Development, Modeling, Analysis, and Optimization of a Novel Inland Desalination with Zero Liquid Discharge for Brackish Groundwaters

by

Khaled Elsaid

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT

Groundwater is considered the major source of domestic water supply in many countries worldwide. In the absence of surface water supplies, the use of groundwater for domestic, agricultural, and even for industrial purposes becomes essential, especially in rural communities. Groundwater supplies typically are of good quality, and the quality is reasonably uniform throughout the year compared to that of surface water, thus making it suitable for direct use, or simple to treat. A disadvantage of groundwater is the content of dissolved salt as many have a moderate-to-high salinity. The high salinity makes water brackish and thus it requires desalination before use. This has led to wide use of groundwater desalination to produce good-quality water in many regions around the world.

Nevertheless, a problem of desalination processes is the generation of a concentrate stream, sometimes called brine or reject, which must be properly managed. The management of brine from brackish groundwater desalination is a significant issue if located far from the coast (i.e. inland plants) or far from public channel to discharge such brine.

Some options for brine disposal from inland desalination plants are evaporation ponds, deep-well injection, disposal to municipal sewers, and irrigation of plants tolerant to high salinities. Each of these disposal methods may result in many environmental problems such as groundwater contamination, the decline in crop yields from agricultural lands, the formation of eyesores, decreasing the efficiency of biological wastewater treatment, and making treated sewage effluent unsuitable for irrigation. As a result, the brine management from inland desalination of brackish groundwater is very critical, and the need for affordable and environmentally benign inland desalination has become crucial in many regions worldwide.

This work aims to develop an efficient and environmentally benign process for inland desalination of brackish groundwater, which approaches zero liquid discharge (ZLD), maximizing the water produced and minimizing the volume of concentrate effluent. The technical approach involves utilization of two-stage reverse osmosis (RO) units with the intermediate chemical treatment of brine stream that is designed to remove most of the scale-forming constituents, which foul membrane surface in RO and limits its water recovery and hence enable further recovery of water in the secondary RO unit.

The treatment process proposed in this work is based on advanced lime softening processes, which have the ability to effectively remove scale-forming constituents, in addition to heavy metals and natural organic matters that might be present in the brine. The process has been applied to the brine produced from 1st stage RO i.e. primary brine stream, to minimize the volume of the stream to be treated chemically, which in turn reduces the capacity of the treatment equipment.

Analysis of groundwater quality and scale-forming constituents that are present in the brine stream upon desalination of groundwater has been performed. The analysis has revealed that in most cases of brackish groundwater desalination the recovery is limited by scaling due to calcium sulfate i.e. gypsum, and amorphous silica. Thus, the main objective set for the chemical treatment of the brine stream focused on removal of calcium, sulfate, and silica.

Advanced lime softening based on high lime doses along with sodium aluminate, as in ultra-high lime with alumina UHLA process, has been proposed for chemical treatment of brine. Bench-scale experiments conducted to evaluate the effectiveness of the proposed chemical treatment for removal of scale-forming constituents, particularly calcium, sulfate, and silica by studying the different factors affecting the removals efficiency from synthetic solutions containing sulfate-only, silica-only, and model brine solution. The results obtained have revealed that the proposed process was very effective and results generally in high and quick removals of calcium, sulfate, and silica of more than 80% within 2 hrs under different experimental conditions.

In addition, beneficial uses of different solid byproducts formed are investigated, by analyzing the solids resulted to qualitatively and quantitatively to identify the different solids present. This offers the potential to lower both costs and solid disposal problems of solids formed being considered as added value product rather than solid waste that has to be properly managed. Results have shown that the solid precipitate contains a wide range of solids that generally composed of calcium, magnesium, aluminum along with carbonate, sulfate, and silicate, which have several potential applications as soil sub-grade, and in cement industry.

Equilibrium model to simulate the chemical treatment process that is able to predict the required chemical reagents doses, effluent water quality for a given influent water quality and treatment levels has been developed utilizing OLI stream analyzer, the developed model was found to well predict the performance of the chemical treatment at equilibrium conditions.

