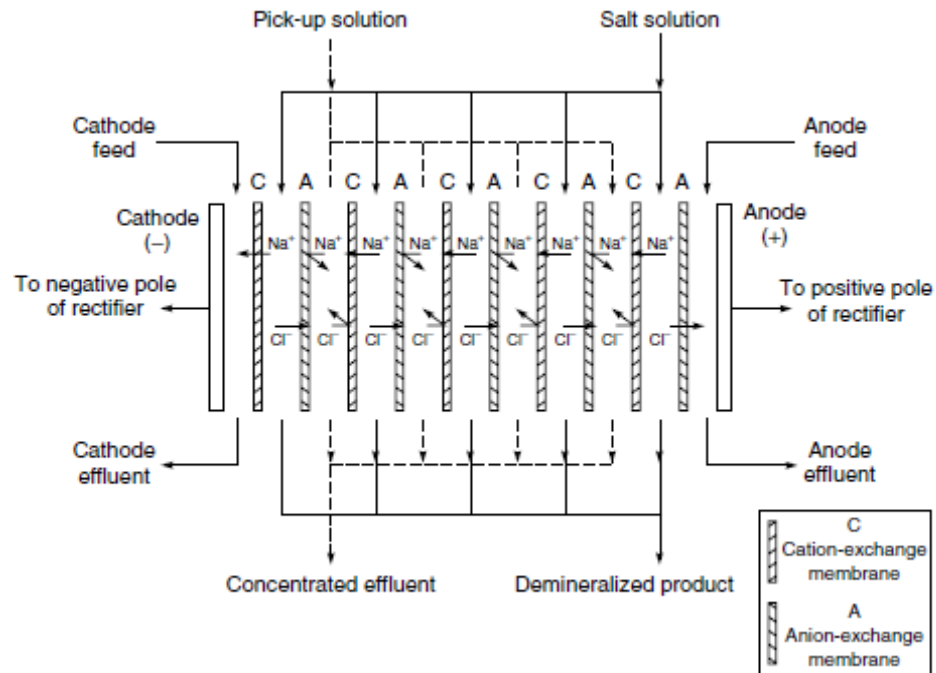


Figure 1.5 Schematic diagram of a plate-and-frame electro dialysis stack. Alternating cation- and anion-permeable membranes are arranged in a stack of up to 100 cell pairs (Baker, 2004).

1.2.5. Reverse Osmosis (RO)

Introduction to reverse osmosis

Reverse Osmosis (RO) is a membrane-based demineralization technique used to separate dissolved solids, such as ions, from solution (most applications involve water-based solutions, which is the focus of this work). Membranes in general act as perm-selective barriers, barriers that allow some species (such as water) to selectively permeate through them while selectively retaining other dissolved species (such as ions) (Kucera, 2010).

In reverse osmosis, a semipermeable membrane is challenged with a pressurised feed stream containing a solute. The pressure exerted is greater than

the osmotic pressure of the feed, causing solvent to flow through the membrane. Figure 1.6 provides a schematic representation of the process (Noble et al, 1995).

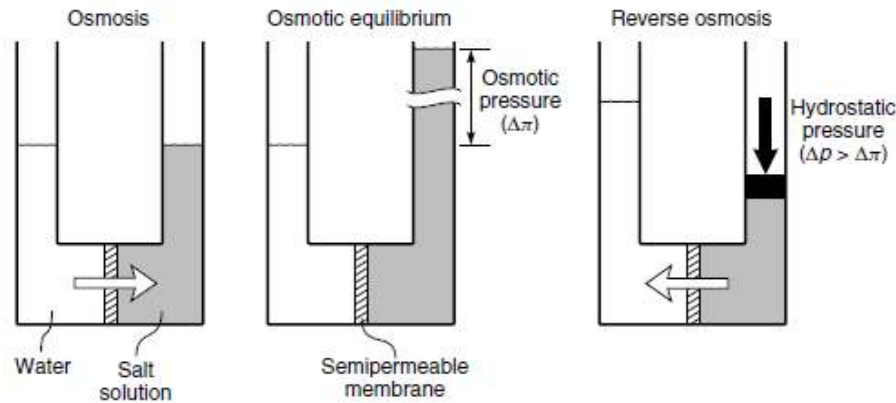


Figure 1.6 Schematic of the reverse osmosis process (Baker, 2004).

History of reverse osmosis

One of the earliest recorded documentation of semipermeable membranes was in 1748, when Abbe Nollet observed the phenomenon of osmosis. Others, including Pfeffer and Traube studied osmotic phenomena using ceramic membranes in the 1850's. However, current technology dates back to the 1940's when Dr. Gerald Hassler at the University of California at Los Angeles (UCLA) began investigation of osmotic properties of cellophane in 1942. He proposed an "air film" bounded by two cellophane membranes. Hassler assumed that osmosis takes place via evaporation at one membrane surface followed by passage through the air gap as a vapor, with condensation on the opposing membrane surface. Today, we know that osmosis does not involve evaporation, but most likely involves solution and diffusion of the solute in the membrane. In 1959, C.E. Reid and E.J. Breton at University of Florida, demonstrated the desalination capabilities of cellulose acetate film. They evaluated candidate semipermeable membranes in a trial-and-error approach, focusing on polymer films containing hydrophilic groups. Materials tested included cellophane, rubber hydrochloride, polystyrene, and cellulose acetate. Many of these materials exhibited no permeate flow, under pressures as high as 800 psi, and had chloride rejections of less than 35%. Cellulose acetate (specifically the DuPont 88 CA-43), however, exhibited chloride rejections of greater than 96%, even at pressures as low as 400 psi. Fluxes ranged from about 2 gallons per square foot-day (gfd) for a 22-micron

thickness cellulose acetate film to greater than 14 gfd for a 3.7 micron thick film when tested at 600 psi on a 0.1 M sodium chloride solution. Reid and Breton's conclusions were that cellulose acetate showed requisite semipermeability properties for practical application, but that improvements in flux and durability were required for commercial viability. A decade after Dr. Hasslefs efforts, Sidney Loeb and Srinivasa Sourirajan at UCLA attempted an approach to osmosis and reverse osmosis that differed from that of Dr. Hassler. Their approach consisted of pressurizing a solution directly against a flat, plastic film. Their work led to the development of the first asymmetric cellulose acetate membrane in 1960. This membrane made RO a commercial viability due to the significantly improved flux, which was 10 times that of other known membrane materials at the time (such as Reid and Breton's membranes). These membranes were first cast by hand as flat sheets. Continued development in this area led to casting of tubular membranes. Following the lead of Loeb and Sourirajan, researchers in the 1960's and early 1970's made rapid progress in the development of commercially-viable RO membranes. Harry Lonsdale, U. Merten, and Robert Riley formulated the "solution-diffusion" model of mass transport through RO membranes. Although most membranes at the time were cellulose acetate, this model represented empirical data very well, even with respect to presentday polyamide membrane. Understanding transport mechanisms was important to the development of membranes that exhibit improved performance (flux and rejection) (Kucera, 2010).

Anisotropic cellulose acetate membranes were the industry standard through the 1960s to the mid-1970s, until Cadotte, then at North Star Research, developed the interfacial polymerization method of producing composite membranes (Cadotte et al., 1985). Interfacial composite membranes had extremely high salt rejections, combined with good water fluxes. Fluid Systems introduced the first commercial interfacial composite membrane in 1975. The construction of a large seawater desalination plant at Jiddah, Saudi Arabia using these membranes was a milestone in reverse osmosis development (Muirhead et al., 1982). Later, at FilmTec, Cadotte developed a fully aromatic interfacial composite membrane based on the reaction of phenylene diamine and trimesoyl chloride (Larson et al., 1981 and Cadotte, 1981). This membrane has become the new industry standard. The most recent development, beginning in the mid-1980s, was the introduction of low pressure nanofiltration membranes by all of the major reverse osmosis companies (Eriksson, 1988 and Kamiyama et al., 1984). These

membranes are used to separate trace amounts of salts and other dissolved solutes from already good-quality water to produce ultrapure water for the electronics industry. An important recent advance by Grace Davison working with Mobil Oil, now Exxon Mobil, is the development of a reverse osmosis (hyperfiltration) process to separate a solution of methyl ethyl ketone and lube oil. A plant installed at a Beaumont, Texas, refinery in 1998 was the first large-scale use of pressure-driven membranes to separate organic solvent mixtures (Baker, 2004).

Recent advances in reverse osmosis

Since the 1970's, the membrane industry has focused on developing membranes that exhibit ever greater rejection of solutes while at the same time exhibiting higher throughput (flux) at lower operating pressure. Table 1.11 shows the growth in RO membrane development with respect to rejection, flux, and operating pressure. Along with advances in membrane performance, membrane costs have also improved. In addition to the progress shown in Table 1.11, some membranes now exhibit up to 99.75% rejection (a drop of 17% in salt passage over membranes exhibiting 99.7% rejection) (Kucera, 2010).

Table 1.11 Development of RO membranes for brackish water desalination (Kucera, 2010).

Year	Pressure (psi)	Relative	Rejection (%)	Membrane Material
1970's	435	1	97.0	Cellulose acetate
1980's	290	1.9	99.0	Cross-linked polyamide composite
1987	220	3.0	99.7	Cross-linked aromatic polyamide composite
1988	145	4.2	99.7	Cross-linked aromatic polyamide composite
1996	110	5.6	99.7	Cross-linked aromatic polyamide composite
1999	75	8.0	99.7	Cross-linked aromatic polyamide composite

1.2.5.1. Theoretical background of reverse osmosis

Osmotic pressure is defined as:

$$\pi = -\frac{R \cdot T}{V_b} \ln(x_w) \quad (1.1)$$

with the osmotic pressure π , the molar volume of water V_b , the mole fraction of water x_w and the ideal gas constant R .

In dilute solutions, the osmotic pressure can be estimated using van't Hoff's law, which is of the same form as the ideal gas law:

$$\pi = \frac{n_s}{V} R \cdot T \quad \text{or} \quad \pi = C \cdot R \cdot T \quad (1.2, 1.3)$$

Taking into account non-ideality and dissociation of the ions in solution, van't Hoff's law can be rewritten as:

$$\pi = i\phi C \cdot R \cdot T \quad (1.4)$$

i representing the dissociation parameter, which is equal to the number of ions and molecules per mole of solute produced by dissolution of the solute and ϕ representing the correction factor that takes into account non-idealities (Fritzman et al., 2006).

It is not yet possible to determine the structure of the skin layer of a reverse osmosis membrane by electron microscopy and there remains some controversy over the possible existence of pores. Current thinking is that the solvent passes through the gaps between polymer chains, which are of the order of 2-5 Å. However, the most commonly applied model at present is the solution-diffusion model, which gives the following relationships:

$$J_i = A(\Delta p - \Delta \pi) \quad (1.5)$$

for water flux. Where Δp is the pressure difference across the membrane, $\Delta \pi$ is the osmotic pressure differential across the membrane, and A is a constant.

The salt flux, J_j , across a reverse osmosis membrane is described by the equation:

$$J_j = B(c_{j0} - c_{jl}) \quad (1.6)$$

where B is the salt permeability constant and c_{j0} and c_{jl} , respectively, are the salt concentrations on the feed and permeate sides of the membrane.

The water flux is proportional to the applied pressure, but the salt flux is independent of pressure. This means that the membrane becomes more selective as the pressure increases. Selectivity can be measured in a number of ways, but conventionally, it is measured as the salt rejection coefficient R ,

$$R = \left[1 - \frac{c_{jl}}{c_{j0}} \right] \times 100\% \quad (1.7)$$

Basic terms and definitions in reverse osmosis

Some basic terms are used in RO systems to define the performance and specifications of the system.

Recovery

Recovery (sometime referred to as "conversion") is a term used to describe what volume percentage of influent water is "recovered" as permeate. Generally, RO system recoveries range from about 50% to 85%, with the majority of systems designed for 75% recovery. Recovery is calculated using the following equation:

$$\text{Recovery, \%} = (\text{permeate flow} / \text{feed flow}) \times 100 \quad (1.8)$$

Rejection

Rejection is a term used to describe what percentage of an influent species a membrane retains. For example, 98% rejection of silica means that the membrane will retain 98% of the influent silica. It also means that 2% of influent silica will pass through the membrane into the permeate (known as "salt passage"). Rejection of a given species is calculated using the following equation:

$$\text{Rejection, \%} = [(C_f - C_p) / C_f] \times 100 \quad (1.9)$$

C_f = influent concentration of a specific component

C_p = permeate concentration of a specific component (Kucera, 2010).

Flux

Flux is defined as the volumetric flow rate of a fluid through a given area. In the case of RO, the fluid is water and the area is that of the membrane. In the language of RO, flux is expressed as liters of water per square meter of membrane area per hour, (L/m²h). The flux of water through an RO membrane is proportional to the net pressure driving force applied to the water

$$J = K (\Delta P - \Delta \pi) \quad (1.10)$$

where: J = water flux K = water transport coefficient = permeability / thickness of the membrane active layer ΔP = pressure difference across the membrane $\Delta \pi$ = osmotic pressure difference across the membrane (Kucera, 2010).

1.2.5.2 Concentration polarization

Reverse osmosis is a cross-flow process and, as in any dynamic hydraulic process, the fluid adjacent to the membrane moves slower than the main stream. This thin, laminar flow film is called the boundary layer (Figure 1.7). When water permeates through the membrane, nearly all of the salt remains behind in the boundary layer next to the membrane. The salt must then diffuse across the boundary layer and back into the bulk stream. This results in a boundary layer with a salt concentration which is more concentrated than the bulk stream. The effect has been termed concentration polarization, and it is defined by the following equation (Porter, 1990):

$$\beta = C_B / C_M \quad (1.11)$$

Where β = Concentration polarization

C_M = Concentration in the main stream

C_B = Concentration in the boundary layer

1.2.5.3 Reverse osmosis membranes and materials

1.2.5.4 Cellulose acetate membranes-asymmetric membranes

Early cellulose acetate membranes were created by Loeb and Sourirajan using the non-solvent phase separation or "phase inversion" method. Cellulose acetate was the first high-performance reverse osmosis membrane material discovered. The flux and rejection of cellulose acetate membranes have now been surpassed by interfacial composite membranes. However, cellulose acetate membranes still maintain a small fraction of the market because they are easy to

make, mechanically tough, and resistant to degradation by chlorine and other oxidants, a problem with interfacial composite membranes. Cellulose acetate membranes can tolerate up to 1 mg/L chlorine, so chlorination can be used to sterilize the feed water, a major advantage with feed streams having significant bacterial loading (Baker, 2004).

The thickness of the skin is typically about 0.2 microns, while the thickness of the entire membrane is about 100 microns. Figure 1.8 shows the chemical structure of CA membranes and Table 1.12 shows the characteristics of CA membranes (Kucera, 2010).

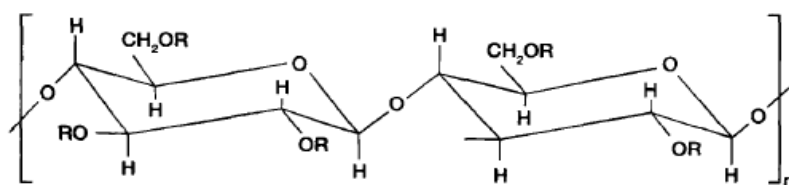


Figure 1.8 Chemical structure of cellulose acetate RO membranes

Table 1.12 Characteristics of cellulose acetate RO membranes (Kucero, 2010).

Property	Value for CA Membranes
Membrane Type	Homogenous asymmetric
Salt Rejection (%)	-95
Silica Rejection (%)	-85
pH Range	4-6
Feed Pressure (brackish membrane)	220-440 psi
Temperature Tolerance Up to 30°C	Up to 30°C
Chlorine Tolerance	Up to 1 ppm continuously
Surface Charge	Neutral
Biological Growth	Metabolized membrane
Fouling Tolerance	Good
Surface Roughness	Smooth

1.2.5.5 Polyamide and composite membranes

Polyamide membranes were developed in an effort to improve upon the performance of CA membranes. In particular, the higher operating pressure and relatively low salt rejection of CA membranes were holding back RO technology from becoming more commercially viable. Cellulose acetate membranes were the dominant choice for RO membranes until the advent of thin film composite (TFC)

RO membranes were developed in 1972. Based on aromatic polyamides, TFC membrane fluxes and rejections surpassed those of CA. For example, a CA-based membrane has a flux of 22 GFD at 425 psig feed pressure and an average NaCl rejection of 97.5% using a 2000 mg/L NaCl feed solution at 77°F and pH 7.5. A polyamide TFC membrane with the same feed solution exhibits a flux of 27 GFD at only 225 psig feed pressure and an average rejection of 99.5% (GE Osmonics, 2004). Most TFC membranes are made with a porous, highly permeable support such as polysulfone, which is coated with a cross-linked aromatic polyamide thin film (Baker, 2004). The coating provides the salt rejection properties of the membrane. This polyamide coating was based on the reaction between m-phenyl diamine and trimesoyl chloride (Cadotte, 1985). Variations of this chemistry are still used today to produce cross-linked membranes for commercial RO membranes and Table 1.13 shows the characteristics of PA membranes. Chemical structure of commercial polyamide membranes was shown in Figure 1.9 (Cadotte, 1985).

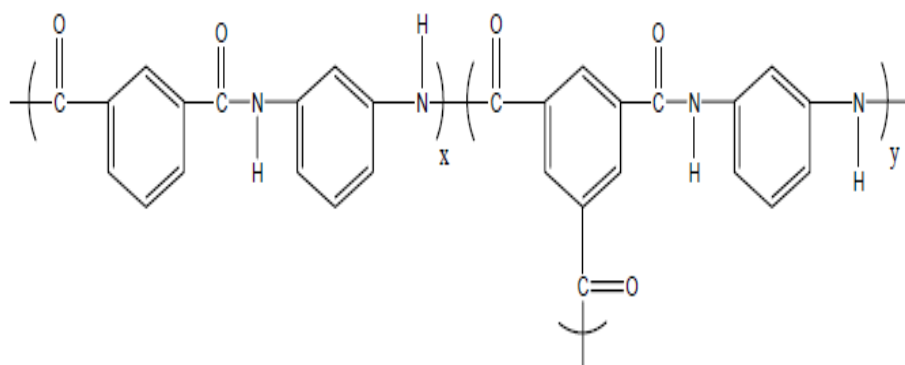


Figure 1.9 Representative chemical structure of commercial polyamide membranes used as the separation layer in thin film composite membranes (Cadotte, 1985).

Table 1.13 Characteristics of polyamide composite RO membranes (Kucero, 2010).

Property	Value for PA Membranes
Membrane type	Homogenous asymmetric, thin film composite
Salt rejection (%)	98
Silica rejection (%)	96
pH range	2-12*
Feed pressure (brackish membrane)	145-400 psi
Temperature tolerance up to 30°C	Up to 45°C**
Chlorine tolerance	<0.02 ppm
Surface charge	Negative (anionic)
Biological growth	Causes membrane fouling
Fouling tolerance	Fair
Surface roughness	Rough

* Broader range possible for cleaning. Check with membrane manufacturer.

** Higher temperature possible for "heat sanitisable" membranes. Check with manufacturer.

All membrane materials available on the market have only limited stability to oxidants used in pre-treatment such as free chlorine or ozone. In separation of organics from water, membrane deterioration can also occur due to the presence of solvents as acetonitrile, vinyl acetate, dioxane, DMF, NMP and a number of chlorinated solvents, substances that usually are not present in drinking water feed streams. Table 1.14 summarizes chemical resistances of the available membrane materials (Fritzman, 2006).

Table 1.14 Membrane damaging conditions (Fritzmman, 2006).

Membrane damaging conditions		
	Cellulose acetate membrane (CA)	Composite membrane (TFC)
pH value	4–5	3–11
Continuous free chlorine	<1 mg/L	200–1000 ppm-h
Bacteria	Not resistant	Resistant
Free oxygen	Resistant	Resistant

1.2.5.6 Other membrane materials

Polyether urea (PEU) is another type of thin-film membrane. This membrane differs from polyamide membranes in the surface charge and morphology. Polyether urea membranes have a slightly positive charge to them.

Further, the surface of a PEU membrane is smooth, similar to a CA membrane, thereby minimizing the potential for fouling. Hydranautics CPA membrane is an example of a polyamide/polyurea composite membrane (Kucera, 2010).

1.2.5.7 Reverse osmosis modules

Reverse osmosis membranes for industrial applications are typically modularized using configurations that pack a large amount of membrane area into a relatively small volume. This makes the RO system more economical to use in that the system requires a smaller footprint, and membranes can be replaced in smaller modules rather than system wide (Kucera, 2010).

The earliest designs were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press: these are called plate-and-frame modules. Membranes in the form of 1 to 3 cm diameter tubes were developed at about the same time. Both designs are still used, but because of their relatively high cost they have been largely displaced in most applications by two other designs the spiral-wound module and the hollow fiber module (Kucera, 2010).

There are four main types of modules: plate-and-frame, tubular, spiral wound, and hollow fiber. These four configurations were summarized in Table 1.15 and discussed below (Singh, 2006).

Table 1.15 Brief comparison of four basic RO membrane module configurations (Singh, 2006).

Property	Plate and Frame	Tubular	Spiral Wound	Hollow Fine Fiber
Packing Density, ft ² /ft ³	45-150	6-120	150-380	150-1,500
Potential for Fouling	Moderate	Low	High	Very High
Ease of Cleaning	Good	Excellent	Poor	Poor
Relative Manufacturing Cost	High	High	Moderate	Low

Plate and frame modules

Plate and frame RO modules are typically used for speciality, high suspended solids applications and are not generally found in water purification facilities. These modules consist of flat sheets of membrane that are modularized into plates, typically two membranes placed back to back per plate. The plates are then stacked within a framework for support. There are patterned spacers materials that are used to keep the membranes from sticking to each other and providing open channels for the feed and product water to flow through (Kucero, 2010).

Plate-and-frame units have been developed for some small-scale applications, but these units are expensive compared to the alternatives, and leak through the gaskets required for each plate are serious problem. Plate-and-frame modules are now only used in electrodialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration applications with highly fouling feeds. An example of one of these reverse osmosis units was shown in Figure 1.10 (Porter, 1990).

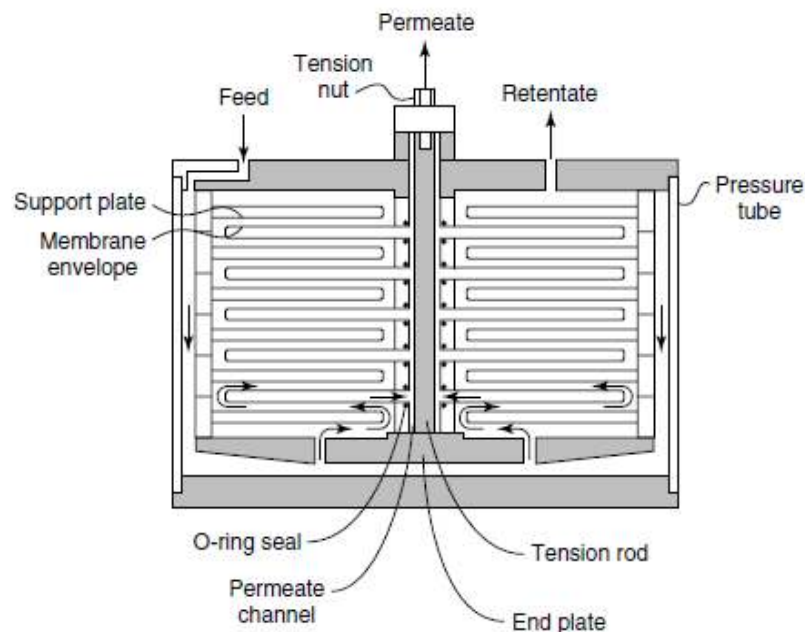


Figure 1.10 Schematic of a plate-and-frame module.

Spiral wound modules

Basically, the spiral wound element consists of two sheets of membrane separated by a grooved, polymer reinforced fabric material. This fabric both supports the membrane against the operating pressure and provides a flow path for product water. The membrane envelope is sealed with an adhesive on three sides to prevent contamination of the product water. The fourth side is attached to a product water tube which has perforations within the edge seal so that product water can be removed from the porous product water carrier material. The membrane envelope is rolled up around central product water tube, with a plastic mesh spacer between the facing membrane surfaces, in a spiral. The mesh spacer not only serves to separate membrane surfaces but it provides a flow path and turbulence in the feed/reject stream of each element. The elements have an outer wrap to contain the feed/reject stream in the mesh passage way and brine seal to insure that the feed/reject stream goes through the element and not around it. Spiral wound elements are available in lengths from 12 to 60 inches and diameters from 2 to 12 inches. Packaging densities of up to 300 square feet of membrane to 1 cubic foot of pressure vessel have been attained. Reverse osmosis plants with a capacity from 100,000 to 5,000,000 gpd of product would normally use elements with an 8-inch diameter by a 40 inch or 60 inch length (Porter, 1990).

However, most membranes to be installed in RO membrane desalination use flat sheet membranes in a spiral wound module (SWM) configuration in spite of its smaller packing density of $<1000 \text{ m}^2/\text{m}^3$. SWMs offer a good balance in terms of permeability, packing density, fouling control and ease of operation. A summary of advantages and disadvantages of spiral wound modules was shown in Table 1.16 (Fritzman, 2006).

Table 1.16 Spiral wound modules advantages and disadvantages (Fritzman, 2006).

Advantages	Disadvantages
Cheap and relatively simple production	High feed side pressure loss
High packing density $<1000 \text{ m}^2/\text{m}^3$	Susceptible to fouling
High mass transfer rates due to feed spacers	Hard to clean

The basic assembly of an RO spiral wound module (SWM) was shown in Figure 1.11.

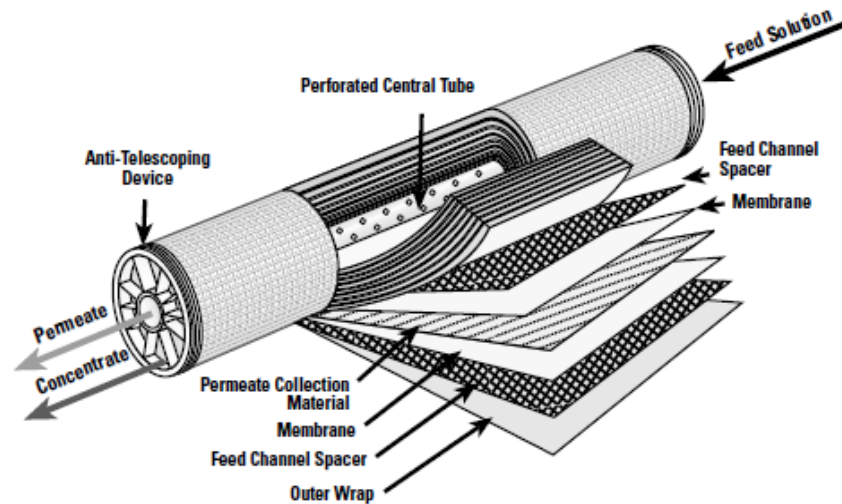


Figure 1.11 An illustration of spiral-wound module (Melin, 2003).

Hollow fine fiber modules

Early RO desalination plants often used hollow fibre reverse osmosis membranes due to the optimal membrane area to volume ratio. Feed water passes at the outside and is forced through the membrane, while permeate is processed inside the lumen. Originally, hollow fibre RO membranes were produced by DuPont, who stopped their commitment in RO membrane development and production. Today, this type of module is still available from the Japanese company Toyobo, which also has supplied several recently installed SW desalination plants with their capillary membranes [e.g., Fukukoa (Japan) 2005, Ad Dur (Bahrain) 2005] (Fritzman, 2006).

Hollow fine fiber synthetic filaments have been prepared for use in the textile industry for a long time. This well-known technology was adapted to

prepare polymers, which are suitable for reverse osmosis desalination, into hollow fine fibers. The most readily available polymers in hollow fine fiber elements are aromatic polyamide, cellulose diacetate and cellulose triacetate. The fibers are indeed very fine in that they approach the diameter of a single human hair. The aromatic polyamide hollow fine fiber has an outside diameter of 85 micrometers for the brackish water fiber and an outside diameter of 95 micrometers for the seawater fiber. Both of the fibers have an internal diameter of 42 micrometers. The ratio of outside to inside diameter exceeds two. The fibers are thick walled cylinders that have the compressive strength necessary to withstand the operating pressures. This concept is capable of achieving a high packaging density of 3,000 square feet per cubic foot but the flux is considerably lower than with sheet membrane (Porter, 1990).

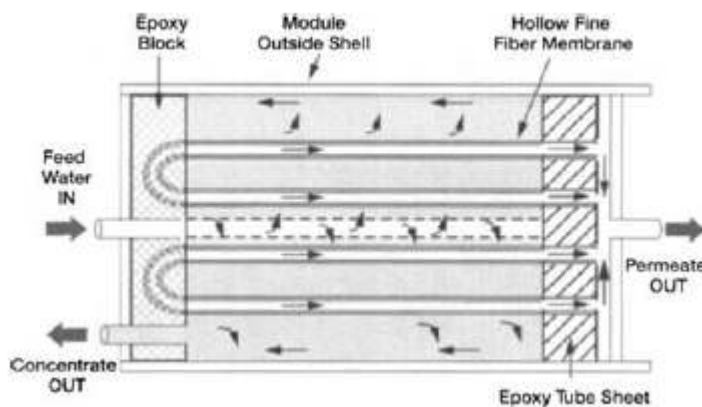


Figure 1.12 Simplified cross section of a hollow fine fiber RO membrane module (Kucera, 2010).

Tubular modules

Tubular modules are also used for specialty, high-solids applications typically found in the food and biological processing industries. Tubular modules range from 1.3 - 2.6 cm in diameter with the membrane feed side on the inside of the tube. Packing densities run about 6-120 ft²/ft³ (Singh, 2006).

The tube serves as the pressure vessel and the membrane is installed inside the tube. Tubes with inside diameters of 0.5 and 1 inch have been used. Uniformly porous fiberglass reinforced plastic tubes have been used and nonporous but perforated copper, stainless steel and fiberglass tubes have also been successfully used. The membrane can be bonded to the tube in which case it is

cast in situ or the membrane can be loose. The loose membrane is cast in sheet form and a cylindrical section is formed and placed in the tube. Packing densities for the 0.5 inch diameter tube are about 100 square feet per cubic foot and about 50 square feet per cubic foot for the 1 inch diameter tube (Porter, 1990).

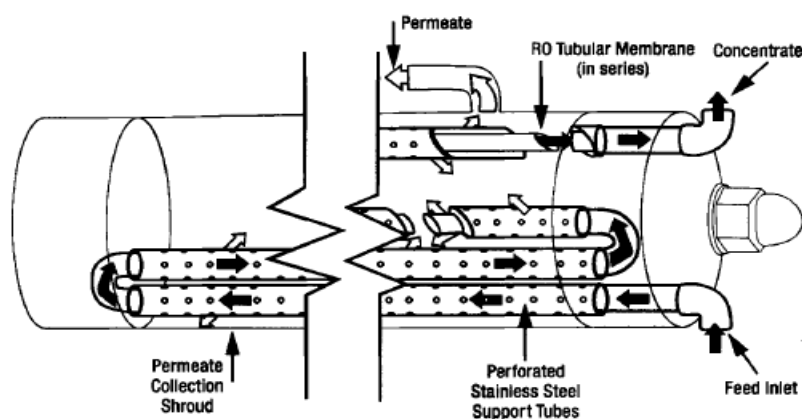


Figure 1.13 Tubular RO membrane module. Membrane tubes are placed in series in housing (Kucera, 2010).

1.2.5.8 Limiting factors to reverse osmosis

Performance of an RO system, depend on a function of membrane fouling, scaling and degradation (Kucera, 2010).

Membrane fouling

A major problem shared by both CA and TFC membranes is fouling. In general, fouling occurs either on the surface of a membrane or within its pores, and it causes a decrease in flux.

Membrane fouling involves the deposition of suspended solids, including bacteria, on the membrane or components within the membrane module. These foulants form a layer on the surface of the membrane that becomes an additional barrier for water to flow through to the permeate side of the membrane. Hence, if the feed pressure is held constant, the permeate flow will decrease (Kucero, 2010).

One of the most important issues in the development of membrane filtration has been fouling. The main reasons for membrane :

- ❖ Organic molecules adsorption (organicfouling, e.g. proteins, humic substances)

- Particulate deposition (colloidal fouling, e.g. clay, iron, and alumina silicate)
- Microbial adhesion (biofouling, e.g. bacteria) (Singh, 2006).

In general, sources of fouling can be divided into four principal categories: scale, silt, bacteria, and organic. More than one category may occur in the same plant (Baker, 2004).

Biological fouling is the growth of bacteria on the membrane surface. The susceptibility of membranes to biological fouling is a strong function of the membrane composition.

Silt is formed by suspended particulates of all types that accumulate on the membrane surface. Typical sources of silt are organic colloids, iron corrosion products, precipitated iron hydroxide, algae, and fine particulate matter.

Membrane scaling

Scaling of the membrane is caused by super-saturation of inorganic compounds concentrated on the feed side. Super-saturated salts can precipitate on the membrane surface building a thin layer, which hinders mass transfer through the membrane. Scaling always occurs at the membrane surface because of the increased salt concentration near the membrane caused by concentration polarisation. Some of the most important scaling substances are CaCO_3 , CaSO_4 , BaSO_4 and silica. Scaling can dramatically reduce permeate flux, and has to be avoided by all means. Most susceptible to scaling is the downstream part of the RO stage where concentration in the feed solution is the highest (Fritzman, 2006).

1.2.5.9 General applications of reverse osmosis

Approximately one-half of the reverse osmosis systems currently installed are desalinating brackish or seawater. Another 40% are producing ultrapure water for the electronics, pharmaceutical, and power generation industries. The remainder are used in small niche applications such as pollution control and food processing (Baker, 2004). The following list enumerates a wide variety of applications for which the reverse osmosis process may be considered:

(1) Municipal Potable Water

General quality improvement of present supplies

Upgrade total municipal supply

Potable water from degraded supplies

Brackish water desalination

Seawater desalination

Removal of nitrates, fluorides, heavy metals, etc.

Bottled water production

(2) Industrial Water

Provide usable water where none available

Brackish water desalination

Seawater desalination

Pure water production

Industrial rinse waters

Food industry

Electroplating

Power plant boiler feed

Beverage production

Medical

Ultrapure water production

Pharmaceutical

Electronics

Medical

(3) Municipal Wastes

Reclaim municipal wastewaters (sewage) for

Ground water recharging

Agricultural or landscape irrigation

Industrial process water

Improve effluent quality to meet discharge requirements

(4) Industrial Wastes

Reclaim industrial wastewaters for

Reuse within industrial plant

Zero discharge

Agricultural or landscape irrigation

Removal of toxic substances prior to discharge

Resource recovery

Separate or concentrate valuable materials

Electroplating industry

Dairy industry

(5) Miscellaneous

Production of pure water for high value crops

Recovery of agricultural irrigation drainage

Production of shipboard drinking water (Porter, 1990).

1.2.5.10 Removal of boron from water by reverse osmosis

The potential sources of boron contamination in water resources are either anthropogenic (pollution from sewage effluents, boron enriched fertilizers, landfill leachates and discharge from the soap and detergent manufacturing) or natural (e.g. water-rock interaction, seawater enrichment, mixing with fossil brines or hydrothermal fluids) (ATSDR, 2007).

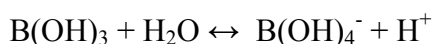
Boron compounds are often present in surface and groundwaters as well as wastewaters at concentration levels of 5–100 mg/L and higher. On the one hand, this is caused by a highly widespread character of boron in Earth's crust, and on the other hand-by a wide application of its compounds in different branches of industry: at production of glass, enamels, glazes, skin, synthetic detergents, microfertilizers (DHS, 1996 and Smith et al., 1995).

Boron in drinking water is suspected as teratogenic. The 1993 WHO guidelines for drinking-water quality proposed a 0.3 mg/L standard for boron in

drinking water. Later, this standard was revised to 0.5 mg/L because it would be difficult to achieve in areas with high natural boron levels with the treatment technology available. Recently boron has been classified by the European Union (EU) as a pollutant of drinking water in national and international drinking water directives. The EU adopted a standard of 1 mg/L boron for drinking water. World Health Organization had originally proposed boron limits of 0.3–0.5 mg/L, but recent developments indicate that in future revisions, the limit might be as high as 2.4 mg/L (Busch et al, 2009).

Therefore, it is necessary to remove the excess amount of boron from water by a suitable method. The treatment methods used for the removal of boron from water can be divided into several categories. The first is coagulation and electrocoagulation processes. The next two categories are adsorption and ion-exchange processes. The last category consists of membranes processes such as Donnan dialysis, electrodialysis and reverse osmosis (RO) (Cengeloglu et al, 2008).

In sea water boron is usually present as boric acid H_3BO_3 and the following equilibrium reaction takes place in water:



Typical RO membranes have a high rejection of the charged form, dominating at pH-values above pK_a , whereas rejection is low for the uncharged species, which dominates at lower pH (Fritzman, 2006).

Removal of boron with RO membrane therefore requires elevated pH values. In a single pass RO operation, high pH is however problematic due to high alkalinity resulting in an excessive consumption of caustic and high hardness which could cause precipitation of scaling layers. Increased pH is therefore used primarily in double pass operation at the second RO pass. Alternatively boron selective resins can be used instead of a second RO stage (Fritzman, 2006).

The main options for boron removal are:

- ❖ Single pass RO with high boron rejection membranes
- ❖ SWRO followed by BWRO
- ❖ SWRO followed by boron selective ion exchange resin (BSR)

- ❖ SWRO followed by a hybrid process of BSR and BWRO
- ❖ SWRO followed by electro dialysis reversal EDR

In recent years, membrane manufactures have developed RO membranes with boron rejections of 91–96%. However, most of the current desalination plants have to implement the additional treatment steps such as pH adjustment of feed water, post-treatment of RO permeate with ion exchange or several pass stage of permeate in order to improve boron rejection. In addition, several process configurations have been proposed to obtain the low boron concentration of the permeate from RO plant (Cengeloglu et al., 2008).

Kabay et al., investigated the effect of operating pressure and temperature on efficiency of seawater desalination. The tests were carried out at different pressures (55–62 bar) using a single RO module at different feed seawater temperatures. Variables such as pH, conductivity, TDS, salinity, turbidity, relative rejection of some ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^-) and B levels in permeates collected were measured. Quality of permeate was highly dependent on feed seawater temperature. As temperature decreased, lower conductivity, lower turbidity but higher mineral rejections were obtained for the permeate stream. In terms of boron removal, higher values of rejection were obtained for decreasing values of temperature. However, boron removal was about 80%, which is the lowest level among the studied species. (Guler et al., 2008).

1.3. Aim of the study

In this study, we aim to investigate the effect of applied pressure and membrane configuration on removal of boron from geothermal water by a small scale brackish reverse osmosis (BWRO) system. The small scale spiral wound reverse osmosis system was installed at Izmir-Balçova geothermal field. One of the most important parameters affecting performance of reverse osmosis system was membrane configuration. The system contained two parallel mounted Film-Tec™ BW30-2540 membranes. This design provided us to work with both single and double membrane configurations at 200 L/h constant concentrate flow rate. The effect of operating pressure on performance of reverse osmosis system was investigated for 12 bar and 15 bar of constant operating pressure for both membrane configurations. The performance of the reverse osmosis system was investigated in terms of permeate quality and quantity. Permeate quality was investigated in terms of salt and boron rejections. In addition, chemical composition of permeate was investigated using various analytical and instrumental methods. The quantity of permeate was checked by permeate flux and permeate recovery.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Feed geothermal water

Geothermal water was obtained from discharge lines of geothermal plant of Izmir Geothermal Co.. Characteristics of the geothermal water were summarized in Table 2.1.

Table 2.1 Characteristics of the feed geothermal water

Test Number	Temperature (°C)	Conductivity (μ S/cm)	TDS (mg/L)	pH	Salinity (‰)	B (mg/L)
1	25.5	1757	879	7.4	0.7	9.15
2	26.5	1679	840	7.3	0.7	9.15
3	28.6	1719	860	7.2	0.7	9.26
4	27.6	1731	866	7.3	0.7	8.80
5	27.8	1726	863	7.2	0.7	8.89
6	31.5	1764	882	6.9	0.7	9.11
7	31.4	1772	887	7.3	0.7	8.91
8	28.9	1770	885	7.4	0.7	10.1
9	27.8	1762	881	7.4	0.7	11.5
10	25.9	1900	950	8.00	0.8	10.4
11	24.0	1891	945	8.40	0.8	10.4
12	24.7	2060	1031	8.84	0.9	9.98
13	22.7	2260	1128	9.40	1.0	10.4
14	22.2	2740	1372	9.96	1.3	9.89
15	22.3	3280	1640	10.47	1.6	9.57
16	20.8	1994	997	8.10	0.8	10.3
17	17.6	2030	1018	8.48	0.9	10.2
18	17.8	2260	1132	9.20	1.0	10.3

Table 2.1 (continued) Characteristics of the feed geothermal water

Test Number	Temperature (°C)	Conductivity ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	pH	Salinity (‰)	B (mg/L)
19	18.7	2500	1251	9.60	1.1	10.4
20	17.0	2850	1424	9.96	1.3	10.4
21	15.7	3180	1590	10.50	0.9	9.96
22	19.7	1898	949	6.80	0.8	10.9
23	16.4	1871	937	7.00	0.8	11.3
24	12.6	1813	906	6.90	0.7	11.3
25	8.00	1770	885	7.00	0.7	11.0
26	13.9	1762	881	7.00	0.7	10.6
27	16.7	1757	876	7.00	0.7	10.3
28	18.1	1752	879	7.00	0.7	10.3
29	19.1	1757	877	7.10	0.7	10.3
30	17.5	1749	875	7.10	0.7	10.8
31	16.9	1750	876	7.00	0.7	10.4

Tests 1-9 was carried out between (14.05.09-03.09.09).

Tests 10-31 was carried out between (14.09.09-27.02.09)

2.1.2 Chemicals

- Antiscalant PC100
- Azomethine-H Monosodium salt hydrate: $\text{C}_{17}\text{H}_{12}\text{NNaO}_8\text{S}_2$, Fluka
- H_3BO_3 : 99.8 %, (Merck)
- NaOH : 99.9 %, Merck
- NaCl : (Merck)
- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$: (Merck)
- KCl (J.T.Baker)
- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (J.T.Baker)
- Na_2SO_4 (ANALAR)
- HCl (37%), (Baker)
- Ultra pure water

2.2 Equipments

2.2.1 Brackish water reverse osmosis (BWRO) equipment

2.2.1.1 Feed tanks

Two connected feed tanks (950 L + 950 L=1900 L) were used (Figure 2.1).



Figure 2.1 Geothermal water storage tanks

2.2.1.2 Pumps

Low pressure pump: Grundfos CH2-60 with capacity 2.5 m³/h max (Figure 2.2)



Figure 2.2 Low pressure pump

High pressure pump: GAMAK MSD 7141- Fluidotech PO/PA 074 with Pressure: 16 bar and Volume: 100 L/sec (Figure 2.3).



Figure 2.3 High pressure pump

2.2.1.3 Sand Filter

For primary filtration a sand filtration was performed (Figure 2.4).



Figure 2.4 Sand filter

2.2.1.4 Cartridge filters

10-micron and 5-micron cartridge filters were used for further filtration (Figure 2.5).



Figure 2.5 Cartridge filters

2.2.1.5 BWRO membranes

Reverse osmosis system contained two parallel mounted brackish reverse osmosis membranes. The membranes were spiral wound produced by Dow Chem. Co. Specifications of FilmTec SW30-2540 membranes were given in Table 2.2.

The dimensions of these membranes were shown in Figure 2.6 while membrane modules in Figure 2.7.

Table 2.2 Properties of FilmTec BW30-2540 membranes (Dow liquid separations, 2005).

Membrane Type (BW30-2540)	Polyamide Thin-Film Composite
Maximum Operating Temperature	113°F (45°C)
Maximum Operating Pressure	600 psi (41bar)
Maximum Pressure Drop	15 psig (1.0 bar)
pH Range, Continuous Operation ^a	2-11
pH Range, Short Term Cleaning ^b	1-13
Maximum Feed Silt Density Index	SDI 5
Free Chlorine Tolerance ^c	<0.1 ppm
Active Area	28 ft ² (2.6 m ²)
Permeate Flow Rate ^b	850 gpd (3.2 m ³ /d)
Stabilized Salt Rejection	99.5 %

^a : Maximum temperature for continuous operation above pH 10 is (35°C).

^b : Refer to Cleaning Guidelines in specification sheet 609-23010.

^c : Under certain conditions, the presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty, FilmTec recommends removing residual free chlorine by pretreatment prior to membrane exposure. Please refer to technical bulletin 609-22010 for more information.

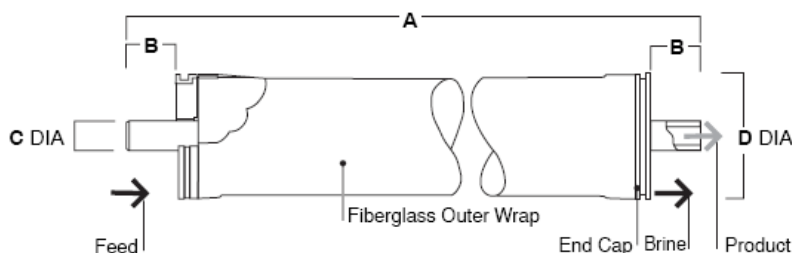


Figure 2.6 Dimensions of FilmTec spiral wound RO membrane BW30 2540 [A: 40 Inches (1016 mm), B: 1.19 Inches (30.2 mm), C: 0.75 Inches (19 mm), D: 2.4 Inches (61 mm)].



Figure 2.7 Spiral wound BWRO membranes

2.2.1.6 Control panel and dosage pumps

Control panel contains two manometers, two flow-meters. Dosage pumps were shown in Figures 2.8 and 2.9. A photo of whole SWRO system was given in Figure 2.10.



Figure 2.8 Control Panel

Figure 2.9 Dosage Pumps



Figure 2.10 BWRO system

2.3 Analytical Methods for Water Analysis

2.3.1 TDS, salinity, conductivity, pH measurements

Measuring some parameters such as TDS, electrical conductivity, salinity to determine the quality of product water and feed water were performed by portable conductivity meter (WTW Cond 330i/SET). pH values of water samples were measured by a portable digital pH meter (WTW pH 315i/SET).

2.3.2 Analysis of Boron

2.3.2.1 Azomethine-H method

Boron concentration in the samples of Balçova BWRO system was determined by Azomethine-H method. Jasco SSE-343, V-530 UV/VIS Spectrophotometer was used in order to perform the spectrophotometric analyses.

Reagents:

Azomethine-H solution: 0.5 g of Azomethine-H and 1 g of ascorbic acid are dissolved in 50 mL pure water and immediately transferred to a plastic bottle. (This solution was made up at each analysis day).

Buffer solution: This solution is prepared by dissolving 50 g of ammonium acetate in 100 mL of pure water and by adding to this solution 25 mL of glacial acetic acid and 1.4 g of EDTA di-sodium salt.

The procedure:

1. 10 mL of sample, 2.5 mL of Azomethine-H solution, and 2.5 mL of buffer solution and are added into a plastic bottle.
2. This mixture is kept at room temperature and in the dark without shaking.
3. After 1 h, absorbances of the samples are read at 415 nm using the spectrophotometer.

The analyses were performed in the calibration range of 0.1-2.0 mg B/L at 415 nm.

Azomethine-H method was highly linear with a regression coefficient of 1.000 as shown in Figure 2.11.

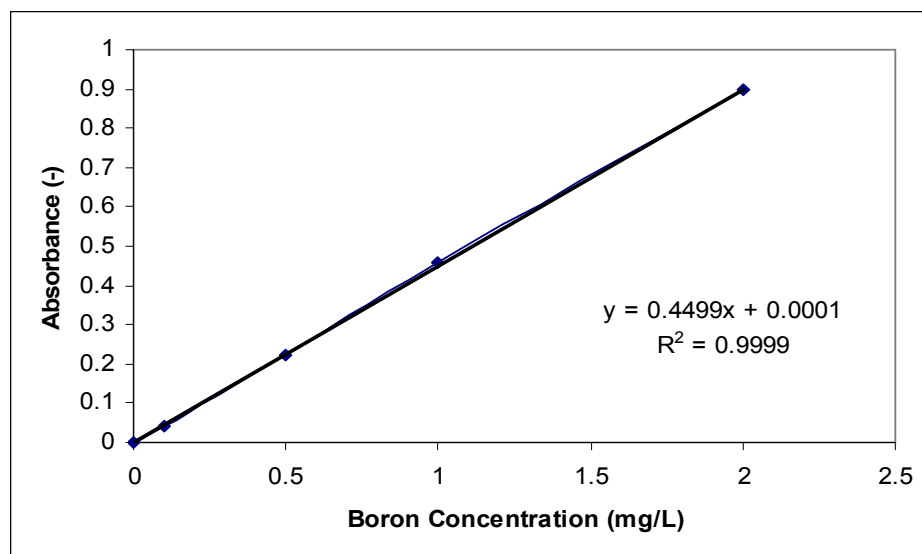


Figure 2.11 Calibration curve obtained at 415 nm using Azomethine-H method

2.3.3 Anion analysis (Cl^- , SO_4^{2-}) by Ion Chromatography

The concentration of chloride and sulfate was determined by Shimadzu model ion chromatography equipment (Figure 2.12).



Figure 2.12 Shimadzu LC-10 Ai model Chromatography

The equipment contains an LC 10Ai liquid delivery pump, a CDD 6A conductivity detector, a CTA 10A oven and a CBM 10A system controller.

The concentrations of chloride and sulfate in permeate and feed water samples were determined with used MCI GEL column. The column contains NR_3^+ functional group. For analysis of anions, a mobil phase which contains vanillic acid (3mM) and N-methyldiethanolamine (2.8mM) was prapered. Mobil phase was passed through the column with 1.2 ml/min of flow rate.

Before injecting the samples, a prefiltration was occured with 0.25 μm membrane filter in order to prevent to fouling in the column by some small particles. Calibration curves were obtained by giving standart solutions of both chloride and sulfate ions.

The concentrations of unknown samples were calculated from calibration curves obtained (Figure 2.13 and 2.14).

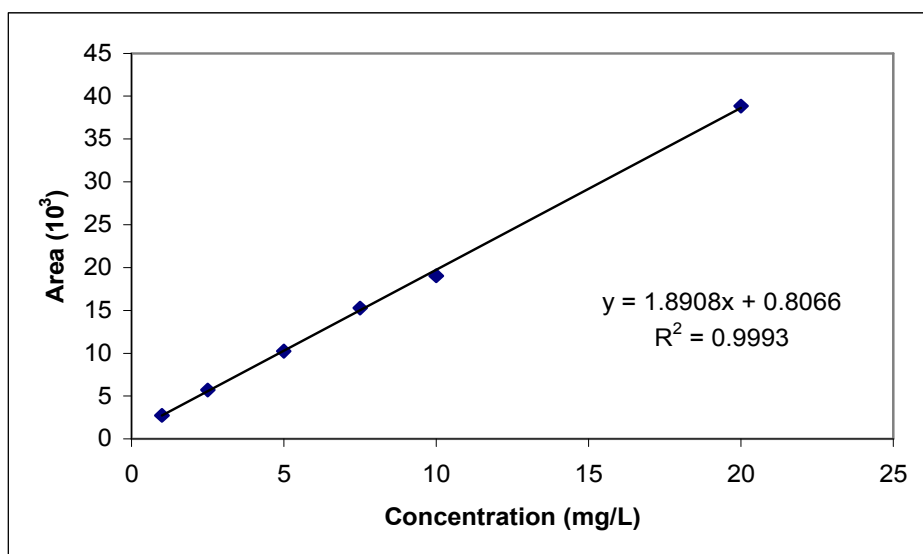


Figure 2.13 Calibration curve of chloride.

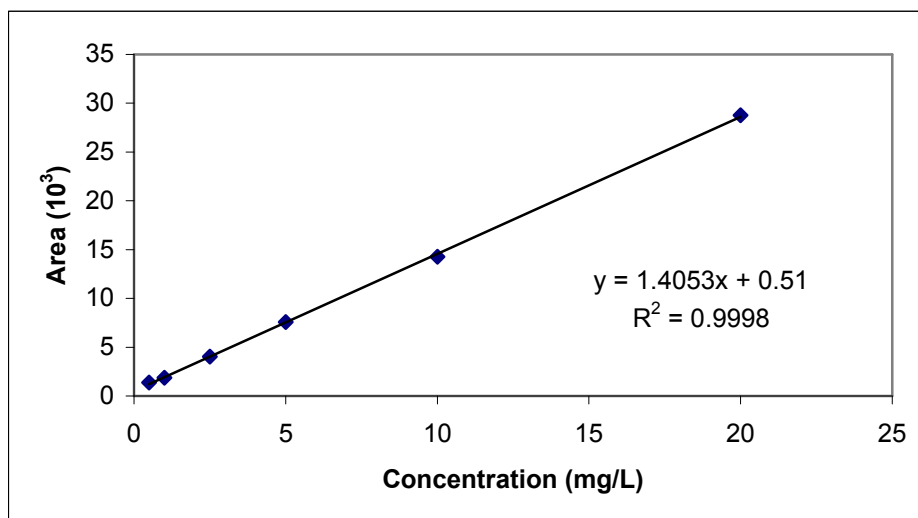


Figure 2.14 Calibration curve of sulfate.

2.3.4 Cation (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) analysis by AAS

The concentrations of cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were determined by Varian 10 Plus Model Atomic Absorption Spectrophotometer (Figure 2.15).

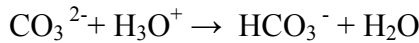
The concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} in permeate and feed water samples were analysed by using calibration curves which were obtained by standart solutions. Feed water samples were diluted 25 times and permeate samples were measured without dilution.