Rigorous membrane separation model has developed in Aspen Custom Modeler to more accurately model RO desalination, which is to be combined with the developed equilibrium model to formulate a complete 1st Stage RO–Chemical Treatment–2nd Stage RO process model. The developed complete and validated model has been then used to fully and accurately simulate the performance of the proposed Zero Liquid Discharge desalination process.

The present work results in three novel achievements: first, introducing a very effective intermediate chemical treatment, which efficiently remove sulfate, particularly from brine. Most of the previously proposed intermediate treatment processes remove sulfate as calcium sulfate i.e. gypsum, however in the introduced process, sulfate is removed in calcium-aluminum-sulfate complexes, which has very low solubility, making the brine highly undersaturated with respect to gypsum, and hence lowering the fouling propensity in the secondary RO, leading to maximizing the overall recovery. In addition, the chemical treatment has been successfully modeled for better simulate of its performance for different brine qualities, which are usually encountered in brackish ground desalination due to the high location-specific nature of groundwater quality.

Second, the developed membrane model has treated the species present in water as ions, accounting for monovalent and divalent ions separately, and obtaining a different permeability coefficient for their transport through the membrane. This is different from most developed RO models, which simplify the transport through the membranes to only water and salt permeability coefficients. This treatment results in better and more refined modeling and simulation of the RO membrane separation, as the RO membrane interact differently to ions present in water.

Third, the complete process model, results from combining the developed equilibrium model of the chemical treatment, and membrane separation model, has revealed very promising results of achieving high recovery desalination of about 93.5% suitable for drinking water purposes, which is higher by about 90% than most of the reported literature, whose result in reducing the brine volume from 25% in conventional desalination to only 6.5% in the proposed process, i.e. brine volume reduction of 74% relative to conventional inland desalination, and 35% relative to other high recovery processes, at reasonable chemical treatment levels.

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DEDICATION

To my dear parents, my beloved wife, and my lovely children with my everlasting love.

Tables of Contents

Page

Chapter

List of Figures

List of TABLES

List of Abbreviations

ACM	Aspen Custom Modeler
BOD	Biological Oxygen Demand
CAPS	Compact Accelerated Precipitation Softening
CP	Concentration Polarization
CPF	Concentration Polarization Factor
DI	Deionized
EC	Electrical Conductivity
ED	Electrodialysis
EDR	Electrodialysis Reversal
FAO	Food and Agriculture Organization
FO	Forward Osmosis
GCC	Gulf Corporation Council
HDPE	High-Density Polyethylene
IAP	Ion Activity Product
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometer
KSA	Kingdom of Saudi Arabia
LDHs	Layered Double Hydroxides
LSI	Langelier Saturation Index
MCM	Million Cubic Meter
MD	Membrane Distillation
MED	Multi-Effect Distillation
MENA	The Middle East and North Africa
MSF	Multi-Stage Flash Distillation
NDP	Net Driving Pressure
NF	Nano Filtration
NOM	Natural Organic Matter
OLI	OLI Stream Analyzer
RO	Reverse Osmosis
SAR	Sodium Adsorption Ratio

SDSI	Stiff & Davis Saturation Index
SI	Saturation Index
TDS	Total Dissolved Solids
TSE	Treated Sewage Effluent
UAE	United Arab Emirates
US	United States
USGS	United States Geological Survey
USEPA	The United States Environmental Protection Agency
VC	Vapor Compression
WHO	World Health Organization
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
ZLD	Zero Liquid Discharge

Nomenclature

A	Permeability of water through membrane (or Water transport coefficient), m^3/m^2.hr.bar
B	Permeability of salt through membrane (or salt transport coefficient), $m^3/m^2/hr$
B_{idv}	Permeability of divalent ions, $m^3/m^2/hr$
B_{imv}	Permeability of monovalent ions, $m^3/m^2/hr$
B_s	Permeability dissolved salts and solids, $m^3/m^2/hr$
B_g	Permeability dissolved gasses, $m^3/m^2/hr$
C_B	Brine salt concentration, g/m^3
C_F	Feed salt concentration, g/m^3
C_{Fm}	Feed average salt concentration, g/m^3
C_P	Product salt concentration, g/m^3
C_S	Membrane surface salt concentration, g/m^3
DG	set of dissolved gasses
DS	set of dissolved salts and solids
E	Energy consumption, kW
F^B	Molar flowrate on the brine side, kmol/hr
F^P	Molar flowrate on the permeate side, kmol/hr
g	Dissolved gases
H_b	Height of brine channel, m
H_p	Height of permeate channel, m
i	Ion i
i_{dv}	divalent ions
i_{mv}	monovalent ions
I	set of ions
I_{DV}	set of divalent ions
I_{MV}	set of monovalent ions
J^m	Molar flux of ions through membrane, $kmol/m^2/hr$
J^v	Volumetric flux of ions through membrane, $m^3/m^2/hr$
k	Mass transfer coefficient, m/hr
K_B	friction factor in brine channel, $1/m^2$

K_P	friction factor in permeate channel, $1/m^2$
K_{sp}	Solubility product
L	Membrane module length, m
m_i	Molar concentration of constitute i, mol/l
mt	Parameter of Mass transfer coefficient, dimensionless
P^d	Pressure drop across RO element, bar
P^B	Pressure on the brine side, bar
P_F	Feed pressure, bar
P_P	Permeate pressure, bar
P^P	Pressure on the permeate side, bar
Q_B	Brine flowrate, m^3/hr
Q_F	Feed flowrate, m^3/hr
Q_P	Product flowrate, m^3/hr
Q_s	Salt flow through membrane, g/hr
R	Universal gas constant = 0.08314 bar.l/ mol.k
R_P	Product recovery, %
s	Dissolved salts and solids
S	membrane surface area, m^2
SE	Specific energy consumption, kW/m^3
SP	Salt passage, %
SR	Salt rejection, %
T	Absolute temperature, K
V_{H2O}	Partial molal volume of water, l/mol
w	Water
W	Membrane module width, m
x	mole fraction of solute
Z^B	Mole fraction on the brine side, kmol/kmol
Z^P	Mole fraction on the permeate side, kmol/kmol
Z^S	Mole fraction on the membrane surface, kmol/kmol
γ^S	Activity coefficient at membrane surface

$\boldsymbol{\gamma_{H2O}}$	Activity coefficient of water
ΔC	Salt concentration difference across the membrane, g/ m^3
δ	Ions valence
$\boldsymbol{\eta_{pump}}$	Pump combined hydraulic and electrical efficiency
θ	X-ray angle if incidence
μ^B	Viscosity of solution on the brine side, bar.hr
μ^P	Viscosity of solution on the brine side, bar.hr
μ^S	Viscosity of solution on the membrane surface, bar.hr
Π	Osmotic pressure
Π^P	Osmotic pressure on the permeate side, bar
Π_{id}^P	Ideal osmotic pressure on the permeate side, bar
Π^S	Osmotic pressure on the membrane surface, bar
Π_{id}^S	Ideal osmotic pressure on the membrane surface, bar
$\overline{\rho}$	Molar partial density, kmol/m^3
ρ^B	Molar density of solution on the brine side, kmol/m^3
ρ^P	Molar density of solution on the brine side, kmol/m^3
ρ^S	Molar density of solution on the membrane surface, kmol/m^3
Φ^P	Osmotic coefficient on the permeate side
Φ^S	Osmotic coefficient on the membrane surface
ω^B	Velocity of solution on the brine side, m/hr
ω^P	Velocity of solution on the permeate side, m/hr

I. INTRODUCTION

Most of the world population uses surface and/or groundwater resources for public water supply. The common surface water sources are rivers, streams, and lakes. On the other hand, the common groundwater sources are flowing artesian wells, or pumped wells. In the absence of surface water supplies, the use of groundwater for different purposes of drinking and irrigation becomes essential, more specifically in the case of rural communities. In general, groundwater has higher quality compared to surface water, and the quality is quite uniform through the year making it easy to use directly or even to treat.