Figure 2.15 Varian 10 Plus Atomic Absorption Spectrophotometer

2.3.5 CO_3^{2-} and HCO_3^- analysis by titration

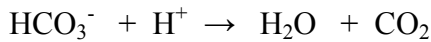
The concentrations of CO_3^{2-} and HCO_3^- in feed and permeate samples was determined by alkalimetric titration method. In this method, a 100.0 ml of water sample (permeate and feed) was measured by a burette and transferred into a 250 ml volumetric flask. 100 μL phenolphthalein indicator was added and sample was titrated with 0.1011 N standard hydrochloric acid until the colorless solution turned into the pink color. Until this point the volume of hydrochloric acid was V_1 . After the first equivalent point methyl orange indicator was added and the same solution was titrated with standard hydrochloric acid solution until the color turned into onion red color. This volume was called V_2 . The related equations are given below:



$$V_{\text{CO}_3^{2-}} = 2V_1$$

$$m_{\text{CO}_3^{2-}} = V_{\text{CO}_3^{2-}} (\text{mL}) \times M_{\text{HCl}} (\text{mol/L}) \times 60 (\text{g/mol}) \times 10 = \dots \text{mg CO}_3^{2-} / \text{L}$$

To calculate the amount of bicarbonate, the following equation was used:



$$V_{\text{HCO}_3^-} = (V_2 - V_1)$$

$$m_{\text{HCO}_3^-} = V_{\text{HCO}_3^-} (\text{mL}) \times M_{\text{HCl}} (\text{mol/L}) \times 61 (\text{g/mol}) \times 10 = \text{mg HCO}_3^- / \text{L}$$

$$\text{MW} (\text{CO}_3^{2-}) = 60 \text{ g/mol}$$

$$\text{MW} (\text{HCO}_3^-) = 61 \text{ g/mol} \quad 10 = \text{Dilution factor}$$

2.3.6 Analysis of Si

Si concentrations of samples were determined by a standard colorimetric method using Merck Nova 60 model colorimeter (Figure 2.16). In sulfuric acid solution, silicate ions react with molybdate ions to form a yellow heteropolyacid. This is reduced to silicomolybdenum blue that is determined colorimetrically. Measuring range was shown in Table 2.3.



Figure 2.16 Spectroquant Nova 60 colorimeter.

Table 2.3 Measuring range: 0.005 - 5.00 mg Si /L

Cell (mm)	Measuring Range	
	SiO ₂ (mg/L)	Si (mg/L)
50	0.011 - 1.600	0.005 - 0.750
20	0.11 - 5.35	0.05 - 2.50
10	0.21 - 10.70	0.10 - 5.00

3. RESULTS AND DISCUSSION

3.1 BWRO Desalination Tests at Balçova, Izmir

Desalination tests were performed at Balçova geothermal field by small scale reverse osmosis system which contained Filmtech BW30-2540 membranes. Membrane modules were spiral wound. Reverse osmosis system contained two parallel mounted brackish water membranes. Desalination performance of reverse osmosis system was investigated as a function of such parameters as applied pressure and membrane configuration.

Desalination tests were performed during 3 h of experimental time period. Water samples were taken at each 20 min. Electrical conductivity, TDS, salinity and pH values of the feed, permeate and concentrate were measured during the experiments by field type portable instruments.

For all the tests, flow rate of concentrate were kept constant at about 200 L/h. Antiscalant solution was added at a dosage rate of 10% with a dosage pump for single membrane configuration and at a dosage rate of 20% for double membrane configuration.

3.1.1 Effect of operating pressure on RO performance

3.1.1.1 Tests performed with single membrane configuration

One of the most important parameters affecting reverse osmosis system performance is operating pressure which is the driving force of reverse osmosis process. In this study, the effect of applied pressure on desalination and boron removal performances was investigated at 12 bar and 15 bar of operating pressures. The effect of applied pressure on reverse osmosis performance was investigated for both single and double membrane configurations. Parallel tests for each experiment were carried out. Desalination performance of reverse osmosis system was determined by the quality and quantity analyses of product water. The qualities of feed and product waters were checked by measuring electrical conductivity, total dissolved solid (TDS), pH, salinity during each experiment in the field and also by determining concentrations of some anions (SO_4^{2-} , Cl^- , HCO_3^-), cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), B and Si in the laboratory after each

experiment was completed. Quantity of product water was defined in terms of permeate flux and water recovery.

Average values of the measured quantities for feed geothermal water and permeate samples were given in Tables 3.1 and 3.2.

Table 3.1 Experimental data for feed geothermal water during single membrane operation at pressures of 12 bar and 15 bar (Tests 3, 4, 5, 9).

Feed Geothermal Water							
P (bar)	t (°C)	EC (μ S/cm)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)
12	28.6	1719	7.2	860	0.7	317.7	9.26
12	27.6	1731	7.3	866	0.7	262.6	8.80
15	27.8	1726	7.2	863	0.7	334.5	8.89
15	27.8	1762	7.4	881	0.7	325.7	11.5

Table 3.2 Experimental data for permeate for single membrane operation at pressure of 12 bar and 15 bar (Tests 3,4,5,9).

Permeate									
P (bar)	t ^a (°C)	EC ^b (μ S/cm)	pH	TDS ^c (mg/L)	Salinity ^d (‰)	Q ^e (L/h)	B (mg/L)	Flux (L/m ² h)	Y ^f (%)
12	30.5	25.25	5.39	12.56	0.0	104.0	4.90	40.0	47.0
12	28.9	23.34	5.31	11.89	0.0	98.13	4.67	37.7	46.1
15	29.1	22.53	5.16	11.11	0.0	119.9	4.49	46.1	35.8
15	28.7	17.14	5.69	8.78	0.0	114.8	4.83	43.2	35.3

^a: Temperature, ^b: Electrical conductivity, ^c: Total dissolved solid, ^d: Salinity, ^e: Flow rate, ^f: Permeate recovery.

Figure 3.1 shows the variations of permeate flux with respect to applied pressure for single membrane operation. For each operating pressure (12 and 15 bar), two parallel tests were carried out.

The applied pressure affects the permeate quality and quantity. The flux values increased with increasing pressure. As shown in Figure 3.1, water flux across the membrane increased with increasing pressure. Although the osmotic pressure stayed constant, applied pressure increased. When 15 bar of pressure was applied, the maximum flux 46% was obtained.

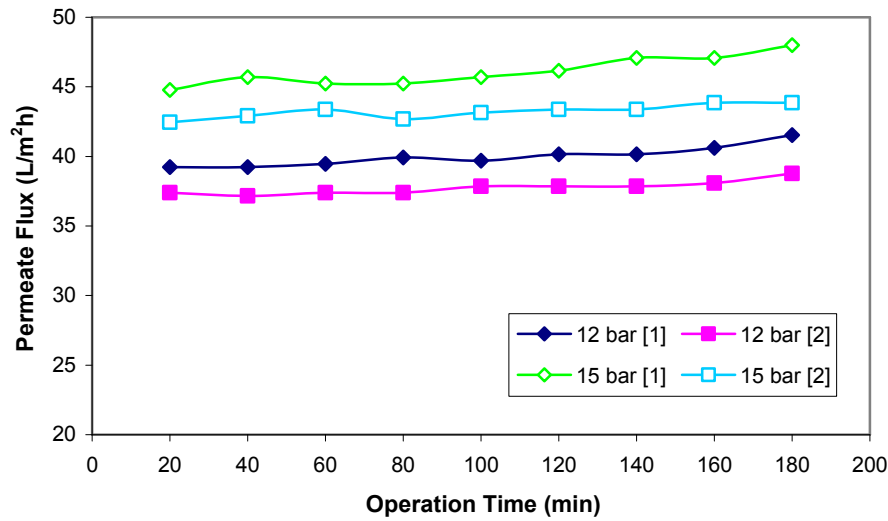


Figure 3.1 Effect of pressure on permeate flux for single membrane operation.

Permeate quantity depends on the applied pressure and thus water recovery values increased with increasing pressure. Figure 3.2 confirmed that permeate recovery increased with increasing pressure. Permeate recovery increased from 32 to 36% by increasing pressure from 12 to 15 bar.

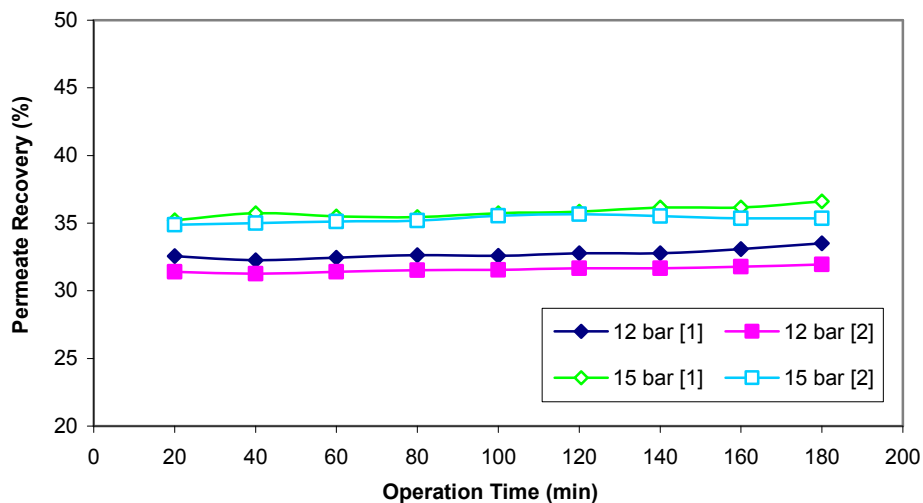


Figure 3.2 Effect of pressure on permeate recovery for single membrane operation.

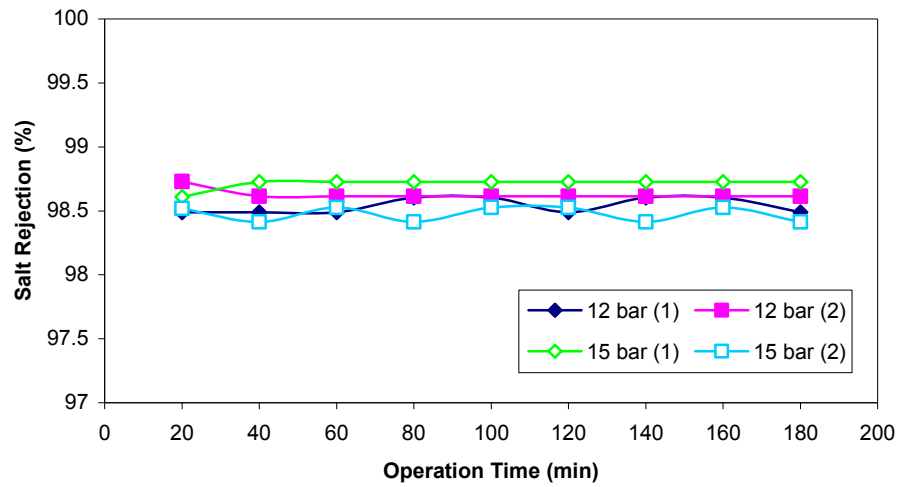


Figure 3.3 Effect of pressure on salt rejection for single membrane operation.

Salt rejection increased with increasing applied pressure. As with increasing pressure water flux increased and the solute flux remained constant so the quality of product water increased with increasing pressure. For 12 bar of operating pressure, average salt rejection values of two parallel tests were 98.5% and 98.6%. For 15 bar of operating pressure, these values were 98.7% and 99.0% (Figure 3.3).

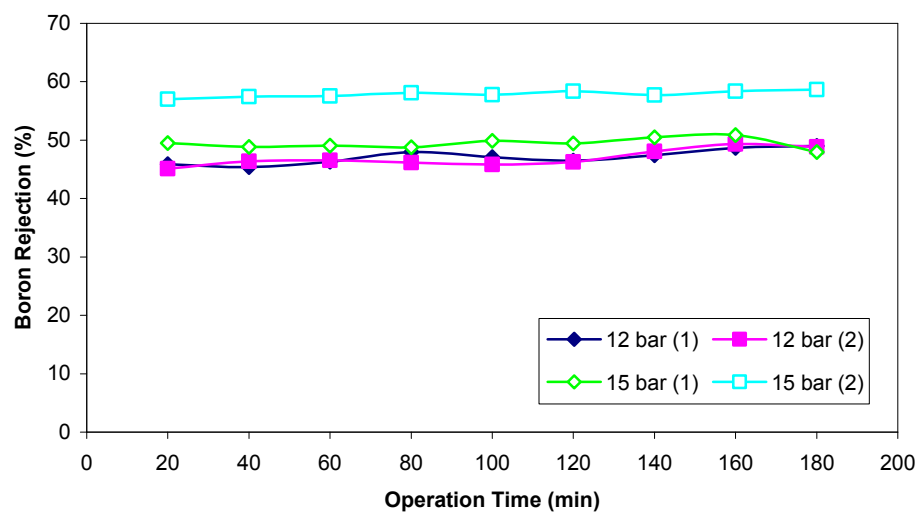


Figure 3.4 Effect of pressure on B rejection for single membrane operation.

Applied pressure also affected the boron rejection performance of reverse osmosis system like salt rejection. As shown in Figure 3.4, average boron rejection of two parallel tests were 47.1% and 47.0% for 12 bar of operating pressure. When operating pressure was 15 bar, the respective values were 49.4 and 57.9%.

In addition, effect of pressure on removal of Cl^- , HCO_3^- , SO_4^{2-} from geothermal water was investigated for single and double membrane configurations. Rejection percentages of ions were calculated using initial feed and permeate concentrations during operation time. The results were given in Figures 3.5-11 as a function of operating time.

At 12 bar of operating pressure, the chloride concentration of feed geothermal water was in the range of 147.2-152.0 mg/L. After desalination test product water contained 2.60-3.23 mg/L of average chloride for parallel tests. At 15 bar of operating pressure conditions, the chloride concentration of feed geothermal water was in the range of 148.3-150.4 mg/L for parallel tests. After desalination test, product water contained 2.21-2.35 mg/L of average chloride for parallel tests.

The chloride rejection was 97.8-98.2% for 12 bar of operating pressure for single membrane operation while the corresponding value was 98.4-98.5% for 15 bar of operating pressure (Figure 3.5).

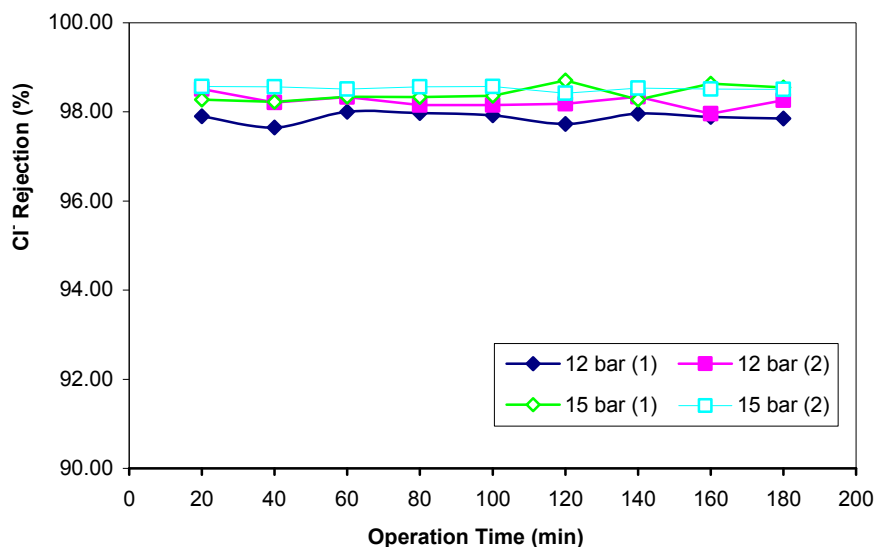


Figure 3.5 Effect of pressure on Cl⁻ rejection for single membrane operation.

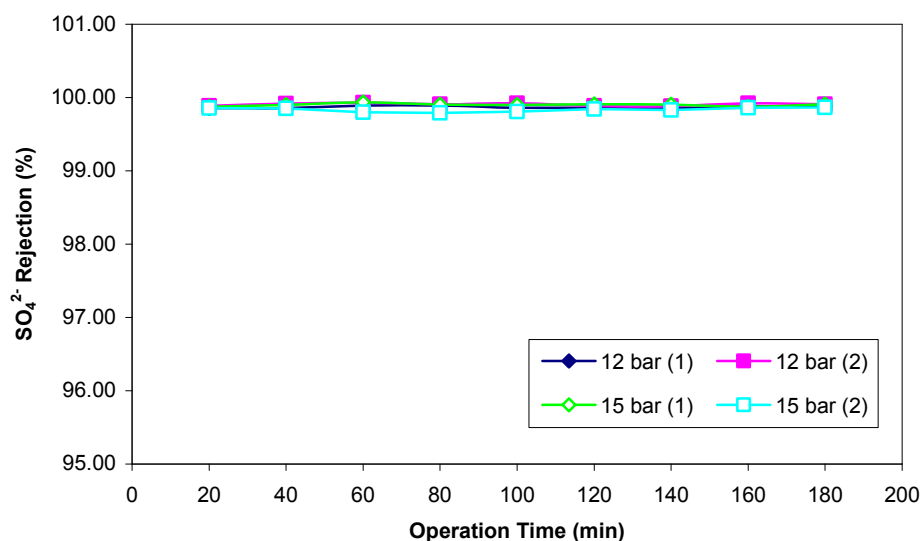


Figure 3.6 Effect of pressure on SO₄²⁻ rejection for single membrane operation.

As seen in Figure 3.6, sulfate rejection was not affected by increased pressure. The carbonate concentration of feed geothermal water was zero because its pH value was below the second pK_a value of carbonic acid. For 12 bar of operating pressure conditions, the bicarbonate concentration of feed geothermal water was in the range of 631.1-632.3 mg/L for parallel tests. After desalination test, product water contained 14.9-16.2 mg/L of bicarbonate for parallel tests. For 15 bar of operating pressure conditions, the bicarbonate concentration of feed geothermal water was 644.0-663.8 mg/L for parallel tests. After desalination test,

product water contained 12.9-14.1 mg/L of bicarbonate. The bicarbonate rejection was 97.4-97.6% for 12 bar of operating pressure for single membrane operation while the corresponding value was 97.8-98.1% for 15 bar of operating pressure (Figure 3.7).

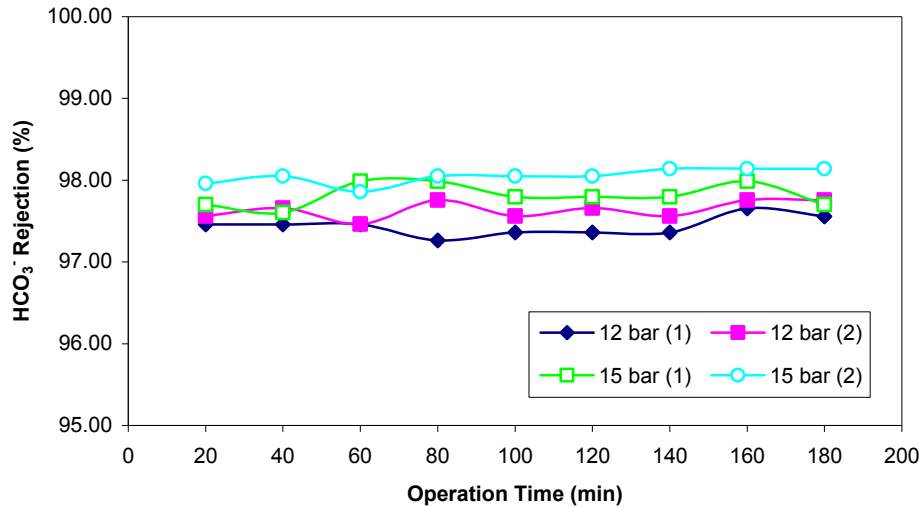


Figure 3.7 Effect of pressure on HCO_3^- rejection for single membrane operation.

Effect of pressure on removal Na^+ , K^+ , Mg^{2+} , Ca^{2+} from geothermal water was investigated for single and double membrane configurations. Percent rejections of ions were calculated using initial feed and permeate concentrations during operation time. The results were given in Figures 3.8-11 as a function of time.

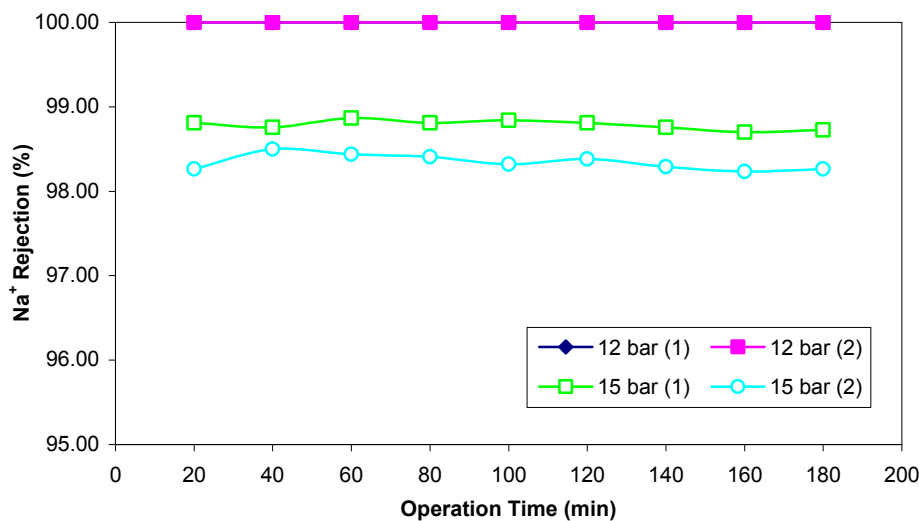


Figure 3.8 Effect of pressure on Na^+ rejection for single membrane operation.

As shown in Figure 3.8, percent Na^+ rejection decreased with an increase in applied pressure. The percent rejection of K^+ increased when the applied pressure increased (Figure 3.9).

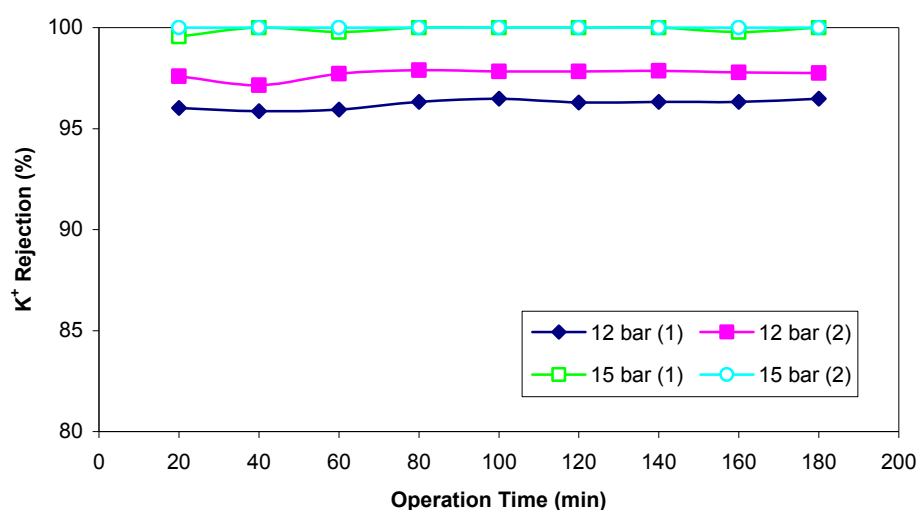


Figure 3.9 Effect of pressure on K^+ rejection for single membrane operation.

When operating pressure increased from 12 bar to 15 bar, Mg^{+2} rejection increased for single membrane configuration as shown in Figure 3.10.

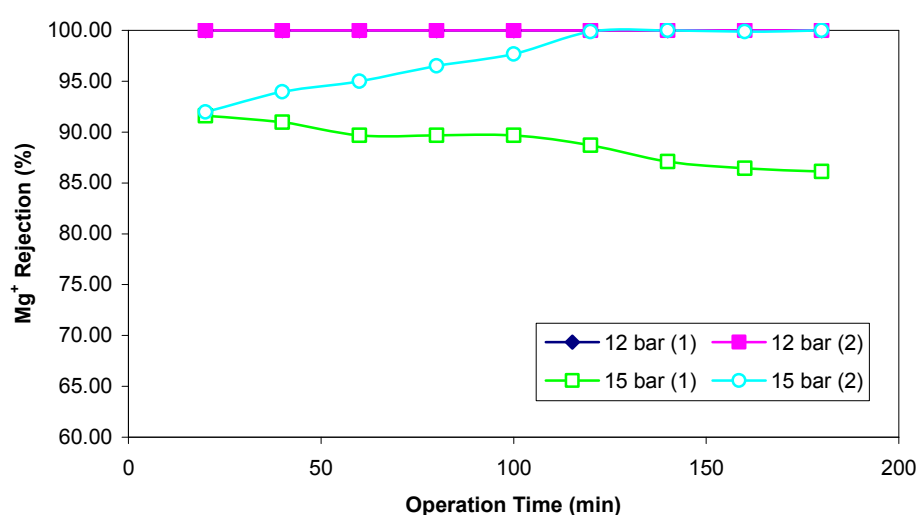


Figure 3.10 Effect of pressure on Mg^{+2} rejection for single membrane operation.

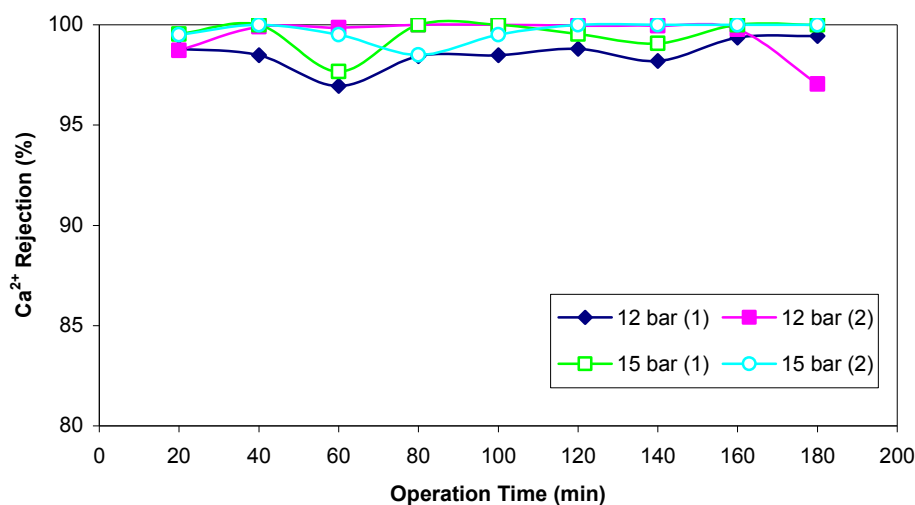


Figure 3.11 Effect of pressure on Ca^{2+} rejection for single membrane operation.

According to the obtained results, the percent rejections were about 98.3-100% for Na^+ , 97.4-99.7% for Ca^{2+} (Figure 3.11), 88.9-100% for Mg^{2+} , 96.2-100% for K^+ using single membrane operation for parallel tests. Si rejection by Filmtec™ BW30-2540 was 99.2% for 12 bar of operating pressure. For 15 bar operating of pressure, Si rejection was 99.3% for single membrane operation. Increasing pressure did not affect the rejection of silica (Figure 3.12).