A major disadvantage is that many groundwater sources have moderate-to-high dissolved salts, due to the direct contact with rocks and formations bearing the mineral of such constituents, especially in areas with low rainfall, and hence less freshwater is recharged to groundwater aquifer. The high dissolved salts make the water brackish, and hence not suitable for drinking purposes, and in many cases not suitable for irrigation purposes as well, which in turn led to utilize desalination to produce good quality water.

Desalination describes a range of processes, which are used to reduce the content of dissolved salts in water that are often referred to as total dissolved solids TDS. Desalination is a reliable method for water supply worldwide and had successfully been applied for many decades with obvious technical and economic feasibility. The common processes for desalination such as multi-stage flash MSF, multi-effect distillation MED, and reverse osmosis RO have turned from being costly techniques, with high energy requirements, to reliable methods for sustainable water supply.

In desalination operations, thermal technologies were the first to be developed with MSF established as the baseline technology. Thermal desalination processes, specifically MSF, used to provide the major portion of the world's desalination capacity. However, as water quality standards become more stringent and the higher cost of energy, along with the recent developments in membrane science, membrane desalination processes in general and RO membranes, in particular, overtook thermal desalination processes as the leading desalination technology. The major factors led to the expansion of commercial RO applications are their favorable low-energy consumption, along with continuous technical improvements in RO membranes, in addition to high capacity flexibility to meet the demand of different communities’ sizes.

Over the last few decades, RO membrane processes have experienced significant developments enabling the massive production of water at a reasonable cost, providing efficient solutions to different necessities for domestic, industrial, and agriculture water supply in terms of capacity and verity of feedwater sources or qualities, as well as product water quality.

Due to flexibility in size or capacity and suitability for different feedwater salinities, and variable-controllable product water quality, RO desalination became the default choice for brackish water desalination for providing a domestic water supply for small and rural communities, as well as for agriculture purposes in many arid areas that lack surface water. Nevertheless, one main problem of RO desalination, like any other desalination process, is concentrate/brine effluent produced, that has to be disposed of properly to avoid many negative environmental impacts.

Fouling by sparingly soluble salts, commonly known as scaling, is a phenomenon that outbreaks the operation of desalination units, especially in RO desalination of brackish groundwater, limiting its recovery, and hence increasing the volume of brine generated from desalination. The deposition of foulants on the surface of RO membrane results in a decline of water production. Therefore as the fouling deposit builds up, the energy consumption has to be increased to maintain the required product flow till the unit is cleaned.

In order to reduce energy consumption, cleaning time and cost, and loss of production during operation interruption, it is important to mitigate fouling. In the case of scaling, the approach is to estimate the saturation levels of scale-forming salts in the feedwater and couple it with the system design recovery and to operate at levels where the solution is undersaturated and stable without of solids precipitation i.e. scaling. However, working at low recovery to avoid membrane scaling will increase the brine flow, which presents the main trade-off for membrane operation.

Although, one of the major problems of desalination is the generation of a brine stream that has to be properly managed; this problem is different in seawater from that of brackish water desalination. In seawater desalination, the problem is readily solved as these plants are always placed near the coast, so brine is discharged back to the sea. However, the management of brine from brackish groundwater desalination plants is a critical issue as they are usually placed far from the coast i.e. inland desalination plants. Some of the options for brine disposal from inland desalination plants are:

1) Evaporation ponds;
2) Deep-well injection;
3) Disposal to municipal sewer systems; and
4) Irrigation of plants tolerant to high salinities.

The major parameters that affect the selection of a certain disposal method are the quantity or the volume of brine, the quality or salinity of such brine, physical and geographical characteristic of plant location, and finally operational and capital costs. Each of these disposal methods poses many challenges and may result in some environmental or operational problems such as:

1) Decline in yields from agricultural lands caused by deposition of airborne salts from dried brine of evaporation ponds.
2) Groundwater contamination, in the case of deep-well injection and irrigation, due to the high salinity and the presence of harmful chemicals added during desalination process.
3) Unsuitability of treated municipal sewage effluent for treatment when a sewerage system is used for disposal of high-salinity brine.

Due to such problems, brine management is usually very critical for brackish water inland desalination, and hence the need for affordable inland desalination has become very crucial worldwide, specifically for rural communities to meet the growing water demands.