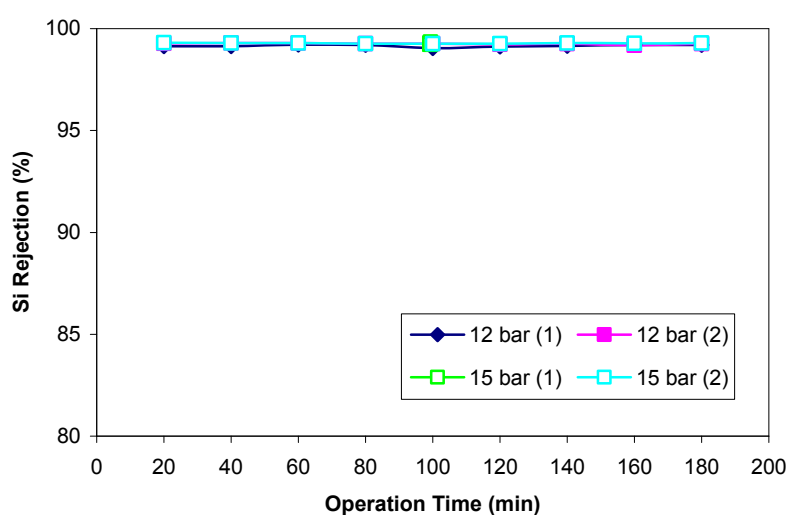


Figure 3.12 Effect of pressure on Si rejection for single membrane operation.

3.1.1.2 Tests performed with double membrane configuration

For double membrane operation, applied pressure affected the desalination performance of the reverse osmosis system. The measured characteristics of feed geothermal water and permeate water were given in Tables 3.3 and 3.4.

Table 3.3 Experimental data of feed geothermal water for double membrane operation at applied pressures of 12 bar and 15 bar (Tests 1,2,7,8).

Feed Geothermal Water							
P (bar)	t (°C)	EC (μS/cm)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)
12	25.5	1757	7.4	879	0.7	400.5	9.15
12	26.5	1731	7.3	840	0.7	392.2	9.15
15	31.4	1772	7.3	887	0.7	450.0	8.91
15	28.9	1770	7.4	885	0.7	425.5	10.1

Table 3.4 Experimental data of permeate for double membrane operation at applied pressure of 12 bar and 15 bar (Tests 1,2,7,8).

Permeate									
P (bar)	t (°C)	EC (μS/cm)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)	Flux (L/m ² h)	Y (%)
12	27.3	31.6	5.5	16.0	0.0	188.2	5.96	36.2	47.0
12	26.3	29.2	5.3	14.6	0.0	180.8	5.73	34.8	46.1
15	32.0	27.9	5.3	14.0	0.0	248.8	5.35	47.8	55.3
15	29.2	24.79	5.4	12.3	0.0	224.8	5.44	43.2	52.8

As operating pressure increased the permeate flux values increased. While the water flux values were in the range of 34.8%-36.2% for 12 bar operating pressure, the respective values were 43.2%-47.8% at 15 bar during parallel tests for double membrane configuration as shown in Figure 3.13.

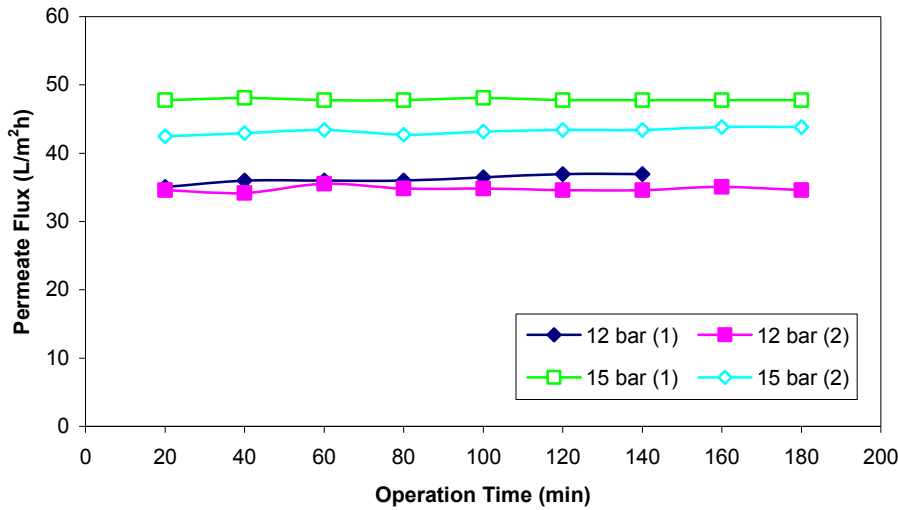


Figure 3.13 Effect of pressure on permeate flux for double membrane operation.

Permeate quantity depends also on operating pressure. When the applied pressure increased, the quantity of product water increased also. For 15 bar of operating pressure permeate recovery was in the range of 52.8-55.3% for parallel tests while the respective values were 46.1-47.0% at 12 bar of operating pressure for double membrane configuration (Figure 3.14).

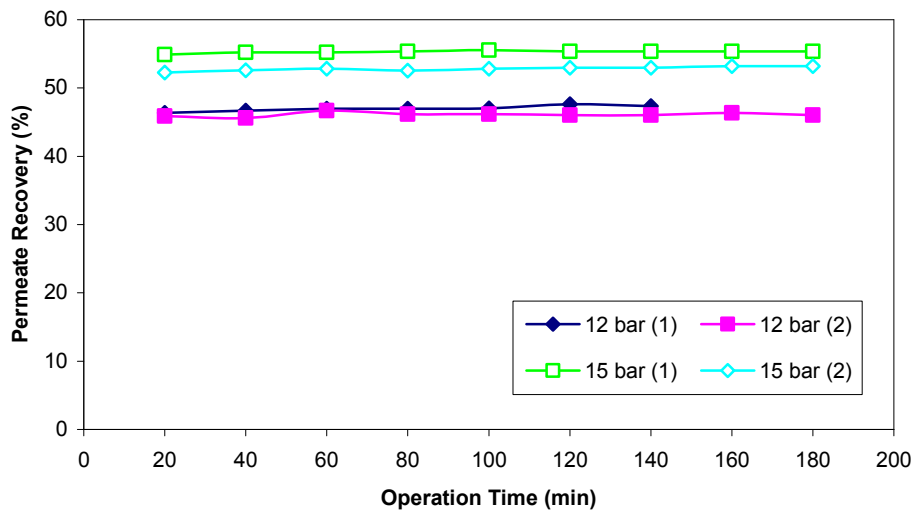


Figure 3.14 Effect of pressure on permeate recovery for double membrane operation.

Applied pressure affects the quality of permeate. The rise in operating pressure was water flux was increasing and the solute flux was constant so the

product water had higher quality. As shown in Figure 3.15, salt rejection increased by increasing applied pressure from 12 to 15 bar.

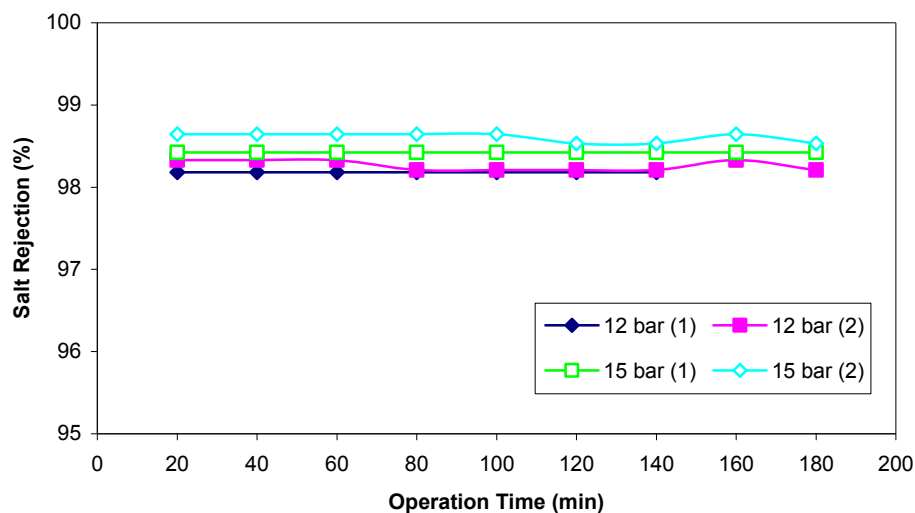


Figure 3.15 Effect of pressure on salt rejection for double membrane operation.

Salt rejection is not affected by pressure. The same amount of salt passes through the membrane at different pressure. However, since more water has passed through the membrane at higher pressure, the absolute salt concentration in the permeate becomes lower. So it appears as if the salt passage decreases and the salt rejection increases when pressure increased. Boron rejection was also affected by applied pressure like salt rejection.

Boron rejection was 34.8% and 37.3% for two parallel operations at 12 bar of operating pressure and the respective values were 39.9% and 46.2% at 15 bar of operating pressure for double membrane configuration as shown in Figure 3.16.

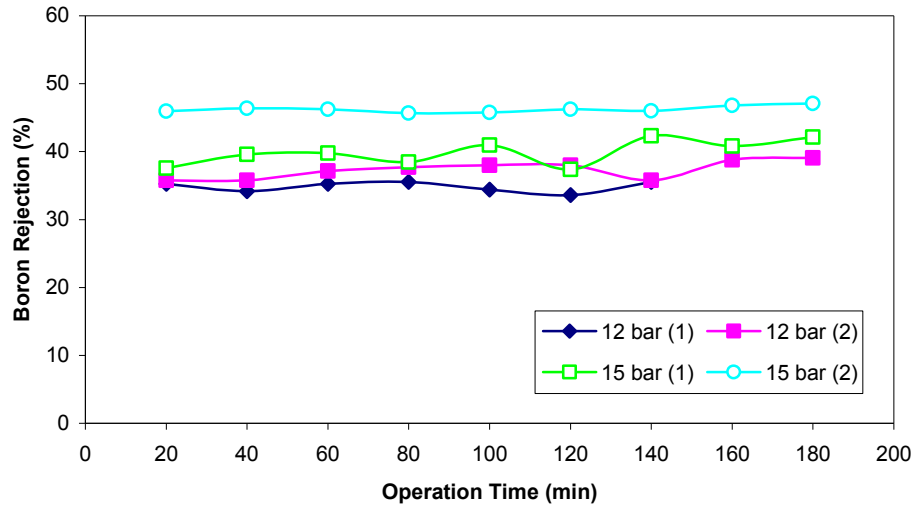


Figure 3.16 Effect of pressure on B rejection for double membrane operation.

The chloride rejection was 96.9% at 12 bar of operating pressure and 98.2% at 15 bar of operating pressure. As shown in Figure 3.17, as the operating pressure increased, the rejection of chloride increased also.

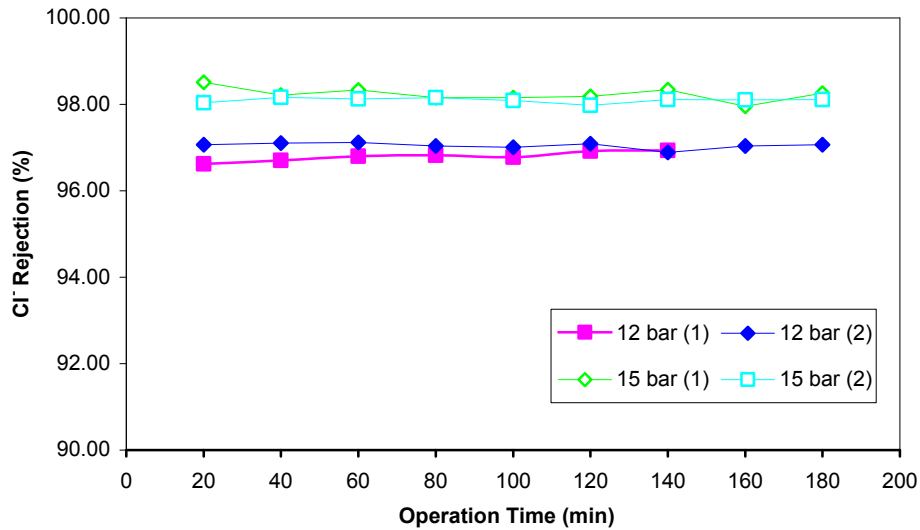


Figure 3.17 Effect of pressure on Cl⁻ rejection for double membrane operation.

Figure 3.18 shows the variation of sulfate rejection with respect to operation time for double membrane configuration. The sulfate rejection was 99.8% for 12 bar of operating pressure and the respective value was 99.9% for 15 bar of operating pressure.

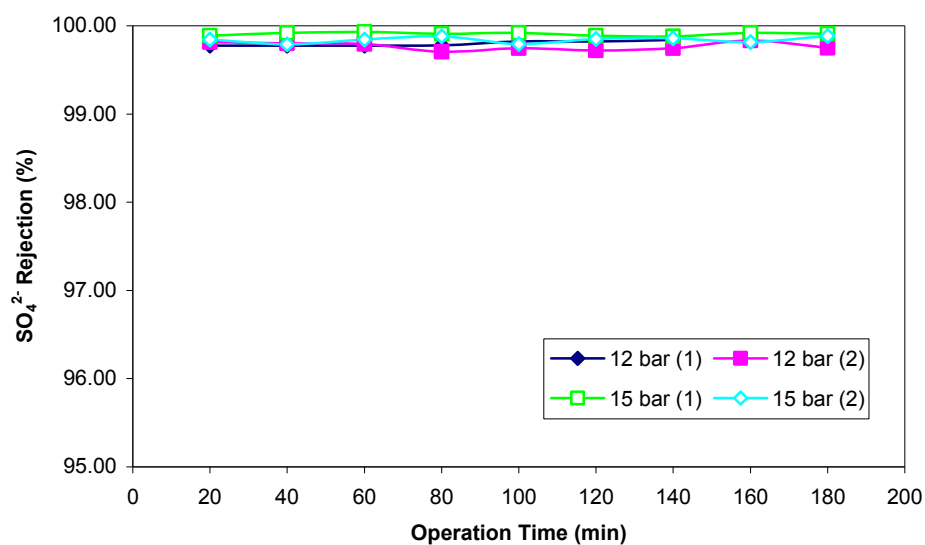


Figure 3.18 Effect of pressure on SO_4^{2-} rejection for double membrane operation.

As seen in Figure 3.19 the rejection of bicarbonate for 12 bar of operating pressure was 97.6% and 98.0% for 15 bar operating pressure.

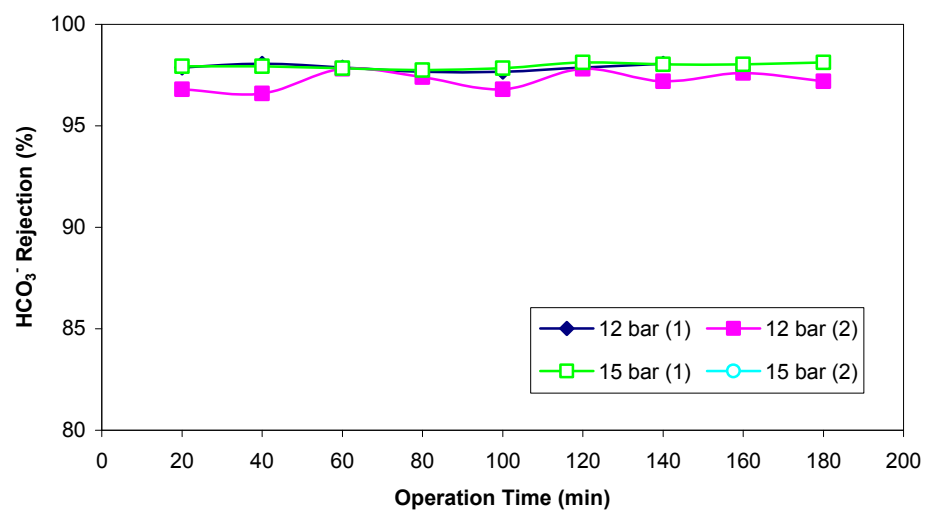


Figure 3.19 Effect of pressure on HCO_3^- rejection for double membrane operation.

Surprisingly, rejection of Na^+ declined by increasing pressure. This was considered to be due to the experimental error during AAS analysis of Na^+ .

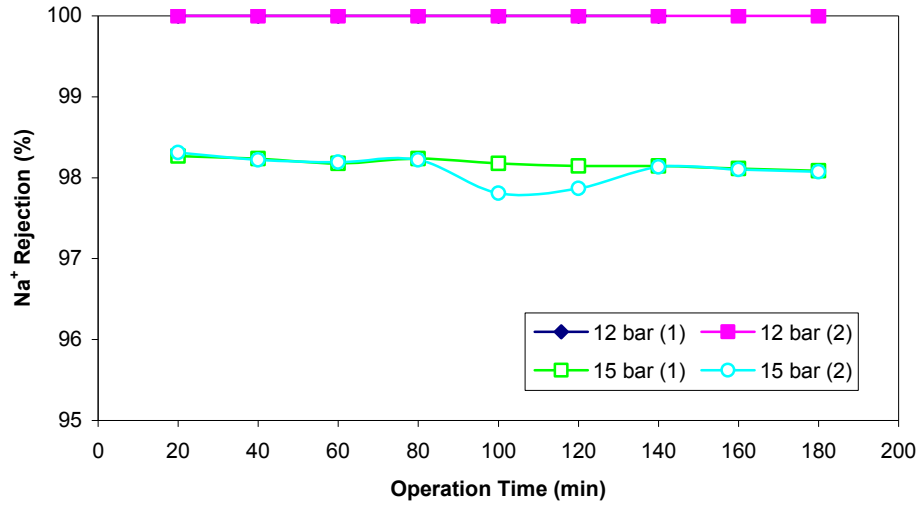


Figure 3.20 Effect of pressure on Na⁺ rejection for double membrane operation.

As shown in Figure 3.21, when operating pressure increased from 12 bar to 15 bar, the rejection of K⁺ increased from 96.3% to 100%.

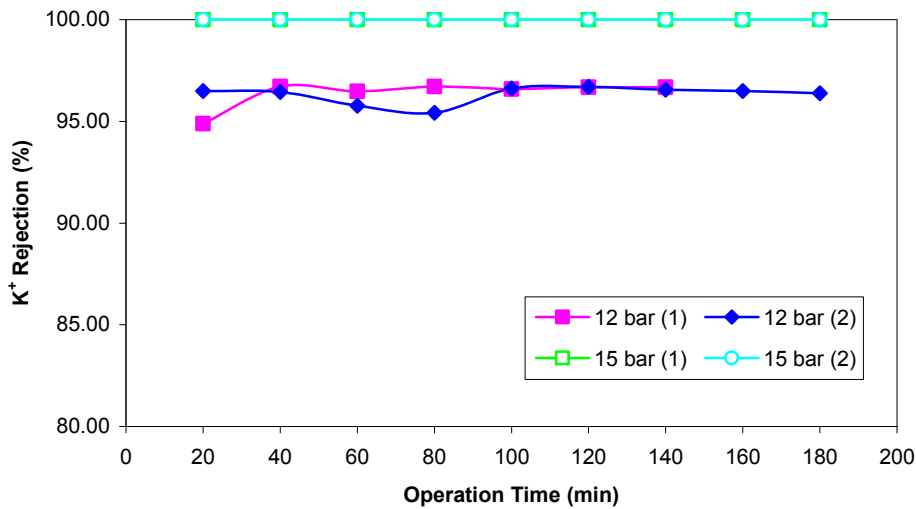


Figure 3.21 Effect of pressure on K⁺ rejection for double membrane operation.

It was obtained that the rejection of Ca²⁺ increased from 97.9 to 99.8% with an increase in applied pressure from 12 to 15 bar for double membrane configuration as shown in Figure 3.22.

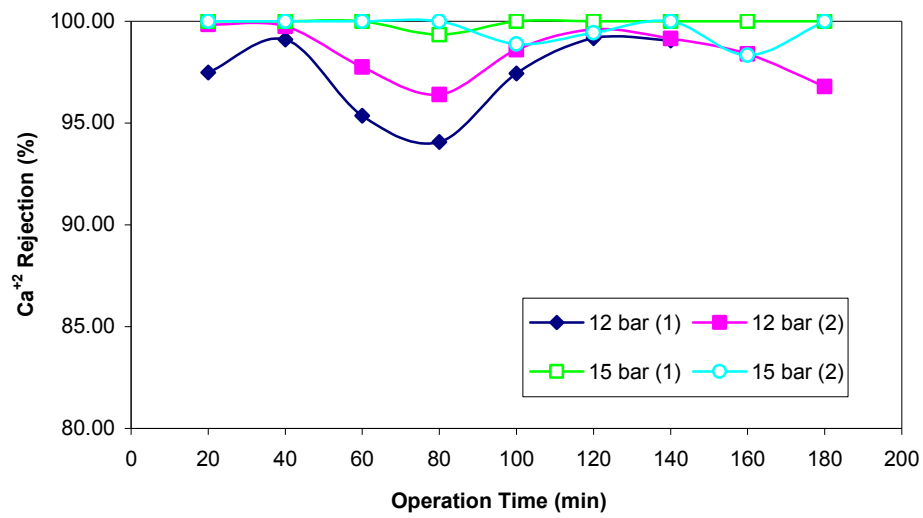


Figure 3.22 Effect of pressure on Ca^{+2} rejection for double membrane operation.

If the applied pressure increased, the rejection of Mg^{+2} was decreased as seen in Figure 3.23.

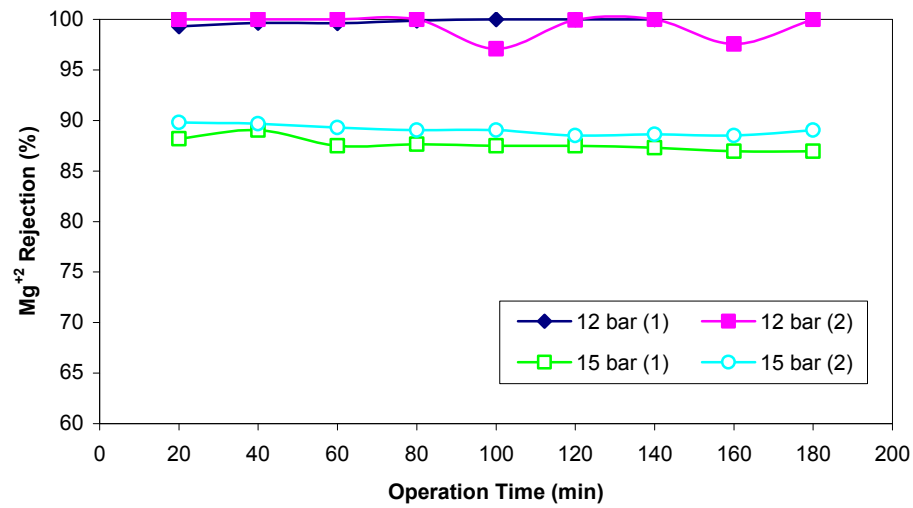


Figure 3.23 Effect of pressure on Mg^{+2} rejection for double membrane operation.

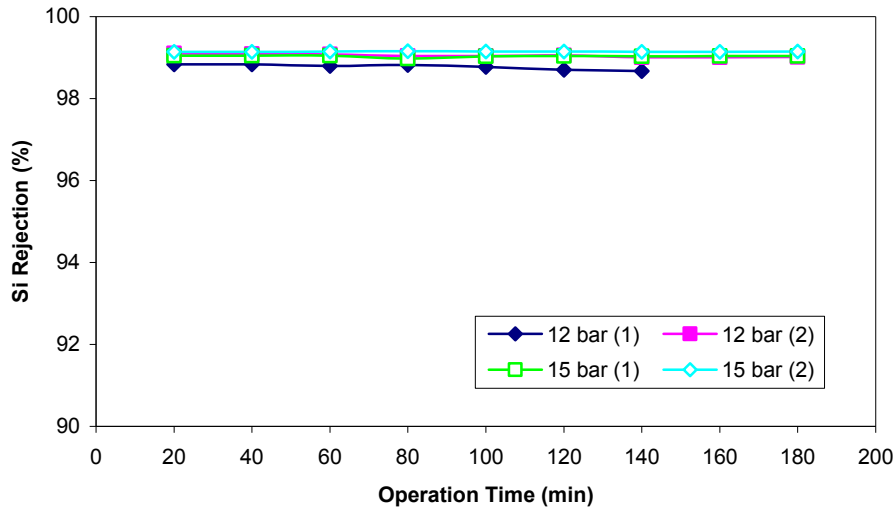


Figure 3.24 Effect of pressure on Si rejection for double membrane operation

At 12 bar of constant operating pressure, Si rejection was 98.9%. With an increase in pressure from 12 to 15 bar, Si rejection increased to 99.1% (Figure 3.24).

3.1.2 Effect of membrane configuration on RO performance

3.1.2.1 Tests performed at 12 bar operating pressure

The effect of membrane configuration on reverse osmosis system performance was investigated for two different membrane configurations: single and double membrane configurations. Reverse osmosis system contained two parallel mounted BWRO membranes so this gave us the chance to investigate the effect of membrane configuration on desalination performance of system for both single and double membrane configurations at constant operating pressure. At 12 bar and 15 bar of operating pressures, the desalination performance was investigated by measuring such characteristics as product water quality and quantity for both membrane configurations, applying 200 L/h of concentrate flow rate.

Experimental data obtained for feed geothermal water and permeate samples for 12 bar of operating pressure were given in Tables 3.5 and 3.6, respectively.

Table 3.5 Experimental data of feed geothermal water at 12 bar of applied pressure for single and double membrane configurations (Tests, 3, 4, 1, 2).

Feed Geothermal Water							
Membrane Configuration	t (°C)	EC (μS/cm)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)
Single	28.6	1719	7.2	860	0.7	317.7	9.26
Single	27.6	1731	7.3	866	0.7	262.6	8.80
Double	25.5	1757	7.4	879	0.7	400.5	9.15
Double	26.5	1679	7.3	840	0.7	392.2	9.15

Table 3.6 Experimental data of feed geothermal water at 12 bar of applied pressure for single and double membrane configurations (Tests, 3, 4, 1, 2).

Permeate									
Membrane Configuration	T (°C)	EC (μS/cm)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)	Flux (L/m ² h)	Y (%)
Single	30.5	25.2	5.39	12.6	0.0	104.0	4.90	40.0	47.0
Single	28.9	23.3	5.31	11.9	0.0	98.13	4.67	37.7	46.1
Double	27.3	31.6	5.51	16.0	0.0	188.2	5.96	36.2	47.0
Double	26.3	29.2	5.39	14.6	0.0	180.8	5.73	34.8	46.1

At 12 bar of operating pressure conditions, the membrane configuration affects the quantity of permeate. For the same concentrate flow rate (200 L/h), permeate volume was larger with two membranes because of the increasing effective membrane area (Figure 3.25).

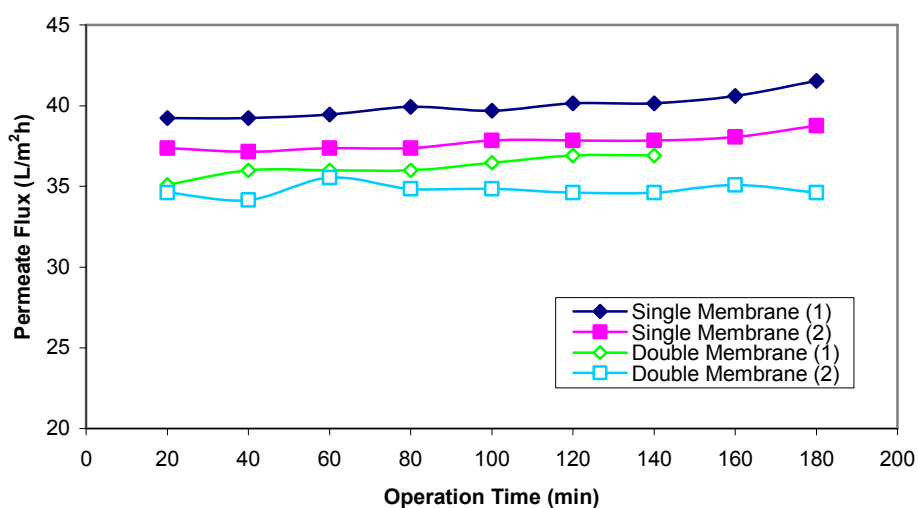


Figure 3.25 Effect of membrane configuration on permeate flux for 12 bar of operating pressure.

If the flow rate of retentate is kept constant for both membrane configurations at the same operating pressure, the permeate recovery was expected to increase with double membrane configuration because the effective membrane area of double membrane configuration is larger than that of single membrane configuration. Figure 3.26 proved this expectation.

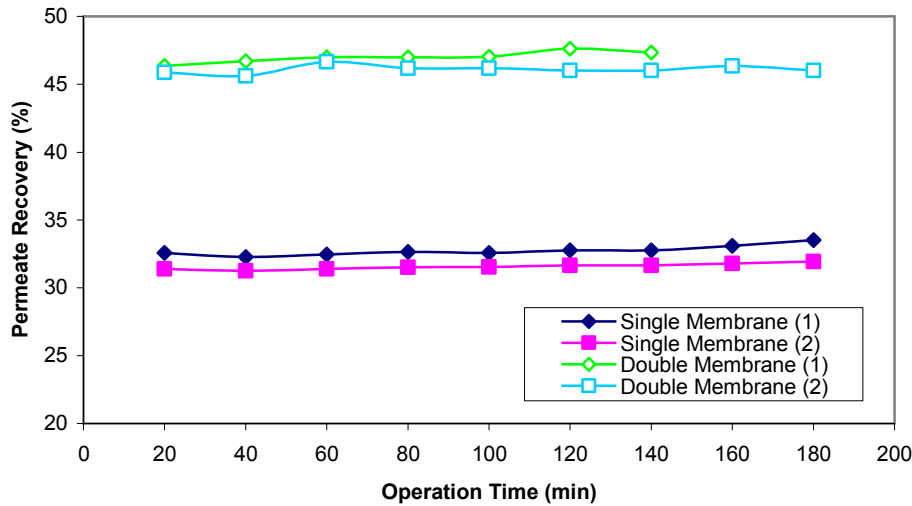


Figure 3.26 Effect of membrane configuration on permeate recovery for 12 bar of operating pressure.

When the larger volume of permeate passed through the membranes of BWRO system with double membranes configuration, the larger amount of salt starts to pass through membrane also. Because of this reason, the salt rejection decreased for BWRO membrane with double membrane configuration (Figure 3.27).

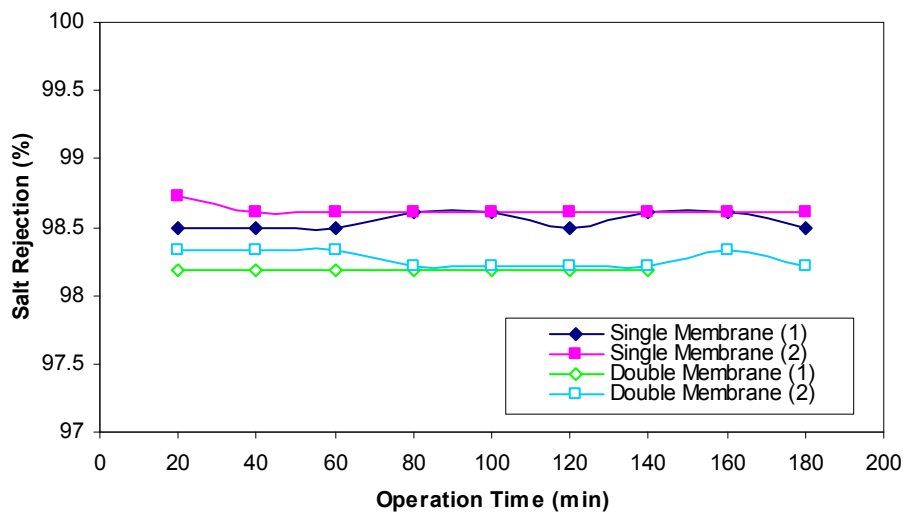


Figure 3.27 Effect of membrane configuration on salt rejection for 12 bar of operating pressure.

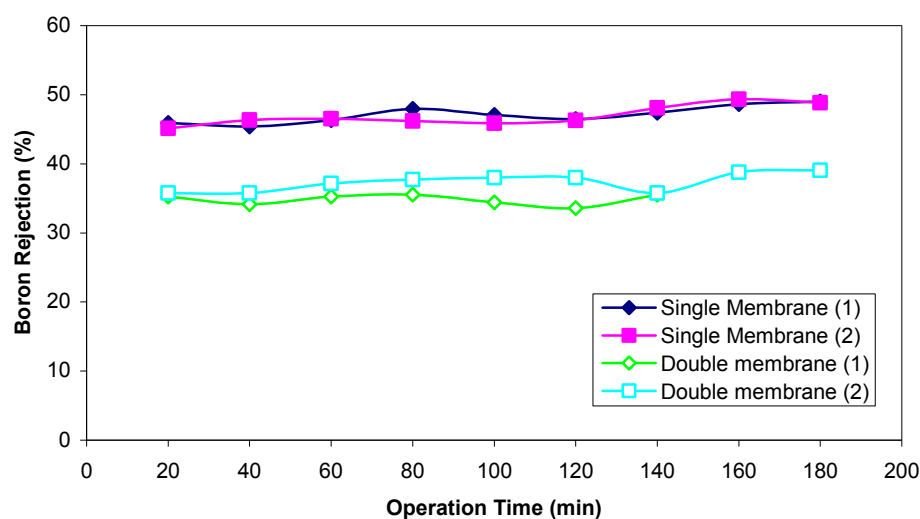


Figure 3.28 Effect of membrane configuration on B rejection for 12 bar of operating pressure.

Boron rejection showed the same trend like salt rejection. If the permeate recovery increased working with two membranes, the rejection of boron decreased also. For double membranes configuration, 36.1% of average boron rejection was achieved at 12 bar of operating pressure and 47% of average boron rejection was obtained for single membrane configuration (Figure 3.28).

The chloride rejection decreased when worked with the double membranes configuration as similar to salt rejection. The chloride rejection value was 98.1% for single membrane configuration and 96.9% of chloride rejection was obtained for double membranes configuration as shown in (Figure 3.29).

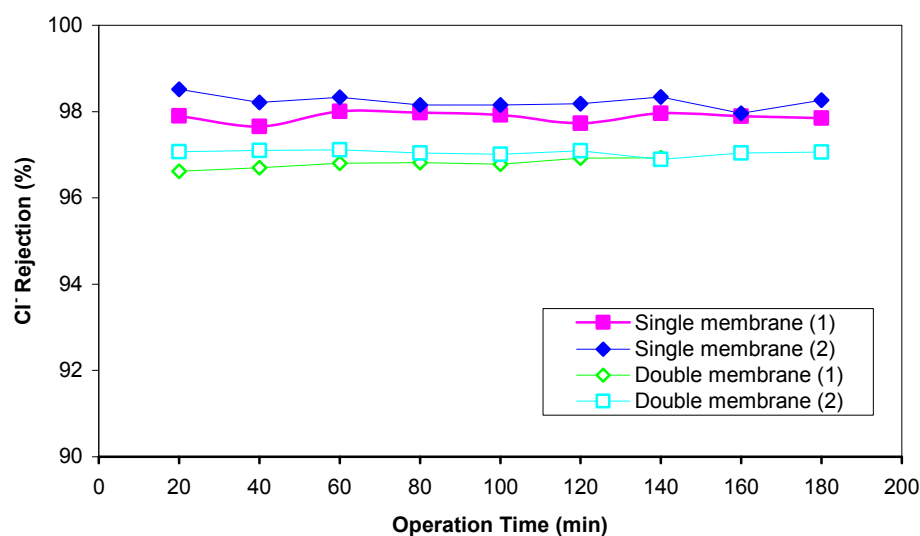


Figure 3.29 Effect of membrane configuration on Cl⁻ rejection for 12 bar of operating pressure.

The sulfate rejection did not change too much when the membrane configuration changed from single membrane configuration to double membranes configuration as seen in Figure 3.30.

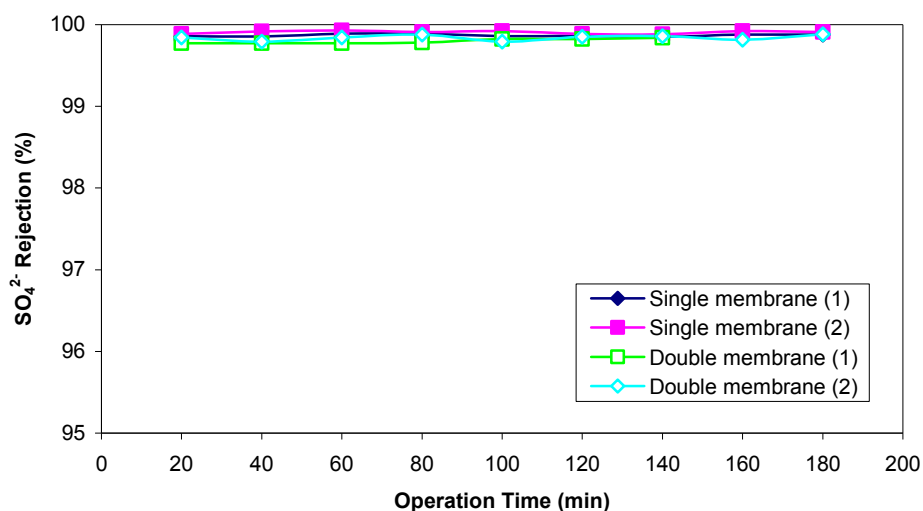


Figure 3.30 Effect of membrane configuration on SO_4^{2-} rejection for 12 bar of operating pressure.

Bicarbonate rejection was 97.5% for both single and double membranes configurations. As shown in Figure 3.31, bicarbonate rejection did not change by changing membrane configuration.

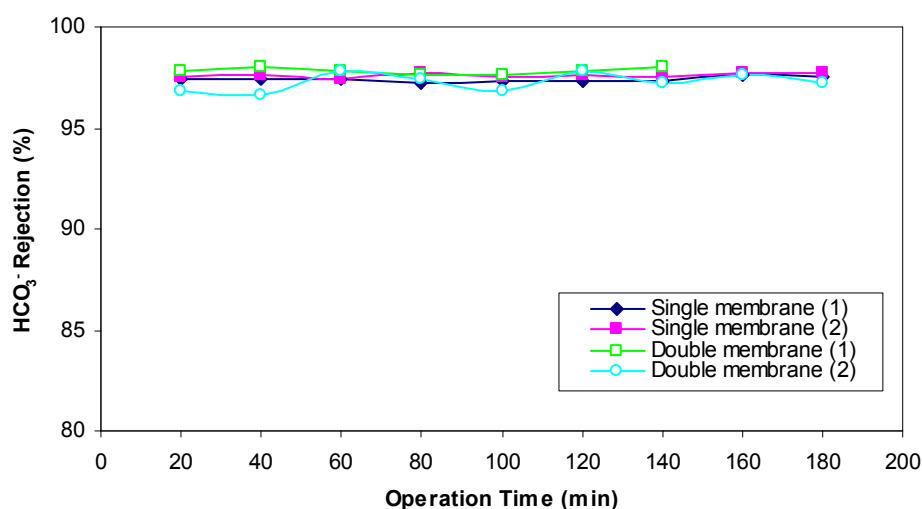


Figure 3.31 Effect of membrane configuration on HCO_3^- rejection for 12 bar of operating pressure.

Sodium rejection did not change also when membrane configuration changed from single membrane to double membrane configuration (Figure 3.32).

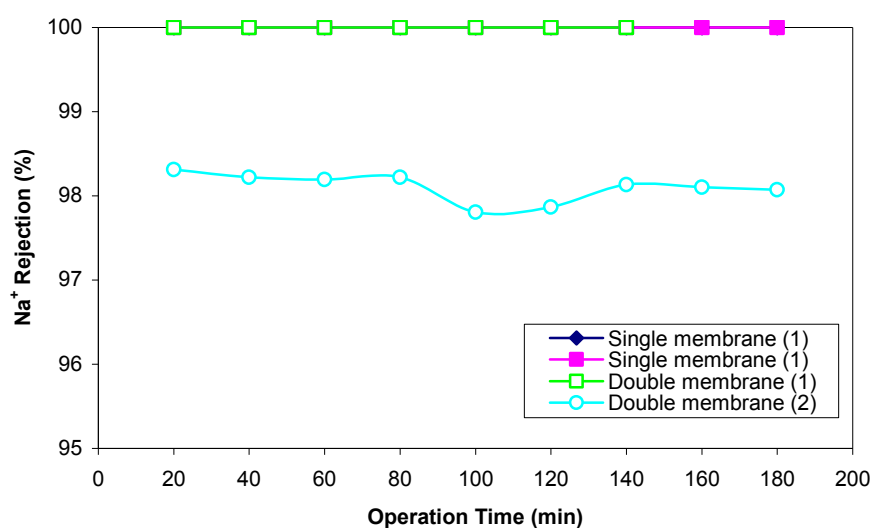


Figure 3.32 Effect of membrane configuration on Na⁺ rejection for 12 bar of operating pressure.

The rejection of K⁺ declined with double membranes configuration as similar to salt rejection (Figure 3.33).

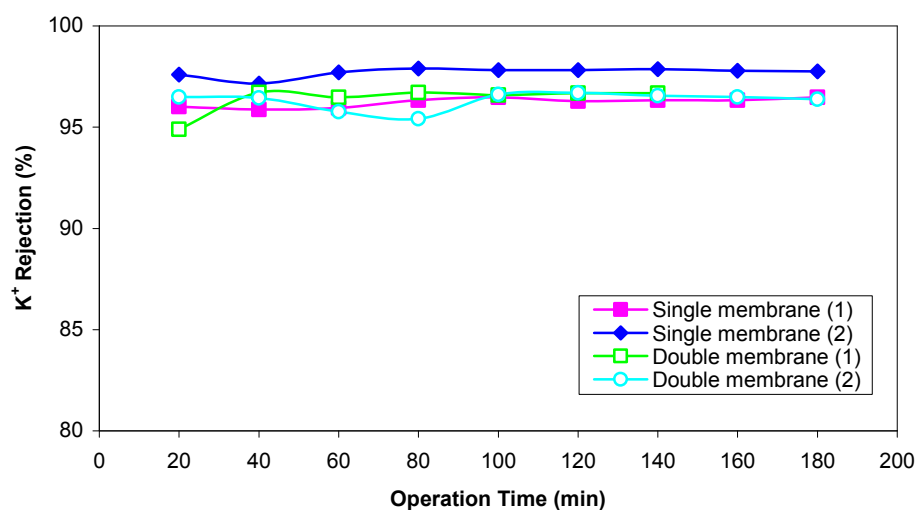


Figure 3.33 Effect of membrane configuration on K⁺ rejection for 12 bar of operating pressure.

The rejection of Mg^{2+} did not change with changing membrane configuration (Figure 3.34).

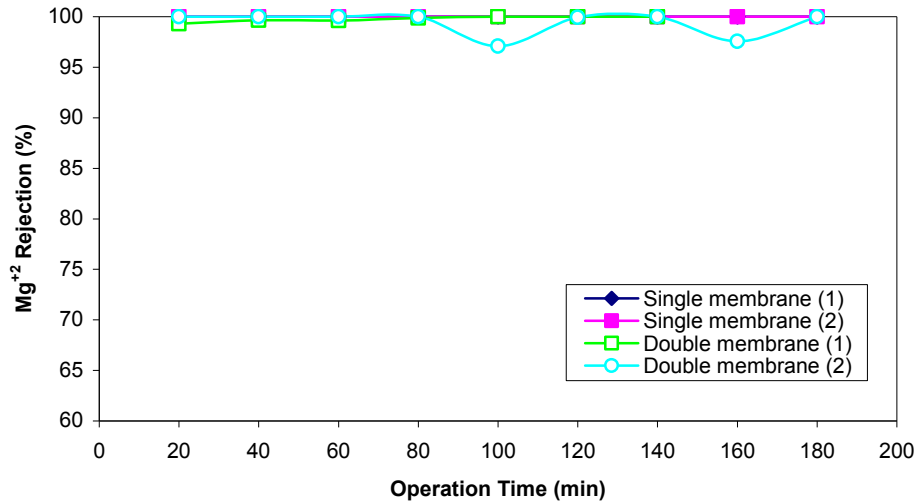


Figure 3.34 Effect of membrane configuration on Mg^{2+} rejection for 12 bar of operating pressure.

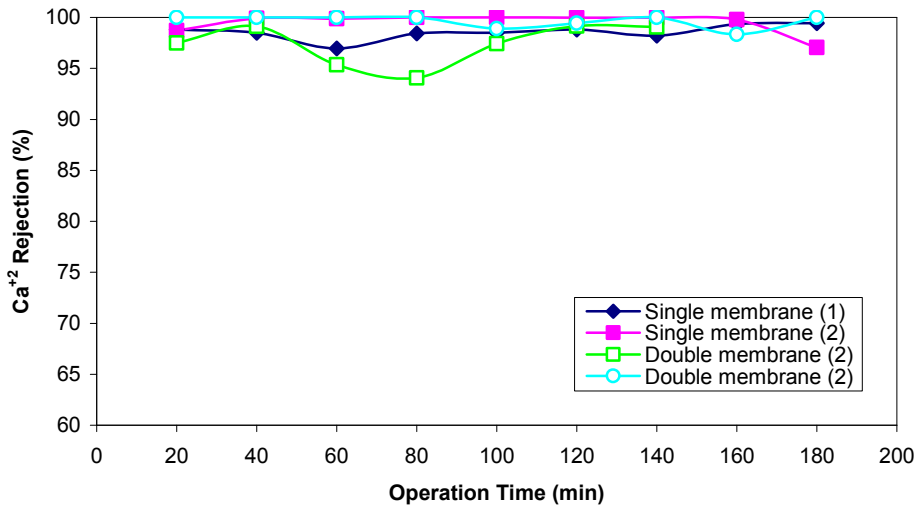


Figure 3.35 Effect of membrane configuration on Ca^{2+} rejection for 12 bar of operating pressure.

For double membranes configuration, average value of Ca^{2+} rejection was 97.1% and the respective value for single membrane configuration was 99.0%. As seen in Figure 3.35, the Ca^{2+} rejection declined if the membrane configuration changed from single to double.

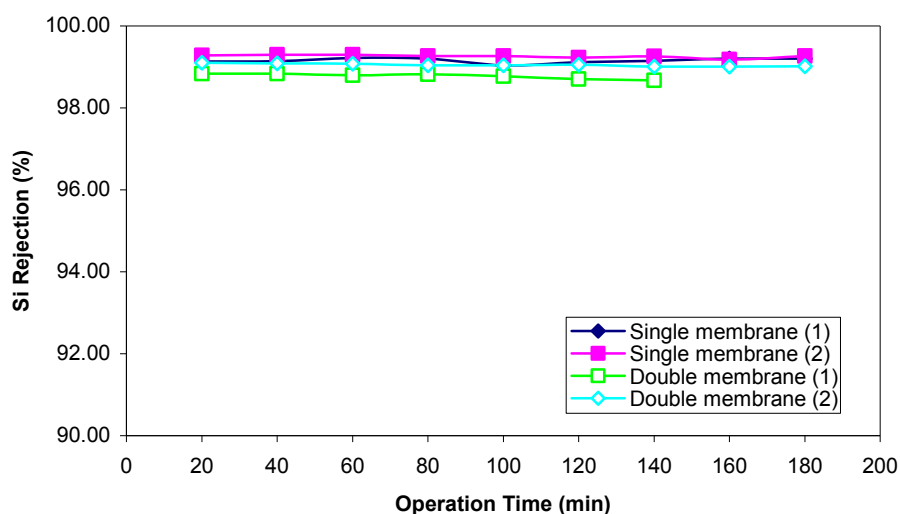


Figure 3.36 Effect of membrane configuration on Si rejection for 12 bar of operating pressure.

When the membrane configuration changed from single to double membranes configuration, the rejection of Si decreased. The rejection of Si was 99.2% for single membrane configuration and 98.9% for double membranes configuration as seen in Figure 3.36.

The effect of membrane configuration on the performance of BWRO system was investigated for 15 bar of operating pressure also. The data obtained for feed seawater and permeate water for single and double membranes operations were given in Tables 3.7 and 3.8.

Table 3.7 Experimental data of feed geothermal water at 15 bar of applied pressure for single and double membranes configurations (Tests 5, 9, 7, 8).

Feed Geothermal Water							
Membrane Configuration	t (°C)	EC (μS/cm)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)
Single	27.8	1726	7.2	863	0.7	334.5	8.89
Single	27.8	1762	7.4	881	0.7	325.7	11.5
Double	31.4	1772	7.3	887	0.7	450.0	8.91
Double	28.9	1770	7.4	885	0.7	425.5	10.1

Table 3.8 Experimental data of permeate water at 15 bar of applied pressure for single and double membranes configurations (Tests 5, 9, 7, 8).

Memb. Config.	t (°C)	Permeate							
		EC ($\mu\text{S}/\text{cm}$)	pH	TDS (mg/L)	Salinity (‰)	Q (L/h)	B (mg/L)	Flux (L/m ² h)	Y (%)
Single	29.1	22.53	5.16	11.11	0.0	119.9	4.49	46.10	35.8
Single	28.7	17.14	5.69	8.78	0.0	114.8	4.83	43.23	35.3
Double	32.0	27.90	5.33	14.0	0.0	248.8	5.35	47.85	55.3
Double	29.2	24.79	5.48	12.3	0.0	224.8	5.44	43.23	52.8

The effect of membrane configuration affected permeate quantity when the operation pressure was 15 bar. For the same flow rate of retentate (200 L/h), permeate volume was larger with double membranes configuration because of the increasing effective membrane area as seen in Figure 3.37.

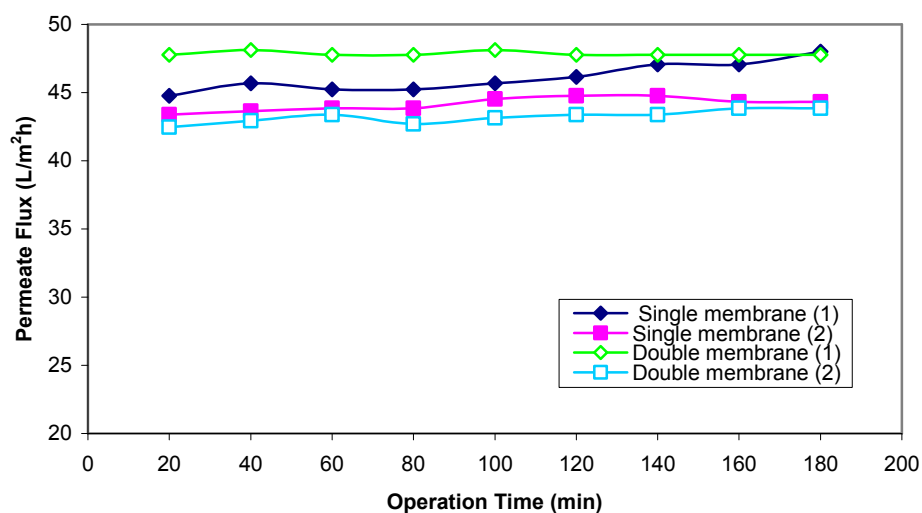


Figure 3.37 Effect of membrane configuration on permeate flux for 15 bar of operating pressure.

When the flow rate of retentate was kept constant for both membrane configurations at 15 bar of operating pressure, permeate recovery for double membranes configuration was larger than that of single membrane configuration (Figure 3.38).

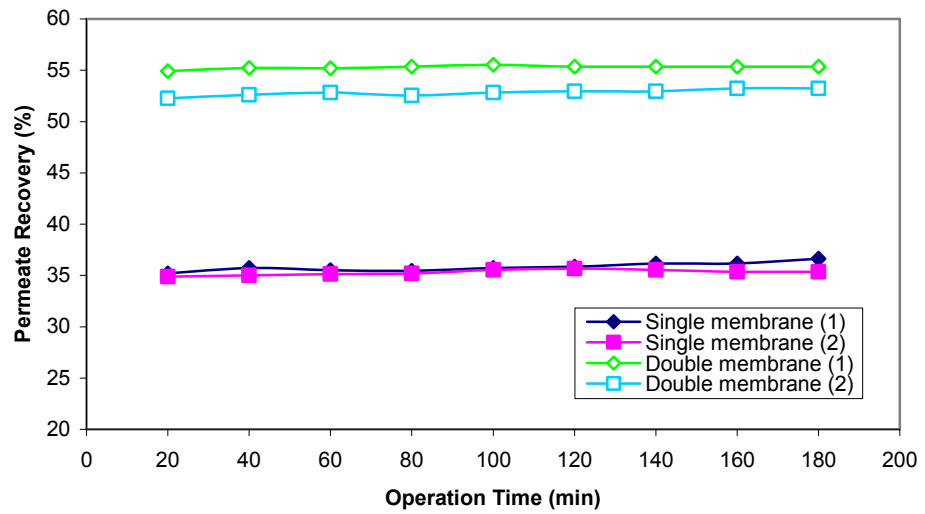


Figure 3.38 Effect of membrane configuration on permeate recovery for 15 bar of operating pressure.

As the larger volume of permeate passed through the membranes of BWRO system with double membranes configuration, the larger amount of salts started to pass through membrane also. Because of this reason, the salt rejection decreased for double membranes configuration.