When concentrate management is an issue, the ultimate solution is Zero Liquid Discharge, ZLD, in which concentrate or brine stream is treated for further water production, leaving basically dry or semi-dry solids, and hence there is no discharge of liquid waste from the site. Most ZLD applications today are for the treatment of industrial wastewater using thermal and/or membrane processes. Thermal processes have been practiced for a long time especially where energy is relatively inexpensive. Although it generates high-quality product water, it is energy-intensive, with high capital and operating costs. The developments in ZLD processes and associated cost reduction will be of remarkable benefit and will resolve water supply challenges faced worldwide.

In conclusion, as groundwater is the main source of potable water in the absence surface water, its quality, more specifically its salinity, is deteriorating that to the utilization of desalination processes to provide good-quality water. The use of RO desalination systems is very beneficial due to the high flexibility with capacity and feedwater quality, low energy consumption, and low cost. However, the generation of brine is the major obstacle facing the efficient utilization of desalination process, more specifically inland plants. Developing an efficient inland desalination with zero liquid discharge presents the ultimate solution to approach an efficient and environment benign inland desalination process. Given such need, it is utmost to develop a zero liquid discharge process that provides environmental and affordable concentrate management at a reasonable cost.

Therefore, the goal of this work is to develop a highly efficient and environmentally benign process for brackish groundwater inland desalination that approaches zero liquid discharge ZLD. The technical approach proposed in this study is to combine two-stage reverse osmosis (RO) units with highly efficient intermediate brine treatment process to remove the scale-forming constituents, making the brine suitable for further and more efficient processing in secondary RO unit. The application of intermediate treatment is to enable maximizing water recovery and minimizing the final concentrate stream that needs to be managed at an affordable cost.

This goal is to be achieved by accomplishing the following objectives:

1) Preliminary process analysis of groundwater: with respect to different quality parameters such as salinity, investigating its suitability for drinking and irrigation purposes.
2) Preliminary process analysis of brackish groundwater desalination: with respect to recovery limitation and scaling tendency of different water constituents.
3) Studying the kinetics and equilibrium of the removal of scale-forming material constituents in the proposed advanced lime-softening based chemical treatment processes at bench scale.
4) Developing equilibrium model to simulate the chemical treatment process, to predict the effluent water quality and solid precipitates formed under different treatment conditions, and brine qualities.
5) Identifying beneficial uses of solids produced during the intermediate chemical treatment as potential added value product.
6) Developing a rigorous and highly accurate membrane separation model to model the RO membrane desalination process and combine it with the developed equilibrium model of the chemical treatment to produce a complete processes model for the proposed ZLD scheme investigating the overall system recovery for a given brackish groundwater quality and flowrate.

Figure 1.1 below shows a scheme of the proposed research methodology to be followed to achieve the set goal of developing ZLD process for brackish groundwater desalination through the development of highly efficient intermediate chemical treatment.

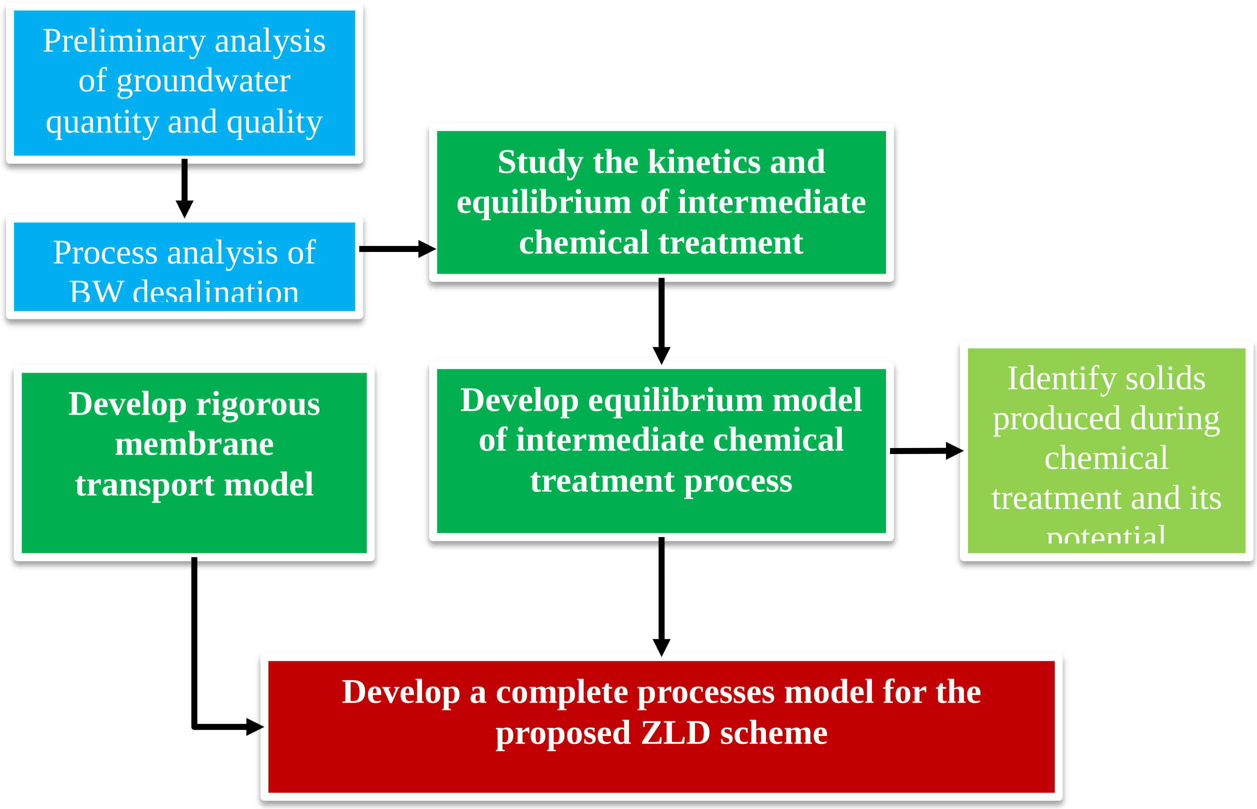


Figure 1.1 Schematic diagram of the research methodology.

Six-task program is to be conducted to achieve the six research objectives. The first task is the preliminary process analysis, which focuses on studying groundwater resources in arid and semi-arid areas both quantitatively and qualitatively in terms of salinity in general, and other constituents related to suitability for drinking and irrigation purposes. Due to the high variability and location-specific nature of groundwater quality from one location to another worldwide, regionally, and even locally, and in many times within the same groundwater aquifer, groundwater resources in the State of Qatar, as an example to a very arid region with high challenges for groundwater resources, has been chosen as case study for analyzing the quality of groundwater resources.

The second task is to focus on preliminary process analysis of brackish groundwater RO desalination, for the same case-study area i.e. groundwater resources in the State of Qatar, with a focus on the maximum achievable recovery. More attention is being paid to scaling tendency by different sparingly soluble salts in specific, which helps to determine the target components to be removed from brine stream during the chemical treatment process.

The third task is to study the kinetics and equilibrium of scale-forming constituent removals during the proposed chemical treatment process. Advanced lime softening processes, specifically high lime with alumina UHLA process is proposed for this purpose. The proposed UHLA process is a novel application of advanced lime softening for the treatment of brine stream in brackish groundwater desalination. The task is to focus on the effect of different parameters such as feedwater quality i.e. salinity and initial concentrations of such scale-forming constituents, doses of chemical reagents and other factors are to be studied. The experimental work mainly focuses on the removal efficiency of different scale-forming constituents from model saline solutions of brackish groundwater brine at different treatment conditions.

The fourth task is to develop an equilibrium model for the chemical treatment process to predict the effluent water quality and formed solid precipitates at specific influent water quality, chemical reagents, and reagent doses. Due to the high ionic strength of brine stream and the fast reacting nature of the ionic reactions, equilibrium rather than kinetic modeling has been assumed for the chemical treatment. The development of equilibrium model for the chemical treatment is very crucial for the development of complete process model, as the chemical treatment process is the key solution to approach the ZLD goal of brackish water desalination. OLI stream analyzer is to be utilized for this purpose which is a powerful tool for modeling aqueous systems, newly applied here for modeling of UHLA advanced lime softening.