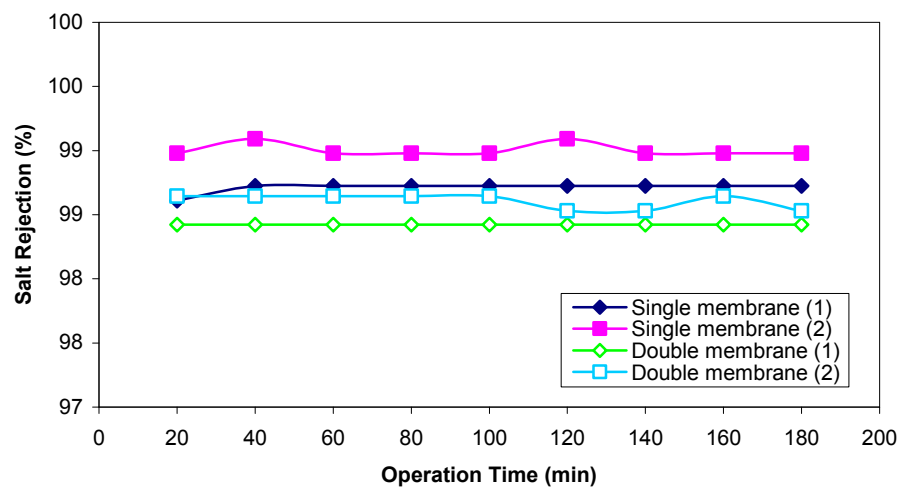


Figure 3.39 Effect of membrane configuration on salt rejection for 15 bar of operating pressure.

As shown in Figure 3.39, with double membranes configuration, permeate volume and thus permeate recovery increased but the permeate quality decreased.

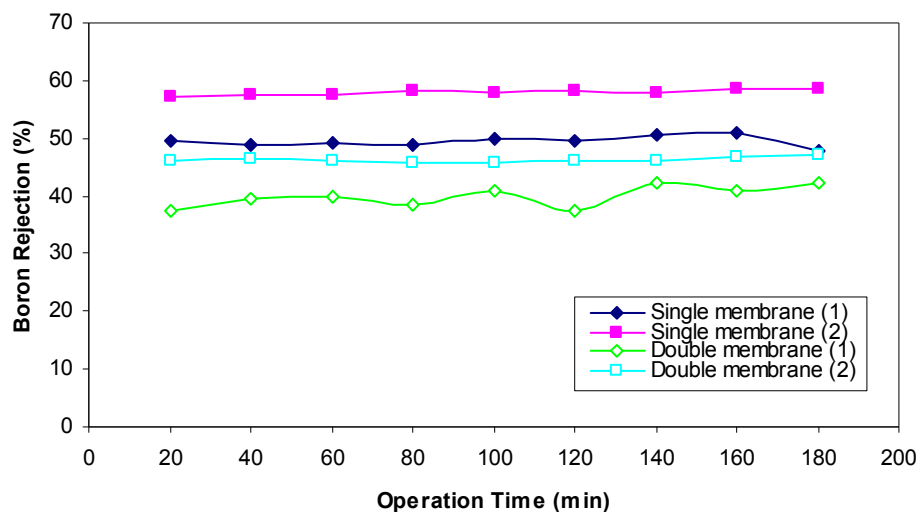


Figure 3.40 Effect of membrane configuration on B rejection for 15 bar of operating pressure.

As similar to salt rejection, boron rejection decreased for double membranes configuration also. Average value of boron rejection was 53.7% for single membrane configuration and 43.1% for double membranes configuration (Figure 3.40).

Chloride rejection was not affected by changing membrane configuration at 15 bar of operating pressure. Chloride rejection values for single and double membrane configurations were 98.5% and 98.2%, respectively (Figure 3.41).

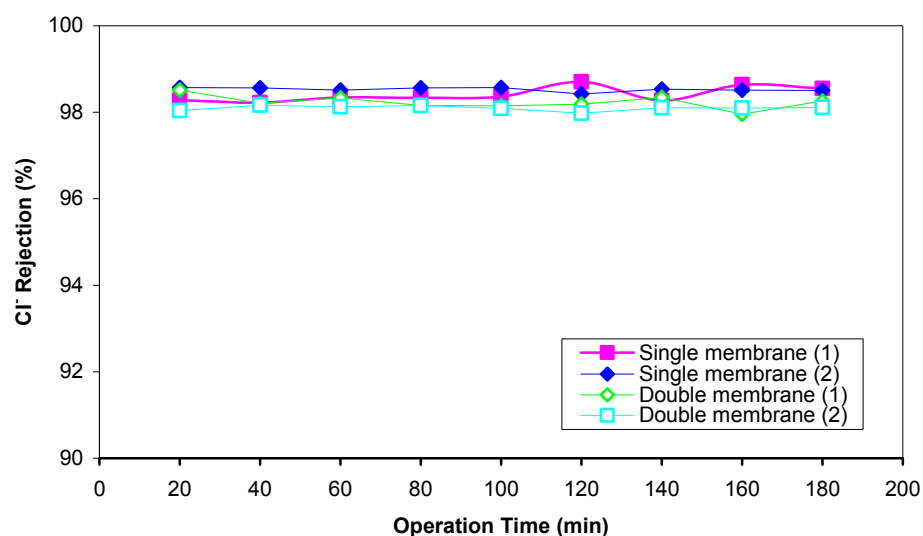


Figure 3.41 Effect of membrane configuration on Cl^- rejection for 15 bar of operating pressure.

Figure 3.42 shows the effect of membrane configuration on sulfate rejection at 15 bar of operating pressure. Sulfate rejection was not affected by changing membrane configuration.

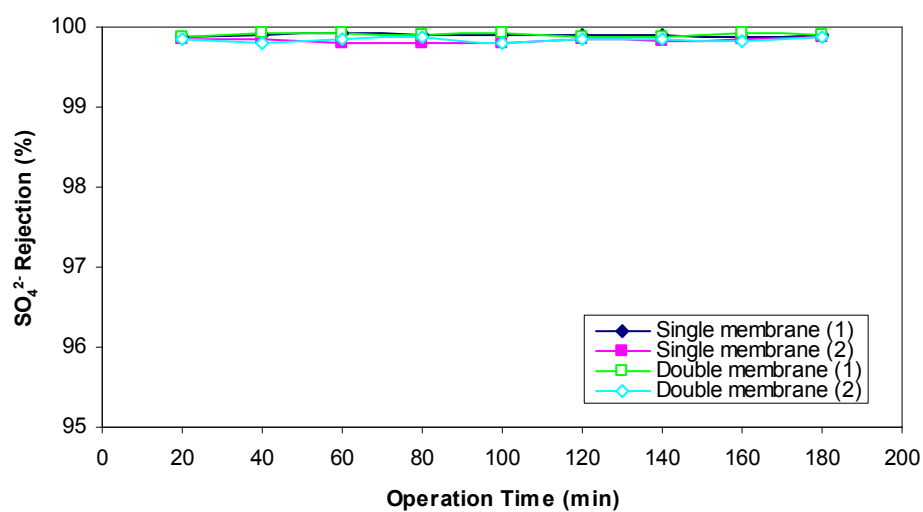


Figure 3.42 Effect of membrane configuration on SO_4^{2-} rejection for 15 bar of operating pressure.

The rejection of HCO_3^- did not change by changing membrane configuration as shown in Figure 3.43.

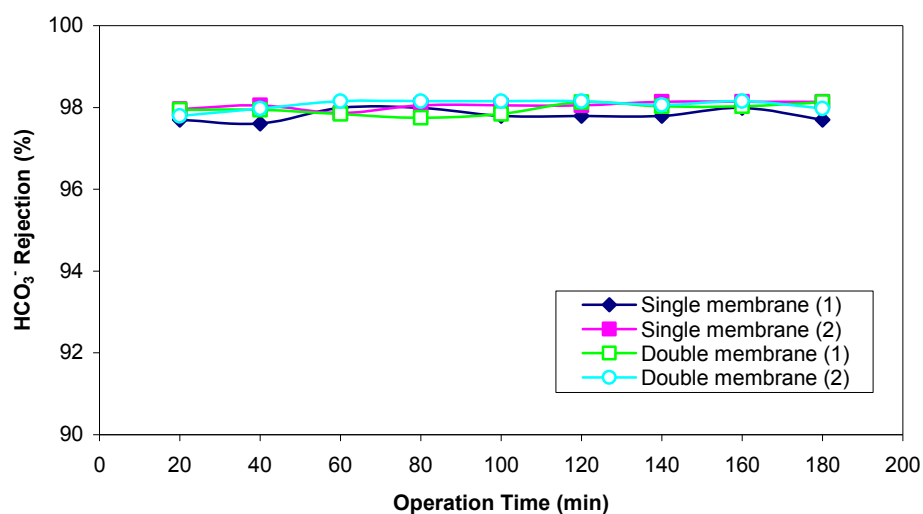


Figure 3.43 Effect of membrane configuration on HCO_3^- rejection for 15 bar of operating pressure.

As shown in Figure 3.44, sodium rejection values were higher for single membrane configuration than those of double membranes configuration.

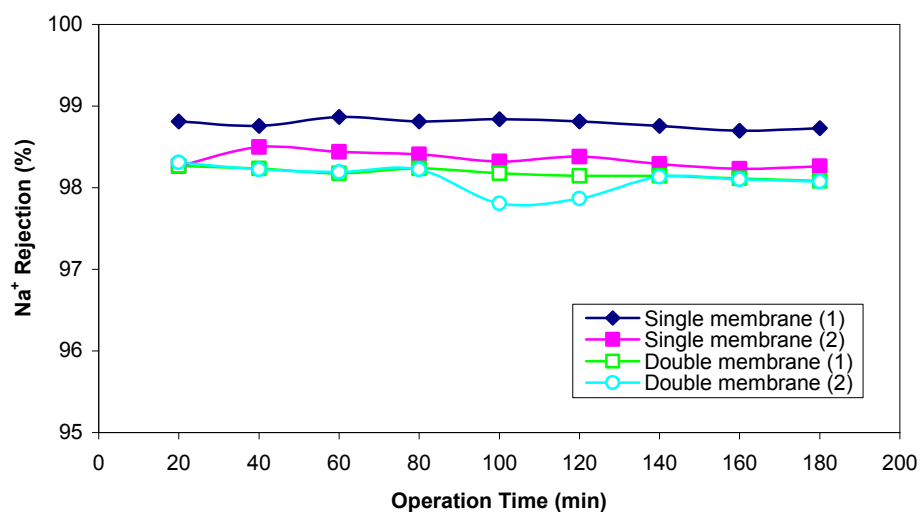


Figure 3.44 Effect of membrane configuration on Na^+ rejection for 15 bar of operating pressure.

The rejection of Mg^{2+} was higher for single membrane configuration than that of double membranes configuration and thus the quality of permeate obtained by single membrane configuration was better than that of double membranes configuration (Figure 3.45).

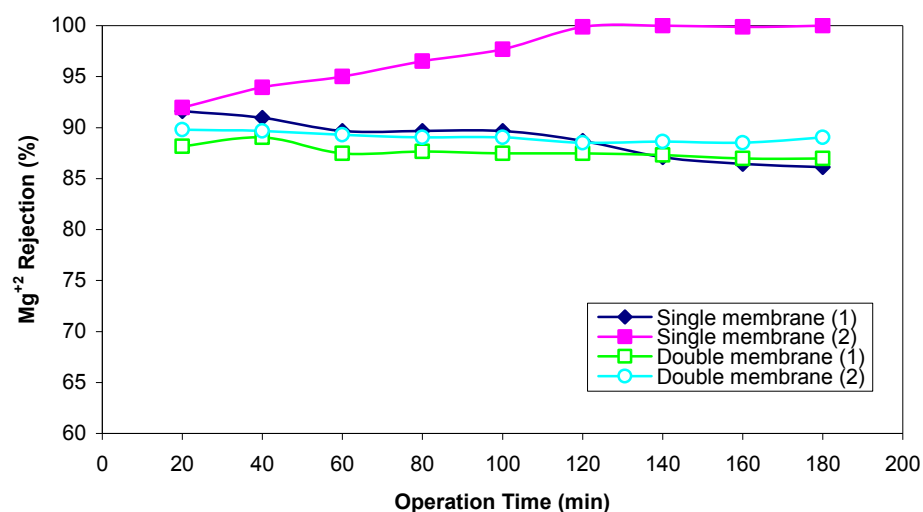


Figure 3.45 Effect of membrane configuration on Mg^{+2} rejection for 15 bar of operating pressure.

The rejection of Ca^{2+} did not change by changing membrane configuration change as shown in Figure 3.46.

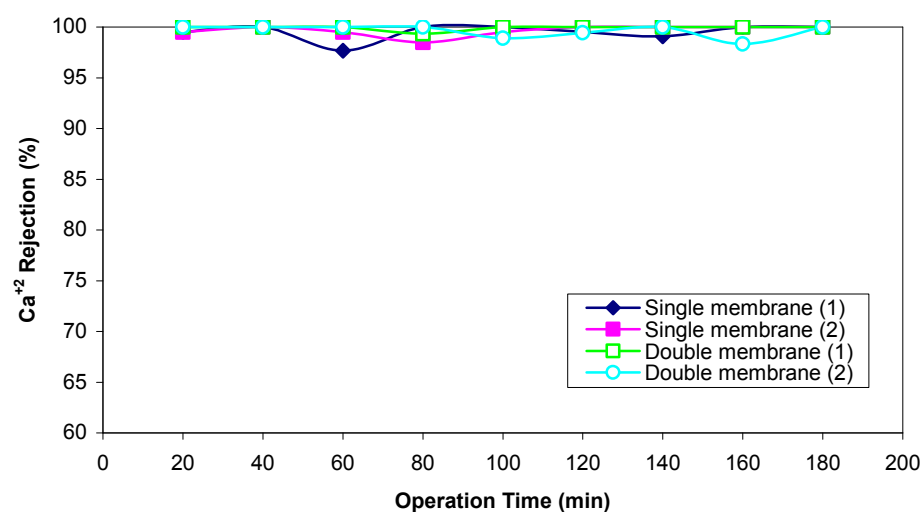


Figure 3.46 Effect of membrane configuration on Ca^{+2} rejection for 15 bar of operating pressure.

At 15 bar of operating pressure, the rejection of K^{+} was lower for double membranes configuration than that of single membrane configuration. The rejection efficiency of K^{+} was 98.1% for double membranes configuration and 98.6% for single membrane configuration (Figure 3.47).

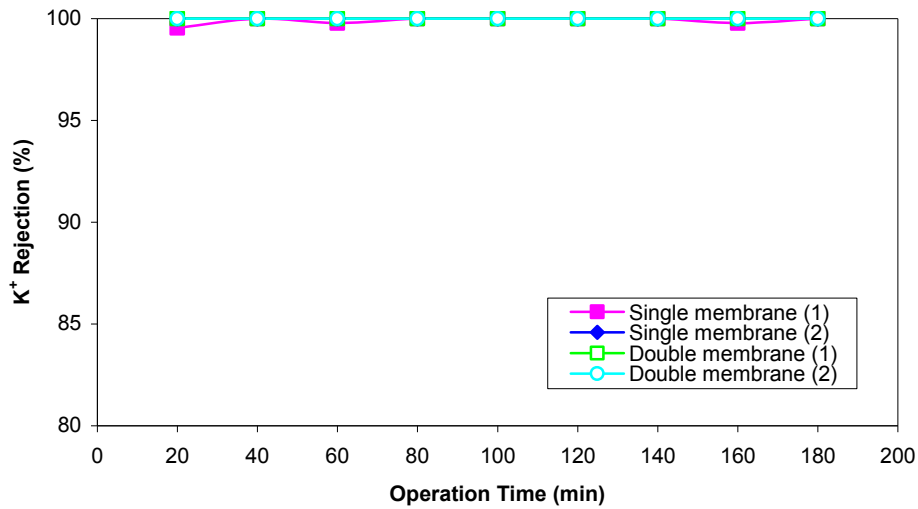


Figure 3.47 Effect of membrane configuration on K^+ rejection for 15 bar of operating pressure.

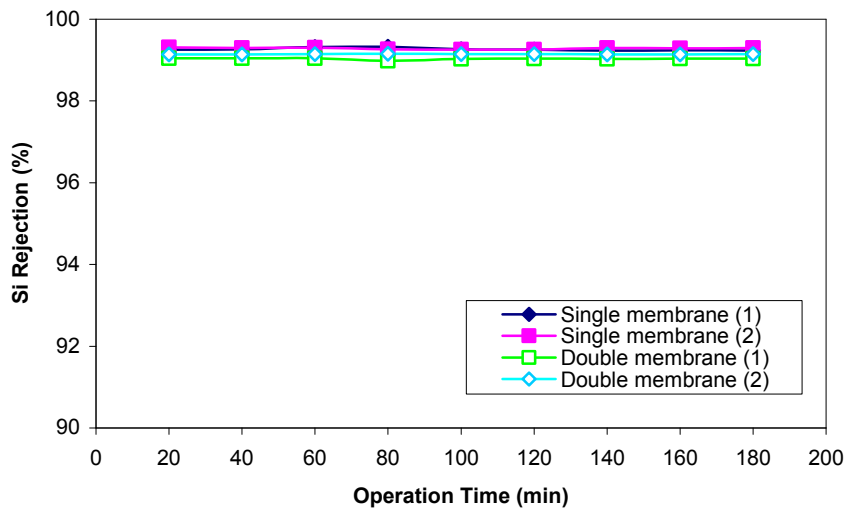


Figure 3.1 Effect of membrane configuration on Si rejection for 15 bar of operating pressure.

The rejection of Si declined when double membranes configuration was employed. The rejection of Si was 99.1% for double membrane configurations and 99.3% for single membrane configuration (Figure 3.48).

4. CONCLUSIONS

Desalination processes have been used for more than forty years to produce fresh water from seawater or brackish water. Reverse osmosis is the most widespread method among the desalination processes. The expanding polymer technology provides some benefits to reverse osmosis membranes such as membranes with higher fluxes and working at lower operating pressures.

Removal of boron by reverse osmosis is not easy because diameter of boric acid molecule is very small and it can pass through the membrane pores easily. Boron is a micronutrient for herbal life in case if it is in small amounts. Excess amount of boron gives some negative effect for growth of some plants.

In this study, some RO tests were performed at Izmir-Balçova geothermal area using a mini-pilot scale BWRO system. The effect of membrane configuration and operating pressure on desalination performance of the reverse osmosis system was investigated.

It was observed that product water quality depends on the operating pressure and membrane configuration. Increasing pressure resulted in higher permeate recoveries and permeate fluxes. Salt rejection also increased with increasing operating pressure for Filmtec™ BW30-2540 membrane.

When a double membranes configuration was employed, a higher permeate recovery was obtained but the quality of product water declined. Working with high permeate recovery values resulted concentration polarization on membrane surface. Also pressure difference between osmotic pressure of the feed solution and applied pressure decreased.

Filmtec™ BW30-2540 membranes were capable of removing boron from geothermal water with an efficiency of 80%. But this value is not enough. The concentration of boron remained in the permeate should be decreased to below 0.5 mg/L if this water is going to be used for irrigation purposes.

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CHAPTER TWO

**ELECTRODIALYTICAL REGENERATION OF HYDROCHLORIC
ACID CONTAINING BORON**

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(15/03/2010 – 12/06/2010)

Gliwice - POLAND

CHAPTER TWO

1. INTRODUCTION

1.1 Environmental effects of spent acids solutions

From the viewpoints of both environmental protection and economy, the usage of waste can reduce the pollution. Waste acid solutions are among the most troublesome waste products produced by a manufacturing process and one of the most expensive to dispose of (Radzi, 2007). Governments and international organisms are more and more concerned with such problems for environmental protection. Quality standards of industrial wastes are now drastic and sometimes conventional depolution techniques become inadequate (Lindheimer, 1993).

Every metal and metallurgical industry is associated with the generation of waste, which may be a solid, liquid or gaseous in nature. Their impacts on the ecological bodies are noticeable due to their complex and hazardous nature affecting the living and non-living environment which is an alarming issue to the environmentalist. The increasingly stringent regulations regarding the discharge of acids and metals into the environment, and the increasing stress upon the recycling/reuse of these effluents after proper treatment have attracted the interest of the research community on the development of new approaches for the recovery of acids and metals from industrial wastes (Agrawal et al., 2009).

1.2 Regeneration of spent acids solutions

The methods used for separation and recovery of acids are crystallization, solvent extraction and membrane technology. The disadvantages of crystallization method were due to the low yield; high chemical costs and waste production. While, solvent extraction is energy intensive, leads to problems of toxic waste disposal, and gives a product that requires further purification. Thus, new extraction technologies need to be established for enhancing recovery yields and reducing cost and environmental impact. The modularity and profitability of membrane technology in a small scale which offered by the third process is a well established technique for the elimination of the pollution.

The principal advantages of membrane processes compared to other separation processes are low energy consumption, simplicity and environmental friendliness. The technology and innovation of membrane separation are rapidly growing. As a result, many different membrane separation processes have been developed and new processes are constantly emerging, which include, besides other techniques, microfiltration, reverse osmosis and electrodialysis (ED). The use of ED, on the treatment of solutions containing complexes, has shown that this technique is effective not only to concentrate ions but also for their separation (Radzi, 2007).

1.3 Recovery and separation of spent acids solutions by electrodialysis

Nowadays electrodialysis can be used for the treatment of acid effluents from industry (chemistry, hydrometallurgy, electroplating). By this process, concentrated acid can be obtained with anion exchange membranes showing a low permeability towards protons (Lindheimer et al., 1991).

ED was a technology that is well-suited for pollution prevention exploitation. It had the capability of separated ionic chemicals from nonionic chemicals in process or waste streams to achieve product purity or eliminate wastes to concentrate the separated chemicals relative to concentration in the initial process or waste streams to aid in reuse of the chemicals and being used as a reactor, both electrolytic and otherwise, to convert chemicals at high efficiencies to more desirable products. This technology does not require any chemicals and is simple to operate. It could be adapted to non-continuous feed supplies at different loads. Besides, it does not dependent on temperature very much (Radzi, 2007). The product could be concentrated up to a certain amount together with the separation process.

In spite of the advantages of ED, there were some problems that can limit the efficiency and separation using electrodialysis. The first problem is regarding the fouling which is become the most important limitation in ED processes. The fouling build-up can reduce the performance of the ED process by increasing the resistance and can eventually lead to membrane integrity alteration. Under certain conditions, fouling and integrity alterations are irreversible and membranes must be replaced. Research on avoiding or preventing fouling have been studied in

order to reduce the cost of cleaning and membrane replacement which is extremely expensive (Morantes, 2004).

Fouling is essentially caused by deposition of some foulants such as organics, minerals, colloids, biomass and particles on the membrane surfaces, causing deterioration in the membrane performance in terms of flux decline and increase in the electrical resistance. Besides, the fouling sometimes causes a loss in selectivity of the membrane. If the fouling is irreversible, the membranes must be changed frequently, adding to the increased energy cost caused by fouling (Morantes, 2004).

The recovery of acids by electrodialysis can be performed using sulfuric acid, hydrofluoric acid, chromic acid and phosphoric acid. Concerning hydrochloric acid, some studies have been carried out in order to improve the electrodialysis efficiency. For this purpose, bipolar membranes as well as modified anion exchange membranes have been used (Bobrinskaya et al., 1985 and Gunjima et al., 1985).

Industrial wastewater with high salinity and pH value can be treated with the combination of electrodialysis and reverse osmosis (RO), while low-salinity wastewater with low pH value can be treated by reverse osmosis. The use of electrodialysis in the purification and reconcentration of spent acid has been limited by the deficiencies of commercial membranes: they suffer from an important proton leakage through the anion exchange membrane (AEM), limiting the reconcentration capacity (Cherif et al., 1988), while a poor selectivity of the cation exchange membrane (CEM) affecting the proton/bivalent cation separation. In recent years, new AEMs with lower proton leakage have appeared in the market. It is now possible to concentrate mineral acids, such as sulphuric and phosphoric acids, from 2.6 N up to 15 N using these new membranes (Zhou et al., 1999).

2. EXPERIMENTAL

2.1 Materials

2.1.1 Solutions

Boron containing hydrochloric acid solution

For concentrate compartment, boron containing hydrochloric acid solution was prepared. The concentration of hydrochloric acid solution was 17.60 g/L and it contained 2.33 g B/L.

Hydrochloric acid solution

For dilute compartment of electrodialysis system hydrochloric acid solution with 17.60 g/L HCl concentration was prepared.

Sodium Sulfate solution

Na_2SO_4 solution was prepared for electrode rinsing compartment by dissolving 71.2 g of Na_2SO_4 in 1 L of deionized water.

2.1.2 Chemicals

- NaOH (Poch Chemicals pure p.a.)
- Na_2SO_4 (Poch Chemicals pure p.a.)
- HCl (Poch Chemicals pure %35-38)
- Chromotropic Acid Disodium Salt Dihydrate (Poch Chemicals pure p.a.)
- $\text{Na}_2\text{H}_2\text{Y}$ (Poch Chemicals pure p.a.)
- Deionized Water

2.1.3 Experimental equipment

- **ED unit :** Hand made
- **Peristaltic pump:** Zalimp p.p. Type PP1B-05A
- **DC Supply:** Shanghai MCP Corp. MCP M10-TP-305E
- **Amperometers:** Mastech M-838, Mastech M-830B,
- **Voltmeters :** Era LM-3 2302104

The systems which were used in batch mode and single pass mode experiments were shown in Figures 1.1 and 1.2, respectively.



Figure 1.1 Electrodialysis system for batch mode experiments

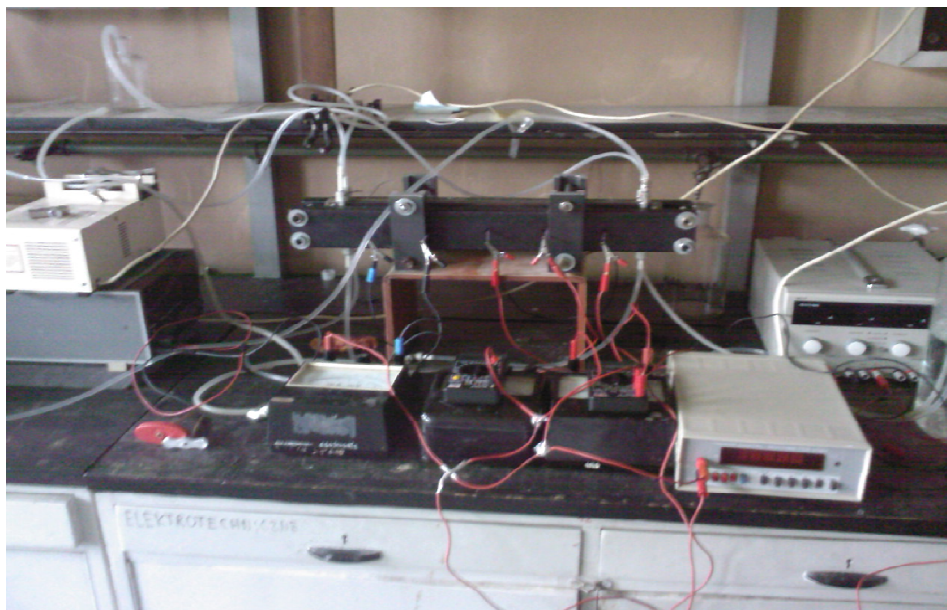


Figure 1.2 Electrodeialysis system for single pass mode experiments

2.1.4 Membranes

The specifications of the membranes used in batch mode and single pass mode electrodeialysis experiments were given in Table 1.1.

Table 1.1 Neosepta AMX and CMX membrane specifications.

Grade	CMX	AMX
Type	Strongly acidic cation permeable	Strongly basic anion permeable
Characteristics	High mechanical strength (Na-form)	High mechanical strength (Cl-form)
Electrical Resistance In 0.5 M NaCl solution at 25°C ($\Omega \text{ cm}^2$)	3.0	2.4
Burst Strength Mullen Burst Strength (MPa)	> 0.40	>0.25
Thickness (mm)	0.17	0.14
Application	Demineralization of whey Purification of organics Concentration of inorganics Demineralization of sucrose Desalination of ground water	Demineralization of whey Purification of organics Concentration of inorganics

2.2 Boron analysis

Boron concentration of samples were determined by fluorimetric flow injection method.

Reagents:

EDTA and chromotropic acid mixture solution: 56 g of EDTA disodium salt and 0.11 g of chromotropic acid disodium salt dihydrate were dissolved in 1 L of deionized water.

NaOH solution : 4 g of NaOH was dissolved in 1 L of deionized water.

Mobil phase : 1 L of deionized water was used as a mobil phase.

The procedure:

1. Each solution was transferred into a glass bottle. Each solution was transferred into a quartz cell with tubings through a peristaltic pump.
2. Sample was injected into tubing by mobil phase and then it was transferred to fluorimeter.
3. Chromotropic acid and boron gives a reaction and a complex is obtained. This complex is excited at 313 nm and at 354 nm. An emission is obtained.
4. Emission intensity of standard solutions and samples are measured and finally B concentrations of samples are calculated.

The equipment for B analysis was shown in Figure 1.3.



Figure 1.3 Fluorimetric flow injection analysis system

2.3 Calculations

2.3.1 Current Efficiency

Current efficiency is a ratio of moles of ions transported through membranes during process to the theoretical value of transport (Equation 1). In this equation, theoretical number of transported ions is related to the charge transferred through all cells of electrodialyser (Equation 2), whereas practical mole numbers of transported ions relates to the difference of ions for given species at the beginning and at the end of process (Equation 3). Having all these values, one can able to determine the current efficiency.

$$\xi = \frac{T}{T_t} \quad (1)$$

Where: ξ - current efficiency, T - actual number of mol of transported ions, T_t – theoretical number of mol of transported ions.

$$T_t = \frac{I \cdot \Delta t \cdot n}{F \cdot v_+ \cdot z_+} \quad (2)$$

Where: I – current [A], Δt – time interval [s], n – number of cells, F – Faraday constant (96485 C/mol), z_+ – valence of ion, v_+ – no. of cations in 1 molecule of an electrolyte.

$$T = V_d \cdot \Delta c_d \quad (3)$$

Where: V_d – volume of diluate, ΔC_d – concentration difference of diluate [mol/L] in Δt time [s].

2.3.2 Current Density

Current density is a term to determine the performance of an electro membrane process. Current density was the current passing through a constant membrane area.

2.4 Analysis of HCl

Analysis of HCl was carried out by volumetric titration. Phenolphthalein was used for determination of equivalent point of the titration. Samples were diluted by a hundred times before the analysis.

2.5 Aim of the study

In this study, it was aimed to concentrate hydrochloric acid from boron containing hydrochloric acid model solution by electrodialysis system. The performance of the system was determined by current efficiency, current density and reconcentration level of hydrochloric acid with small and large ED cell containing pairs of Neospta AMX and CMX membranes. The tests were carried out with single pass mode and batch mode to investigate the performance of the electrodialysis system. For the preliminary tests, the effect of concentration of diluate compartment was investigated at 0.8 A of applied current. After the preliminary tests, the performance of the system was investigated by a larger diameter of ED cell. The effect of the flow rate of the diluate compartment and applied current on system performance was investigated.

3. RESULTS AND DISCUSSION

3.1. Batch Mode Experiments

In batch mode experiments, a small electrodialysis cell which has a 4.5 cm^2 of effective membrane area was used. Electrodialysis cell contained 4 pairs of anion and cation exchange membranes. Anion exchange membranes were Neosepta AMX (strongly basic anion exchange membrane) and the cation exchange membranes were Neosepta CMX (strongly acidic cation exchange membrane). Titanium electrodes were used as anode and cathode electrodes. A 0.8 A of current was applied during the tests. The system performance was investigated by calculating current efficiency and current density. The flow rate was 2 cm/s. The tests carried out until the steady state was obtained. A 0.5 M Na_2SO_4 was used for electrode rinsing in order to prevent electrode reactions. The specifications of the solutions which were used in batch mode ED experiments were shown in Table 1.2.

Table 1.2 Specifications of solutions used in ED batch experiments.

Test Number	V_D (ml)	V_C (ml)	Q_D (cm/s)	Q_C (cm/s)	I (A)
1	30	30	2	2	0.8
2	40	20	2	2	0.8
3	60	30	2	2	0.8

The composition of the solutions which are used in electrodialysis system was shown in Table 1.3. For the first test, a small volume of diluate (30 ml) and concentrate (30 ml) solutions were used. When electrodialysis was applied to the boron containing hydrochloric acid solution, two parameters have to be taken into consideration: the current efficiency and the reconcentration level of the hydrochloric acid.

Table 1.3 Composition of solutions used in electro dialysis system (Test 1).

	Diluate Compartment	Concentrate Compartment	Electrode Rinsing Compartment
Solution	2.23 g B /L and 17.64 g HCl /L	16.78 g HCl /L	10 g/L Na ₂ SO ₄
Volume (mL)	30	30	30
Linear Flow Rate (cm/s)	2	2	2

The current efficiency of hydrochloric acid in diluate and concentrate compartments were low as seen in Table 1.4. Boron transport in electro dialysis system was not occurred effectively because the solutions which are used in electro dialysis system were acidic. The transport of molecular species in electro dialysis system is generally very slow. The concentration of the hydrochloric acid in the concentrate compartment was not high at the end of the experiment.

Table 1.4 Experimental data of batch mode experiment for Test 1.

Compartment Parameter		Diluate				Concentrate			
Operation Time (min)	Current Density (mA/cm ²)	HCl		Boron		HCl		Boron	
		Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)
0	177.8	0.00	17.1	0.00	2.23	0.00	16.0	0.00	0.00
10	177.8	27.4	10.3	1.60	1.55	4.56	17.1	0.09	0.04
20	133.3	21.1	6.85	1.01	1.43	18.8	25.1	0.08	0.06
30	111.1	21.6	2.28	0.69	1.48	14.9	26.3	0.06	0.07
40	33.33	17.4	2.74	0.64	1.42	13.8	27.4	0.09	0.11
50	22.22	17.0	1.71	0.53	1.53	12.6	27.4	0.09	0.12
60	15.56	15.8	1.71	0.54	1.49	11.7	27.4	0.10	0.14

As shown in Table 1.5, the volume of the diluate compartment was two times larger than the concentrate compartment. To study with larger volume of

diluate solution than concentration compartment provides higher reconcentration level for hydrochloric acid.

Table 1.5 Composition of solutions used in electrodialysis system (Test 2).

	Diluate Compartment	Concentrate Compartment	Electrode Rinsing Compartment
Solution	2.33 g B /L and 17.13 g HCl /L	17.12 g HCl /L	0.5 M Na ₂ SO ₄
Volume (mL)	40	20	40
Linear Flow Rate (cm/s)	2	2	2

A higher current efficiency was obtained for hydrochloric acid when the volume of the diluate compartment was two times larger than the concentrate compartment. For boron also the current efficiency was low for diluate and concentrate compartments. The transport of boron was low because of being in molecular form (Table 1.6).

Table 1.6 Experimental data of batch mode experiment for Test 2.

Compartment Parameter		Diluate				Concentrate			
Operation Time (min)	Current Density (mA/cm ²)	HCl		Boron		HCl		Boron	
		Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)
0	133.3	0.00	17.5	3.39	2.16	0.00	18.2	0.00	0.13
10	127.8	35.6	14.6	0.04	1.65	4.53	19.7	0.00	0.07
20	55.56	31.8	13.1	0.35	2.15	11.7	23.3	0.17	0.12
30	41.11	38.6	10.9	0.51	2.05	13.8	25.9	0.08	0.14
40	33.33	47.8	8.02	0.31	1.98	14.6	28.1	0.06	0.16
50	22.22	47.4	7.29	0.32	2.04	12.0	28.4	0.08	0.19
60	17.78	64.2	2.19	0.68	2.03	16.6	32.8	0.10	0.23

The effect of diluate compartment volume on performance of electrodialysis for recovery of hydrochloric acid was investigated using a larger volume of diluate compartment (Table 1.7).

Table 1.7 Composition of solutions used electro dialysis system (Test 3).

	Diluate Compartment	Concentrate Compartment	Electrode Rinsing Compartment
Solution	2.16 g B /L and 17.50 g HCl /L	18.23 g HCl /L	0.5 M Na ₂ SO ₄
Volume (mL)	60	30	60
Linear Flow Rate (cm/s)	2	2	2

For Test 3, samples were taken only at the beginning of the experiment and after steady state was obtained. The volume of the diluate was increased for the same flow rate. The current efficiency of hydrochloride acid declined for diluate compartment (Table 1.8).

Table 1.8 Experimental data of batch mode experiment for Test 3.

Compartment Parameter		Diluate				Concentrate			
Operation Time (min)	Current Density (mA/cm ²)	HCl		Boron		HCl		Boron	
		Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)
0	110	0.00	17.1	0.00	2.33	0.00	17.1	0.00	0.00
10	70	--	--	--	--	--	--	--	--
20	50	--	--	--	--	--	--	--	--
30	40	--	--	--	--	--	--	--	--
40	30	--	--	--	--	--	--	--	--
50	20	--	--	--	--	--	--	--	--
60	10	36.37	5.10	2.96	1.35	17.3	31.0	0.19	0.15

3.2. Single pass mode experiments

Single pass mode experiments were carried with the boron containing hydrochloric acid. The experiment was carried out with counter-current flow in single-pass mode. The volumetric flow rate of dilute was decreased properly and concentrate flow rate was kept constant. Current efficiency and density parameters were calculated for determining the performance of ED system. ED cell contained four anion and cation exchange membranes. Anode electrode had five points (wires) and while cathode two wires. Samples were taken at beginning of the experiment and after steady state conditions occurred.

The tests were carried out with a electrodialysis cell which had 4 pairs of anion and cation exchange membranes. The membranes were produced by Neosepta Co. and they had 84 cm² of effective membrane area. Titanium electrodes were used as anode and cathode electrodes. The effect of flow rate of diluate and concentrate compartments was investigated. The effect of applied current was also investigated at 5 A and 7 A of constant currents. Five liter of diluate and concentration solutions and 200 mL of Na₂SO₄ electrode rinsing solution was used for the tests. The specifications of the solutions which were used in single pass mode ED experiments were shown in Table 1.9.

Table 1.9 Specifications of solutions used in ED batch experiments.

Test Number	V _D (L)	V _C (L)	Q _D (ml/min)	Q _C (ml/min)	I (A)
4	5	5	28	14	5
5	5	5	(40-28)	18	5
6	5	5	28	14	7

The composition of the solutions which were used in single pass mode experiments were shown in Table 1.10.

Table 1.10 Composition of solutions used for single pass mode tests in electrodialysis system (Test 4).

	Diluate Compartment	Concentrate Compartment	Electrode Rinsing Compartment
Solution	2.38 g B /L and 16.77 g HCl /L	17.50 g HCl /L	0.5 M Na ₂ SO ₄
Volume (L)	5	5	0.2

Diluate flow rate was kept constant at 28 mL/min and concentrate flow rate at 14 mL/min during the test. Applied current was 5 A during the test. The higher current efficiency was obtained with single pass mode experiments than the batch mode experiments. The effective membrane area was larger for separating hydrochloric acid and the applied current was high enough to obtain a high current efficiency. At the end of the experiment, 0.9 M hydrochloric acid was obtained in the concentrate compartment (Table 1.11).

Table 1.11 Experimental datas for single pass mode experiment for Test 4.

Compartment Parameter		Diluate				Concentrate			
Operation Time (min)	Current Density (mA/cm ²)	HCl		Boron		HCl		Boron	
		Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)
0	0.06	--	17.2	--	2.38	--	17.9	--	0.01
10	0.06	--		--		--		--	
20	0.06	--		--		--		--	
30	0.06	--		--		--		--	
40	0.06	75.3	5.02	1.65	2.11	50.9	30.3	0.16	0.34

The compositions of the solutions which were used in single pass mode experiments were shown in Table 1.12.

Table 1.12 Composition of solutions used for single pass mode tests in electrodialysis system (Test 5).

	Diluate Compartment	Concentrate Compartment	Electrode Rinsing Compartment
Solution	2.43 g B /L and 16.84 g HCl /L	17.92 g HCl /L	0.5 M Na ₂ SO ₄
Volume (L)	5	5	0.2

During the experiment the flow rate of the dilute compartment decreased from 40 ml/min to 28 ml/min and concentrate flow rate was kept constant. The current efficiency increased as the flow rate of the dilute compartment was decreased. Current efficiency of boron was still low. Steady state conditions were obtained after 45 minutes.

Table 1.13 Experimental datas for single pass mode experiment for Test 5

Compartment Parameter		Diluate				Concentrate			
Operation Time (min)	Current Density (mA/cm ²)	HCl		Boron		HCl		Boron	
		Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)	Current Efficiency (%)	Conc. (g/L)
0	60	--	16.8	--	2.43	--	17.2	--	0.00
15	70	46.5	11.0	0.40	2.38	39.6	28.2	0.36	0.13
30	70	54.1	8.24	1.38	2.32	43.8	29.6	0.94	0.17
45	70	67.9	4.50	0.65	2.32	45.8	30.3	0.66	0.24

The effect of applied current on the performance of the electrodialysis system was investigated by increasing the applied current to 7 A. The comparison of the system performance was carried out at 5 A and 7 A of applied current values. The compositions of the solutions which are used for the tests were shown in Table 1.14.

Table 1.14 Composition of solutions used for single pass mode tests in electrodialysis system (Test 6).

	Diluate Compartment	Concentrate Compartment	Electrode Rinsing Compartment
Contain	2.43 g B /L and 16.84 g HCl /L	17.92 g HCl /L	0.5 M Na ₂ SO ₄
Volume	5 L	5 L	200 ml

Increasing the applied current did not effect the system performance as seen in Table 1.15. Current efficiency did not change as the applied current increased from 5 A to 7 A.

Table 1.15 Experimental datas for single pass mode experiment for Test 6

Compartment Parameter		Diluate				Concentrate			
Operation Time (min)	Current Density (mA/cm ²)	HCl		Boron		HCl		Boron	
		Current Ef. (%)	Conc. (g/L)	Current Ef. (%)	Conc. (g/L)	Current Ef. (%)	Conc. (g/L)	Current Ef. (%)	Conc. (g/L)
0	90	--	16.84	--	2.43	--	17.92	--	0.00
15	80	66.85	4.85	1.24	2.23	38.03	30.20	0.52	0.24

4. CONCLUSIONS

We have obtained unequal current efficiency of HCl and we should answer to the question of decreasing in diluate flow rate between the inlet – outlet and increase of concentrate flow rate by the water transport through the electro-osmosis.

Classical type anion exchange membranes exhibit proton leakage due to the fact that water sorbed inside the membrane material acts as a proton conductor.

Dialysis of HCl from concentrate to the diluate also affects negatively the performance of the system.

As concern to the boron, final concentration of boron in diluate is still high because in acidic environment especially when pH of the solution is below 3, transport of boron is very low.

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APPENDIX

Table A.1 Results of pressure effect on permeate flux for single membrane operation (Figure 3.1) (Tests 3,4,5,9).

Time (min)	Permate flux, (L/m²h) (12 Bar)	Permate flux, (L/m²h) (12 Bar)	Permate flux, (L/m²h) (15 Bar)	Permate flux, (L/m²h) (15 Bar)
20	39.23	37.38	44.77	42.46
40	39.23	37.15	45.69	42.92
60	39.46	37.38	45.23	43.38
80	39.92	37.38	45.23	42.69
100	39.69	37.85	45.69	43.15
120	40.15	37.85	46.15	43.38
140	40.15	37.85	47.08	43.38
160	40.62	38.08	47.08	43.85
180	41.54	38.77	48.00	43.85

Table A.2 Results of pressure effect on permeate recovery for single membrane operation (Figure 3.2) (Tests 3,4,5,9).

Time (min)	Permate recovery (%) (12 Bar)	Permate recovery (%) (12 Bar)	Permate recovery (%) (15 Bar)	Permate recovery (%) (15 Bar)
20	32.57	31.40	35.21	34.88
40	32.26	31.26	35.74	35.00
60	32.45	31.40	35.51	35.12
80	32.64	31.52	35.44	35.19
100	32.58	31.54	35.74	35.54
120	32.77	31.66	35.84	35.66
140	32.77	31.66	36.17	35.53
160	33.08	31.79	36.17	35.36
180	33.52	31.94	36.62	35.36

Table A.3 Results of pressure effect on salt rejection for single membrane operation (Figure 3.3) (Tests 3,4,5,9).

Time (min)	Salt rejection (%) (12 Bar)	Salt rejection (%) (12 Bar)	Salt rejection (%) (15 Bar)	Salt rejection (%) (15 Bar)
20	98.49	98.73	98.61	98.98
40	98.49	98.61	98.73	99.09
60	98.49	98.61	98.73	98.98
80	98.60	98.61	98.73	98.98
100	98.60	98.61	98.73	98.98
120	98.49	98.61	98.73	99.09
140	98.60	98.61	98.73	98.98
160	98.60	98.61	98.73	98.98
180	98.49	98.61	98.73	98.98

Table A.4 Results of pressure effect on boron rejection for single membrane operation (Figure 3.4) (Tests 3,4,5,9).

Time (min)	Boron rejection (%) (12 Bar)	Boron rejection (%) (12 Bar)	Boron rejection (%) (15 Bar)	Boron rejection (%) (15 Bar)
20	45.90	45.14	49.47	57.03
40	45.41	46.35	48.86	57.46
60	46.33	46.53	49.06	57.54
80	47.95	46.18	48.76	58.10
100	47.08	45.85	49.87	57.78
120	46.46	46.27	49.43	58.36
140	47.41	48.09	50.50	57.73
160	48.65	49.34	50.87	58.40
180	49.03	48.82	47.98	58.64

Table A.5 Results of pressure effect on chloride rejection for single membrane operation (Figure 3.5) (Tests 3,4,5,9).

Time (min)	Chloride Rejection (%) (12 Bar)	Chloride Rejection (%) (12 Bar)	Chloride Rejection (%) (15 Bar)	Chloride Rejection (%) (15 Bar)
20	97.90	98.51	98.28	98.57
40	97.65	98.21	98.23	98.56
60	98.00	98.33	98.34	98.51
80	97.97	98.16	98.33	98.56
100	97.92	98.15	98.36	98.57
120	97.73	98.19	98.70	98.42
140	97.96	98.34	98.28	98.54
160	97.89	97.96	98.64	98.51
180	97.85	98.26	98.55	98.51

Table A.6 Results of pressure effect on sulfate rejection for single membrane operation (Figure 3.6) (Tests 3,4,5,9).

Time (min)	Sulfate Rejection (%) (12 Bar)	Sulfate Rejection (%) (12 Bar)	Sulfate Rejection (%) (15 Bar)	Sulfate Rejection (%) (15 Bar)
20	99.86	99.89	99.87	99.86
40	99.86	99.92	99.90	99.85
60	99.89	99.93	99.94	99.80
80	99.89	99.91	99.90	99.79
100	99.86	99.92	99.90	99.81
120	99.86	99.89	99.91	99.84
140	99.85	99.88	99.90	99.83
160	99.88	99.92	99.87	99.86
180	99.88	99.91	99.91	99.87

Table A.7 Results of pressure effect on hydrogen carbonate rejection for single membrane operation (Figure 3.7) (Tests 3,4,5,9).

Time (min)	Hydrogencar bonate Rejection (%) (12 Bar)	Hydrogencar bonate rejection (%) (12 Bar)	Hydrogencar bonate rejection (%) (15 Bar)	Hydrogencar bonate rejection (%) (15 Bar)
20	97.46	97.56	97.70	97.96
40	97.46	97.66	97.61	98.05
60	97.46	97.46	97.99	97.86
80	97.26	97.76	97.99	98.05
100	97.36	97.56	97.80	98.05
120	97.36	97.66	97.80	98.05
140	97.36	97.56	97.80	98.14
160	97.65	97.76	97.99	98.14
180	97.56	97.76	97.70	98.14

Table A.8 Results of pressure effect on sodium rejection for single membrane operation (Figure 3.8) (Tests 3,4,5,9).

Time (min)	Sodium rejection (%) (12 Bar)	Sodium rejection (%) (12 Bar)	Sodium rejection (%) (15 Bar)	Sodium rejection (%) (15 Bar)
20	97.46	97.56	97.70	97.96
40	97.46	97.66	97.61	98.05
60	97.46	97.46	97.99	97.86
80	97.26	97.76	97.99	98.05
100	97.36	97.56	97.80	98.05
120	97.36	97.66	97.80	98.05
140	97.36	97.56	97.80	98.14
160	97.65	97.76	97.99	98.14
180	97.56	97.76	97.70	98.14

Table A.9 Results of pressure effect on potassium rejection for single membrane operation (Figure 3.9) (Tests 3,4,5,9).

Time (min)	Potassium rejection (%) (12 Bar)	Potassium rejection (%) (12 Bar)	Potassium rejection (%) (15 Bar)	Potassium rejection (%) (15 Bar)
20	96.02	97.60	99.55	100.00
40	95.87	97.15	100.0	100.00
60	95.95	97.71	99.78	100.00
80	96.33	97.90	100.00	100.00
100	96.48	97.82	100.00	100.00
120	96.29	97.82	100.00	100.00
140	96.33	97.86	100.00	100.00
160	96.33	97.79	99.78	100.00
180	96.48	97.75	100.00	100.00

Table A.10 Results of pressure effect on magnesium rejection for single membrane operation (Figure 3.10) (Tests 3,4,5,9).

Time (min)	Magnesium rejection (%) (12 Bar)	Magnesium rejection (%) (12 Bar)	Magnesium rejection (%) (15 Bar)	Magnesium rejection (%) (15 Bar)
20	100.00	100.00	91.61	91.98
40	100.00	100.00	90.97	93.95
60	100.00	100.00	89.68	95.00
80	100.00	100.00	89.68	96.51
100	100.00	100.00	89.68	97.67
120	100.00	100.00	88.71	99.88
140	100.00	100.00	87.10	100.00
160	100.00	99.99	86.45	99.88
180	100.00	100.00	86.13	100.00

Table A.11 Results of pressure effect on calcium rejection for single membrane operation (Figure 3.11) (Tests 3,4,5,9).

Time (min)	Calcium rejection (%) (12 Bar)	Calcium rejection (%) (12 Bar)	Calcium rejection (%) (15 Bar)	Calcium rejection (%) (15 Bar)
20	98.80	98.73	99.53	99.50
40	98.48	99.91	100.00	100.00
60	96.96	99.86	97.67	99.50
80	98.43	100.00	100.00	98.50
100	98.48	100.00	100.00	99.50
120	98.80	99.95	99.53	100.00
140	98.20	99.95	99.07	100.00
160	99.35	99.77	100.00	100.00
180	99.45	97.05	100.00	100.00

Table A.12 Results of pressure effect on Si rejection for single membrane operation (Figure 3.12) (Tests 3,4,5,9).

Time (min)	Si rejection (%) (12 Bar)	Si rejection (%) (12 Bar)	Si rejection (%) (15 Bar)	Si rejection (%) (15 Bar)
20	99.13	99.28	99.26	99.31
40	99.14	99.30	99.26	99.29
60	99.22	99.30	99.32	99.30
80	99.20	99.26	99.33	99.27
100	99.04	99.26	99.26	99.26
120	99.12	99.23	99.26	99.26
140	99.15	99.25	99.23	99.29
160	99.20	99.18	99.24	99.28
180	99.20	99.26	99.23	99.29

Table A.13 Results of pressure effect on permeate flux for double membrane operation (Figure 3.13) (Tests 1,2,7,8).

Time (min)	Permate flux, (L/m ² h) (12 Bar)	Time (min)	Permate flux, (L/m ² h) (12 Bar)	Permate flux, (L/m ² h) (15 Bar)	Permate flux, (L/m ² h) (15 Bar)
20	35.08	20	34.62	47.77	42.46
40	36.00	40	34.15	48.12	42.92
60	36.00	60	35.54	47.77	43.38
80	36.00	80	34.85	47.77	42.69
100	36.46	100	34.85	48.12	43.15
120	36.92	120	34.62	47.77	43.38
140	36.92	140	34.62	47.77	43.38
		160	35.08	47.77	43.85
		180	34.62	47.77	43.85

Table A.14 Results of pressure effect on permeate recovery for double membrane operation (Figure 3.14) (Tests 1,2,7,8).

Time (min)	Permate recovery, L/m ² h (12 Bar)	Time (min)	Permate recovery, L/m ² h (12 Bar)	Permate recovery, L/m ² h (15 Bar)	Permate recovery, L/m ² h (15 Bar)
20	46.34	20	45.87	54.91	52.27
40	46.71	40	45.61	55.23	52.62
60	46.99	60	46.67	55.20	52.81
80	46.99	80	46.18	55.35	52.56
100	47.02	100	46.18	55.53	52.82
120	47.62	120	46.01	55.35	52.96
140	47.34	140	46.01	55.35	52.96
		160	46.34	55.35	53.22
		180	46.01	55.35	53.22

Table A.15 Results of pressure effect on salt rejection for double membrane operation (Figure 3.15) (Tests 1,2,7,8).

Time (min)	Salt rejection (%) (12 Bar)	Time (min)	Salt rejection (%) (12 Bar)	Salt rejection (%) (15Bar)	Salt rejection (%) (15 Bar)
20	98.18	20	98.33	98.42	98.64
40	98.18	40	98.33	98.42	98.64
60	98.18	60	98.33	98.42	98.64
80	98.18	80	98.21	98.42	98.64
100	98.18	100	98.21	98.42	98.64
120	98.18	120	98.21	98.42	98.53
140	98.18	140	98.21	98.42	98.53
		160	98.33	98.42	98.64
		180	98.21	98.42	98.53

Table A.16 Results of pressure effect on boron rejection for double membrane operation (Figure 3.16) (Tests 1,2,7,8).

Time (min)	Boron rejection (%) (12 Bar)	Time (min)	Boron rejection (%) (12 Bar)	Boron rejection (%) (15 Bar)	Boron rejection (%) (15 Bar)
20	35.25	20	35.79	37.55	45.96
40	34.15	40	35.79	39.58	46.36
60	35.25	60	37.16	39.76	46.22
80	35.52	80	37.7	38.47	45.67
100	34.43	100	37.98	40.97	45.77
120	33.61	120	37.98	37.38	46.25
140	35.52	140	35.79	42.32	45.98
		160	38.8	40.80	46.80
		180	39.07	42.15	47.07

Table A.17 Results of pressure effect on chloride rejection for double membrane operation (Figure 3.17) (Tests 1,2,7,8).

Time (min)	Chloride rejection (%) (12 Bar)	Time (min)	Chloride rejection (%) (12 Bar)	Chloride rejection (%) (15 Bar)	Chloride rejection (%) (15 Bar)
20	96.62	20	97.07	98.51	98.04
40	96.70	40	97.10	98.21	98.17
60	96.80	60	97.12	98.33	98.13
80	96.82	80	97.04	98.16	98.16
100	96.78	100	97.01	98.15	98.09
120	96.92	120	97.09	98.19	97.98
140	96.93	140	96.89	98.34	98.11
		160	97.04	97.96	98.10
		180	97.06	98.26	98.11

Table A.18 Results of pressure effect on sulfate rejection for double membrane operation (Figure 3.18) (Tests 1,2,7,8).

Time (min)	Sulfate rejection (%) (12 Bar)	Time (min)	Sulfate rejection (%) (12 Bar)	Sulfate rejection (%) (15 Bar)	Sulfate rejection (%) (15Bar)
20	99.77	20	99.82	99.89	99.84
40	99.77	40	99.80	99.92	99.79
60	99.77	60	99.79	99.93	99.84
80	99.78	80	99.71	99.91	99.88
100	99.82	100	99.75	99.92	99.79
120	99.82	120	99.72	99.89	99.85
140	99.84	140	99.75	99.88	99.86
		160	99.83	99.92	99.82
		180	99.75	99.91	99.88

Table A.19 Results of pressure effect on hydrogen carbonate rejection for double membrane operation (Figure 3.19) (Tests 1,2,7,8).

Time (min)	Hydrogen carbonate rejection (%) (12 Bar)	Time (min)	Hydrogen carbonate rejection (%) (12 Bar)	Hydrogen carbonate rejection (%) (15 Bar)	Hydrogen carbonate rejection (%) (15 Bar)
20	97.87	20	96.80	97.94	97.79
40	98.06	40	96.60	97.94	97.97
60	97.87	60	97.80	97.84	98.15
80	97.67	80	97.40	97.75	98.15
100	97.67	100	96.80	97.84	98.15
120	97.87	120	97.80	98.13	98.15
140	98.06	140	97.20	98.03	98.06
		160	97.60	98.03	98.15
		180	97.20	98.13	97.97

Table A.20 Results of pressure effect on sodium rejection for double membrane operation (Figure 3.20) (Tests 1,2,7,8).

Time (min)	Sodium rejection (%) (12 Bar)	Time (min)	Sodium rejection (%) (12 Bar)	Sodium rejection (%) (15 Bar)	Sodium rejection (%) (15 Bar)
20	100	20	100	98.27	98.31
40	100	40	100	98.24	98.22
60	100	60	100	98.18	98.19
80	100	80	100	98.24	98.22
100	100	100	100	98.18	97.81
120	100	120	100	98.14	97.87
140	100	140	100	98.14	98.13
		160	100	98.11	98.10
		180	100	98.08	98.07

Table A.21 Results of pressure effect on potassium rejection for double membrane operation (Figure 3.21) (Tests 1,2,7,8).

Time (min)	Potassium rejection (%) (12 Bar)	Time (min)	Potassium rejection (%) (12 Bar)	Potassium rejection (%) (15 Bar)	Potassium rejection (%) (15 Bar)
20	94.89	20	96.50	100.00	100.00
40	96.70	40	96.44	100.00	100.00
60	96.48	60	95.77	100.00	100.00
80	96.70	80	95.42	100.00	100.00
100	96.59	100	96.61	100.00	100.00
120	96.68	120	96.70	100.00	100.00
140	96.68	140	96.55	100.00	100.00
		160	96.50	100.00	100.00
		180	96.38	100.00	100.00

Table A.22 Results of pressure effect on calcium rejection for double membrane operation (Figure 3.22) (Tests 1,2,7,8).

Time (min)	Calcium rejection (%) (12 Bar)	Time (min)	Calcium rejection (%) (12 Bar)	Calcium rejection (%) (15 Bar)	Calcium rejection (%) (15 Bar)
20	97.48	20	99.85	100.00	100.00
40	99.11	40	99.75	100.00	100.00
60	95.36	60	97.75	100.00	100.00
80	94.07	80	96.40	99.33	100.00
100	97.43	100	98.60	100.00	98.89
120	99.16	120	99.60	100.00	99.44
140	99.06	140	99.15	100.00	100.00
		160	98.40	100.00	98.33
		180	96.80	100.00	100.00

Table A.23 Results of pressure effect on magnesium rejection for double membrane operation (Figure 3.23) (Tests 1,2,7,8).

Time (min)	Magnesium rejection (%) (12 Bar)	Time (min)	Magnesium rejection (%) (12 Bar)	Magnesium rejection (%) (15 Bar)	Magnesium rejection (%) (15 Bar)
20	99.30	20	100.00	88.17	89.81
40	99.65	40	100.00	89.04	89.68
60	99.61	60	100.00	87.48	89.29
80	99.87	80	100.00	87.65	89.03
100	100.00	100	97.08	87.48	89.03
120	100.00	120	99.92	87.48	88.52
140	100.00	140	100.00	87.30	88.65
		160	97.57	86.96	88.52
		180	100.00	86.96	89.03

Table A.24 Results of pressure effect on silisium rejection for double membrane operation (Figure 3.24) (Tests 1,2,7,8).

Time (min)	Si rejection (%) (12 Bar)	Time (min)	Si rejection (%) (12 Bar)	Si rejection (%) (15 Bar)	Si rejection (%) (15 Bar)
20	98.84	20	99.10	99.13	99.28
40	98.84	40	99.09	99.14	99.30
60	98.80	60	99.08	99.22	99.30
80	98.82	80	99.04	99.20	99.26
100	98.78	100	99.04	99.04	99.26
120	98.71	120	99.06	99.12	99.23
140	98.67	140	99.01	99.15	99.25
		160	99.01	99.20	99.18
		180	99.02	99.20	99.26

Table A.25 Results of membrane configuration effect on permeate flux for 12 bar of operating pressure (Figure 3.25) (Tests 3,4,1,2).

Time (min)	Permate flux, (L/m²h) (Single)	Permate flux, (L/m²h) (Single)	Permate flux, (L/m²h) (Double)	Time (min)	Permate flux, (L/m²h) (Double)
20	39.23	37.38	34.62	20	35.08
40	39.23	37.15	34.15	40	36.00
60	39.46	37.38	35.54	60	36.00
80	39.92	37.38	34.85	80	36.00
100	39.69	37.85	34.85	100	36.46
120	40.15	37.85	34.62	120	36.92
140	40.15	37.85	34.62	140	36.92
160	40.62	38.08	35.08		
180	41.54	38.77	34.62		

Table A.26 Results of membrane configuration effect on permeate recovery for 12 bar of operating pressure (Figure 3.26) (Tests 3,4,1,2).

Time (min)	Permate recovery, (L/m²h) (Single)	Permate recovery, (L/m²h) (Single)	Permate recovery, (L/m²h) (Double)	Time (min)	Permate recovery, (L/m²h) (Double)
20	32.57	31.40	45.87	20	46.34
40	32.26	31.26	45.61	40	46.71
60	32.45	31.40	46.67	60	46.99
80	32.64	31.52	46.18	80	46.99
100	32.58	31.54	46.18	100	47.02
120	32.77	31.66	46.01	120	47.62
140	32.77	31.66	46.01	140	47.34
160	33.08	31.79	46.34		
180	33.52	31.94	46.01		

Table A.27 Results of membrane configuration effect on salt rejection for 12 bar of operation pressure (Figure 3.27) (Tests 3,4,1,2).

Time (min)	Salt rejection (%) (Single)	Salt rejection (%) (Single)	Salt rejection (%) (Double)	Time (min)	Salt rejection (%) (Double)
20	98.49	98.73	98.33	20	98.18
40	98.49	98.61	98.33	40	98.18
60	98.49	98.61	98.33	60	98.18
80	98.60	98.61	98.21	80	98.18
100	98.60	98.61	98.21	100	98.18
120	98.49	98.61	98.21	120	98.18
140	98.60	98.61	98.21	140	98.18
160	98.60	98.61	98.33		
180	98.49	98.61	98.21		

Table A.28 Results of membrane configuration effect on boron rejection for 12 bar of operating pressure (Figure 3.28) (Tests 3,4,1,2).

Time (min)	Boron Rejection (%) (Single)	Boron Rejection (%) (Single)	Boron Rejection (%) (Double)	Time (min)	Boron Rejection (%) (Double)
20	45.90	45.14	35.79	20	35.25
40	45.41	46.35	35.79	40	34.15
60	46.33	46.53	37.16	60	35.25
80	47.95	46.18	37.7	80	35.52
100	47.08	45.85	37.98	100	34.43
120	46.46	46.27	37.98	120	33.61
140	47.41	48.09	35.79	140	35.52
160	48.65	49.34	38.8		
180	49.03	48.82	39.07		

Table A.29 Results of membrane configuration effect on chloride rejection for 12 bar of operating pressure (Figure 3.29) (Tests 3,4,1,2).

Time (min)	Chloride rejection (%) (Single)	Chloride rejection (%) (Single)	Chloride rejection (%) (Double)	Time (min)	Chloride rejection (%) (Double)
20	97.90	98.51	97.07	20	96.62
40	97.65	98.21	97.10	40	96.70
60	98.00	98.33	97.12	60	96.80
80	97.97	98.16	97.04	80	96.82
100	97.92	98.15	97.01	100	96.78
120	97.73	98.19	97.09	120	96.92
140	97.96	98.34	96.89	140	96.93
160	97.89	97.96	97.04		
180	97.85	98.26	97.06		

Table A.30 Results of membrane configuration effect on sulfate rejection for 12 bar of operating pressure (Figure 3.30) (Tests 3,4,1,2).

Time (min)	Sulfate Rejection (%) (Single)	Sulfate Rejection (%) (Single)	Sulfate Rejection (%) (Double)	Time (min)	Sulfate Rejection (%) (Double)
20	99.89	99.86	99.82	20	99.77
40	99.92	99.86	99.80	40	99.77
60	99.93	99.89	99.79	60	99.77
80	99.91	99.89	99.71	80	99.78
100	99.92	99.86	99.75	100	99.82
120	99.89	99.86	99.72	120	99.82
140	99.88	99.85	99.75	140	99.84
160	99.92	99.88	99.83		
180	99.91	99.88	99.75		

Table A.31 Results of membrane configuration effect on hydrogen carbonate rejection for 12 bar of operating pressure (Figure 3.31) (Tests 3,4,1,2).

Time (min)	Hydrogen carbonate Rejection (%) (Single)	Hydrogenc arbonate Rejection (%) (Single)	Hydrogen carbonate Rejection (%) (Double)	Time (min)	Hydrogen carbonate Rejection (%) (Double)
20	97.46	97.56	96.80	20	97.87
40	97.46	97.66	96.60	40	98.06
60	97.46	97.46	97.80	60	97.87
80	97.26	97.76	97.40	80	97.67
100	97.36	97.56	96.80	100	97.67
120	97.36	97.66	97.80	120	97.87
140	97.36	97.56	97.20	140	98.06
160	97.65	97.76	97.60		
180	97.56	97.76	97.20		

Table A.32 Results of membrane configuration effect on sodium rejection for 12 bar of operating pressure (Figure 3.32) (Tests 3,4,1,2).

Time (min)	Sodium rejection (%) (Single)	Sodium rejection (%) (Single)	Sodium rejection (%) (Double)	Time (min)	Sodium rejection (%) (Double)
20	100.00	100.00	100.00	20	100.00
40	100.00	100.00	100.00	40	100.00
60	100.00	100.00	100.00	60	100.00
80	100.00	100.00	100.00	80	100.00
100	100.00	100.00	100.00	100	100.00
120	100.00	100.00	100.00	120	100.00
140	100.00	100.00	100.00	140	100.00
160	100.00	100.00	100.00		
180	100.00	100.00	100.00		

Table A.33 Results of membrane configuration effect on potassium rejection for 12 bar of operating pressure (Figure 3.33) (Tests 3,4,1,2).

Time (min)	Potassium rejection (%) (Single)	Potassium rejection (%) (Single)	Potassium rejection (%) (Double)	Time (min)	Potassium rejection (%) (Double)
20	96.02	97.60	96.50	20	94.89
40	95.87	97.15	96.44	40	96.70
60	95.95	97.71	95.77	60	96.48
80	96.33	97.90	95.42	80	96.70
100	96.48	97.82	96.61	100	96.59
120	96.29	97.82	96.70	120	96.68
140	96.33	97.86	96.55	140	96.68
160	96.33	97.79	96.50		
180	96.48	97.75	96.38		

Table A.34 Results of membrane configuration effect on magnesium rejection for 12 bar of operating pressure (Figure 3.34) (Tests 3,4,1,2).

Time (min)	Magnesium rejection (%) (Single)	Magnesium rejection (%) (Single)	Magnesium rejection (%) (Double)	Time (min)	Magnesium rejection (%) (Double)
20	100.00	100.00	100.00	20	99.30
40	100.00	100.00	100.00	40	99.65
60	100.00	100.00	100.00	60	99.61
80	100.00	100.00	100.00	80	99.87
100	100.00	100.00	100.00	100	100.00
120	100.00	100.00	100.00	120	100.00
140	100.00	100.00	100.00	140	100.00
160	100.00	99.99	100.00		
180	100.00	100.00	100.00		

Table A.35 Results of membrane configuration effect on calcium rejection for 12 bar of operating pressure (Figure 3.35) (Tests 3,4,1,2).

Time (min)	Calcium Rejection (%) (Single)	Calcium Rejection (%) (Single)	Calcium Rejection (%) (Double)	Time (min)	Calcium Rejection (%) (Double)
20	98.80	98.73	99.85	20	97.48
40	98.48	99.91	99.75	40	99.11
60	96.96	99.86	97.75	60	95.36
80	98.43	100.00	96.40	80	94.07
100	98.48	100.00	98.60	100	97.43
120	98.80	99.95	99.60	120	99.16
140	98.20	99.95	99.15	140	99.06
160	99.35	99.77	98.40		
180	99.45	97.05	96.80		

Table A.36 Results of membrane configuration effect on Si rejection for 12 bar of operating pressure (Figures 3.36) (Tests 3,4,1,2).

Time (min)	Si Rejection (%) (Single)	Si Rejection (%) (Single)	Si Rejection (%) (Double)	Time (min)	Si Rejection (%) (Double)
20	99.13	99.28	99.10	20	98.84
40	99.14	99.30	99.09	40	98.84
60	99.22	99.30	99.08	60	98.80
80	99.20	99.26	99.04	80	98.82
100	99.04	99.26	99.04	100	98.78
120	99.12	99.23	99.06	120	98.71
140	99.15	99.25	99.01	140	98.67
160	99.20	99.18	99.01		
180	99.20	99.26	99.02		

Table A.37 Results of membrane configuration effect on permeate flux for 15 bar of operating pressure (Figure 3.37) (Tests 5,9,7,8).

Time (min)	Permate flux, (L/m²h) (Single)	Permate flux, (L/m²h) (Single)	Permate flux, (L/m²h) (Double)	Permate flux, (L/m²h) (Double)
20	44.77	43.38	47.77	42.46
40	45.69	43.63	48.12	42.92
60	45.23	43.85	47.77	43.38
80	45.23	43.85	47.77	42.69
100	45.69	44.54	48.12	43.15
120	46.15	44.77	47.77	43.38
140	47.08	44.77	47.77	43.38
160	47.08	44.31	47.77	43.85
180	48.00	44.31	47.77	43.85

Table A.38 Results of membrane configuration effect on permeate recovery for 15 bar of operating pressure (Figure 3.38) (Tests 5,9,7,8).

Time (min)	Permate recovery (%) (Single)	Permate recovery (%) (Single)	Permate recovery (%) (Double)	Permate recovery (%) (Double)
20	35.21	34.88	54.91	52.27
40	35.74	35.00	55.23	52.62
60	35.51	35.12	55.20	52.81
80	35.44	35.19	55.35	52.56
100	35.74	35.54	55.53	52.82
120	35.84	35.66	55.35	52.96
140	36.17	35.53	55.35	52.96
160	36.17	35.36	55.35	53.22
180	36.62	35.36	55.35	53.22

Table A.39 Results of membrane configuration effect on salt rejection for 15 bar of operating pressure (Figure 3.39) (Tests 5,9,7,8).

Time (min)	Salt rejection (%) (Single)	Salt rejection (%) (Single)	Salt rejection (%) (Double)	Salt rejection (%) (Double)
20	98.61	98.98	98.42	98.64
40	98.73	99.09	98.42	98.64
60	98.73	98.98	98.42	98.64
80	98.73	98.98	98.42	98.64
100	98.73	98.98	98.42	98.64
120	98.73	99.09	98.42	98.53
140	98.73	98.98	98.42	98.53
160	98.73	98.98	98.42	98.64
180	98.73	98.98	98.42	98.53

Table A.40 Results of membrane configuration effect on boron rejection for 15 bar of operating pressure (Figure 3.40) (Tests 5,9,7,8).

Time (min)	Boron rejection (%) (Single)	Boron rejection (%) (Single)	Boron rejection (%) (Double)	Boron rejection (%) (Double)
20	49.47	57.03	37.55	45.96
40	48.86	57.46	39.58	46.36
60	49.06	57.54	39.76	46.22
80	48.76	58.10	38.47	45.67
100	49.87	57.78	40.97	45.77
120	49.43	58.36	37.38	46.25
140	50.50	57.73	42.32	45.98
160	50.87	58.40	40.80	46.80
180	47.98	58.64	42.15	47.07

Table A.41 Results of membrane configuration effect on chloride rejection for 15 bar of operating pressure (Figure 3.41) (Tests 5,9,7,8).

Time (min)	Chloride rejection (%) (Single)	Chloride rejection (%) (Single)	Chloride rejection (%) (Double)	Chloride rejection (%) (Double)
20	98.28	98.57	98.51	98.04
40	98.23	98.56	98.21	98.17
60	98.34	98.51	98.33	98.13
80	98.33	98.56	98.16	98.16
100	98.36	98.57	98.15	98.09
120	98.70	98.42	98.19	97.98
140	98.28	98.54	98.34	98.11
160	98.64	98.51	97.96	98.10
180	98.55	98.51	98.26	98.11

Table A.42 Results of membrane configuration effect on sulfate rejection for 15 bar of operating pressure (Figure 3.42) (Tests 5,9,7,8).

Time (min)	Sulfate Rejection (%) (Single)	Sulfate Rejection (%) (Single)	Sulfate Rejection (%) (Double)	Sulfate Rejection (%) (Double)
20	99.86	99.87	99.89	99.84
40	99.85	99.90	99.92	99.79
60	99.80	99.94	99.93	99.84
80	99.79	99.90	99.91	99.88
100	99.81	99.90	99.92	99.79
120	99.84	99.91	99.89	99.85
140	99.83	99.90	99.88	99.86
160	99.86	99.87	99.92	99.82
180	99.87	99.91	99.91	99.88

Table A.43 Results of membrane configuration effect on hydrogen carbonate rejection for 15 bar of operating pressure (Figure 3.43) (Tests 5,9,7,8).

Time (min)	Hydrogen carbonate rejection (%) (Single)	Hydrogen carbonate rejection (%) (Single)	Hydrogen carbonate rejection (%) (Double)	Hydrogen carbonate rejection (%) (Double)
20	97.70	97.96	97.94	97.79
40	97.61	98.05	97.94	97.97
60	97.99	97.86	97.84	98.15
80	97.99	98.05	97.75	98.15
100	97.80	98.05	97.84	98.15
120	97.80	98.05	98.13	98.15
140	97.80	98.14	98.03	98.06
160	97.99	98.14	98.03	98.15
180	97.70	98.14	98.13	97.97

Table A.44 Results of membrane configuration effect on sodium rejection for 15 bar of operating pressure (Figure 3.44) (Tests 5,9,7,8).

Time (min)	Sodium rejection (%) (Single)	Sodium rejection (%) (Single)	Sodium rejection (%) (Double)	Sodium rejection (%) (Double)
20	98.81	98.26	98.27	98.31
40	98.76	98.50	98.24	98.22
60	98.87	98.44	98.18	98.19
80	98.81	98.41	98.24	98.22
100	98.84	98.32	98.18	97.81
120	98.81	98.38	98.14	97.87
140	98.76	98.29	98.14	98.13
160	98.70	98.23	98.11	98.10
180	98.73	98.26	98.08	98.07

Table A.45 Results of membrane configuration effect on magnesium rejection for 15 bar of operating pressure (Figure 3.45) (Tests 5,9,7,8).

Time (min)	Magnesium Rejection (%) (Single)	Magnesium Rejection (%) (Single)	Magnesium Rejection (%) (Double)	Magnesium Rejection (%) (Double)
20	91.61	91.98	88.17	89.81
40	90.97	93.95	89.04	89.68
60	89.68	95.00	87.48	89.29
80	89.68	96.51	87.65	89.03
100	89.68	97.67	87.48	89.03
120	88.71	99.88	87.48	88.52
140	87.10	100.00	87.30	88.65
160	86.45	99.88	86.96	88.52
180	86.13	100.00	86.96	89.03

Table A.46 Results of membrane configuration effect on calcium rejection for 15 bar of operating pressure (Figure 3.46) (Tests 5,9,7,8).

Time (min)	Calcium rejection (%) (Single)	Calcium rejection (%) (Single)	Calcium rejection (%) (Double)	Calcium rejection (%) (Double)
20	99.53	99.50	100.00	100.00
40	100.00	100.00	100.00	100.00
60	97.67	99.50	100.00	100.00
80	100.00	98.50	99.33	100.00
100	100.00	99.50	100.00	98.89
120	99.53	100.00	100.00	99.44
140	99.07	100.00	100.00	100.00
160	100.00	100.00	100.00	98.33
180	100.00	100.00	100.00	100.00

Table A.47 Results of membrane configuration effect on potassium rejection for 15 bar of operating pressure (Figure 3.47) (Tests 5,9,7,8).

Time (min)	Potassium rejection (%) (Single)	Potassium rejection (%) (Single)	Potassium rejection (%) (Double)	Potassium rejection (%) (Double)
20	99.55	100.00	100.00	100.00
40	100.00	100.00	100.00	100.00
60	99.78	100.00	100.00	100.00
80	100.00	100.00	100.00	100.00
100	100.00	100.00	100.00	100.00
120	100.00	100.00	100.00	100.00
140	100.00	100.00	100.00	100.00
160	99.78	100.00	100.00	100.00
180	100.00	100.00	100.00	100.00

Table A.48 Results of membrane configuration effect on silisium rejection for 15 bar of operating pressure (Figure 3.48) (Tests 5,9,7,8).

Time (min)	Si rejection (%) (Single)	Si rejection (%) (Single)	Si rejection (%) (Double)	Si rejection (%) (Double)
20	99.26	99.31	99.04	99.14
40	99.26	99.29	99.04	99.14
60	99.32	99.30	99.04	99.15
80	99.33	99.27	98.98	99.15
100	99.26	99.26	99.03	99.15
120	99.26	99.26	99.04	99.15
140	99.23	99.29	99.03	99.14
160	99.24	99.28	99.04	99.14
180	99.23	99.29	99.04	99.15

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Publication at SCI Journals

Ozgur Arar, Emre Yavuz, Umran Yuksel, Nalan Kabay Separation of Low Concentration of Fluoride from Water by Electrodialysis (ED) in the Presence of Chloride and Sulfate Ions, Separation Science and Technology 44: 1562 – 1573, 2009

Awards

Türk Eğitim Vakfı 2007- 2008 öğretim yılı TEV Yüksek Öğrenim Üstün Başarı Ödülü

Presentations in National and International Conferences

1. E. Güler, E. Yavuz, N.Kabay M.Yuksel, U.Yuksel, An Alternative Method for Production of Safe Water: Seawater Reverse Osmosis (SWRO) Technique-Performance Tests for Short and Long Terms, *International Congress on Production of Safe Water*, January 21-23, 2009, İzmir (Poster presentation).
2. O.Arar, E.Yavuz, U.Yuksel, N.Kabay, Separation of Low Concentration of Floride Ion from Water Containing Chloride and Sulfate Ions by Electrodialysis (ED) Method, *International Congress on Production of Safe Water*, January 21-23, 2009, İzmir (Poster presentation).
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4. E.Yavuz, E.Güler, G.Sert, Ö.Arar, M.Yüksel, Ü.Yüksel, M.Kitiş, N.Kabay, Mini-Pilot Ölçek Spiral Sarım Ters Ozmos Sistemiyle Jeotermal Sulardan Bor Giderilmesi, *Membran Teknolojileri ve Uygulamaları Sempozyumu*, November 2-3, 2009, İstanbul (Poster presentation).
5. E.Güler E.Yavuz, S.Solak, G.Sert, M.Arda, , M.Yüksel, Ü.Yüksel, V.Gündoğdu N.Kabay, Deniz Suyundan Kullanım Suyu Üretiminde Ters Ozmos Yöntemi-Doğal Deniz Suyu Ortamında Ters Ozmos Membranlarının Performans Karşılaştırması, *Membran Teknolojileri ve Uygulamaları Sempozyumu*, November 2-3, 2009, İstanbul (Poster presentation).
6. E.Yavuz, Ö.Arar, M.Yüksel, Ü.Yüksel, M. Kitiş, N.Kabay, Boron Removal from Geothermal Water by Using A Small-Scale Reverse Osmosis (RO) Plant - Effect of pH and Membrane Configuration, *Eastern Mediterranean Chemical Engineering Conference (EMCC-6)*, March 12-17, 2010 (Poster presentation).

7. E.Yavuz, S.Solak, G.Sert, Ş.G.Öner, M.Arda, Ü.Yüksel, M.Yüksel, V.Gündoğdu, N.Kabay, A Comparative Study For Long Term Desalination Tests At Urla Bay –Effect of Membrane Type on Product Water Quality, *Eastern Mediterranean Chemical Engineering Conference (EMCC-6)*, March 12-17, 2010 (Poster presentation).
8. E.Yavuz, O. Arar, K. V. Ozdokur, S. Solak, A. Onac, U. Yuksel, M. Arda, N. Kabay, M. Yuksel, Desalination Performance of A Small Scale SWRO System for Geothermal Water – Effect of Applied Pressure, International Student Conference on Advanced Science and Technology ICAST, 25-26 May 2010 (Poster presentation).
9. G.Sert, V.Gündoğdu, E.Yavuz, N.Kabay, Environmental Impact Analysis of Seawater Reverse Osmosis Systems-Case Study for Urla, International Student Conference on Advanced Science and Technology ICAST, 25-26 May 2010 (Poster presentation).
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National Projects Involved

1. Project No: 2009 FEN 040, Scientific Research Project of Ege University, Removal of Boron from Geothermal Waters by Reverse Osmosis Method
2. Project No: BOREN 2008-G-0192, BOREN–Ulusal Bor Araştırma Enstitüsü, Tarımsal Sulamada Kullanım İçin Bor İçeren Sulardan Membran Filtrasyon, İyon Değişirme ve Sorpsiyon-Membran Filtrasyon Hibrit Yöntemleriyle Bor Giderilmesi ve Kazanılması.

Work Experience

1. 09/2007-10/2007 Dyo Boya Fabrikaları San. Tic.A.Ş. Çigli/ İzmir
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