The fifth task is to characterize the solids formed during the chemical treatment step and to investigate the beneficial uses of such solids. Utilization of such solids offers the potential to lower overall process costs and potential environmental problems associated with solid waste disposal, being considered as added value products. The solids produced during the chemical treatment of the brine will be characterized by analysis of solids produced from experiments using X-ray techniques, as well as utilizing the developed equilibrium model, which predicts the solids formed according to their saturation indices.

The sixth task is to develop a complete process model enabling the study of the effect of different process variable on the process performance, and more specifically the overall system recovery. In order to build such complete process model, a rigorous membrane separation model to simulate the RO membrane desalination has to be built. The developed membrane separation model is to be built in Aspen Custom Modeler environment and utilized as a customized model unit. The membrane separation model to be developed here will utilize a novel approach for treating monovalent and divalent ions differently, as the membrane reacts to these two categories of ions differently. This is a distinct improvement to membrane separation modeling, which treats all ions present in water similarly, with only two types of membrane permeability, one for solvent i.e. water and other for salt, regardless of salt type or nature.

Complete process model with Primary RO-Intermediate chemical treatment-Secondary RO is to be built in the process simulation environment of Aspen Plus using Aspen Custom Modeler ACM model for RO membrane process and OLI stream analyzer for chemical treatment equilibrium model. This complete model is developed to simulate and analyze the process performance under different operating conditions.

This thesis is organized into five chapters; Chapter I, provides a general introduction to the thesis subject along with work objectives and the methodology to achieve such objectives.

Chapter II provides background and literature review covering water resources in general, and groundwater resources in particular, with a focus on groundwater quality and the problems leading to the use of desalination. The chapter also tackles desalination technologies, with a focus on RO membrane desalination, along with the limitation of system recovery due to fouling and scaling, with a discussion on the formation of scales during desalination due to saturation of different salts. The chapter covers the chemical equilibrium modeling of dissolution/precipitation phenomena which leads to scale formation. Then the different options for brine disposal are browsed, discussing the advantages and disadvantages of each leading to the crucial demand for affordable ZLD. Later the different approaches and efforts for developing high recovery desalination systems are discussed.

Chapter III explains in details the research methodology with respect to preliminary process analyses performed to estimate the crucial groundwater quality parameters, the desalination process performance and quality of produced concentrate stream, and critical components to be addressed for the chemical treatment of brine stream. The experimental and analytical procedures developed and used during the bench scale experiments and solid characterization is discussed. Then the procedures used to develop the equilibrium model of the chemical treatment of brine. The chapter then explains the methodology to characterize and identify the solids formed during the chemical treatment both qualitatively and quantitatively. Finally, the chapter covers the procedure used for the development of RO membrane separation model and overall process modeling to be used for process simulation.

Chapter IV presents the results obtained and the detailed discussion of preliminary groundwater quality, brackish groundwater desalination process analyses, bench scale experiments along with the results of chemical treatment equilibrium modeling and characterization of solids produced during the chemical treatment. Finally, the results obtained from the performed process modeling of the complete Primary RO – Intermediate chemical treatment – Secondary RO are explained showing the effect of different process variable on overall process performance.

Finally, Chapter V summarizes and concludes the results obtained in this work and their relevance to the improvement of water supply in arid regions of the world in general, and inland desalination of brackish groundwater in particular, and future research needs in this area.

II. BACKGROUND AND LITERATURE REVIEW

Groundwater reservoirs present a major source of fresh water, with respect to storage capacity, as it contains about 99% of the total available fresh water worldwide. Groundwater usually considered as high-quality water resource relative to surface water. However, a major problem of groundwater resources in some areas worldwide is that many have moderate-to-high salinity i.e. brackish, thus has to be treated to have the water suitable for potable use, and this has given rise to the application of brackish groundwater desalination. The demand for affordable groundwater desalination is becoming a vital objective in many regions around the world, given the increasing water demand. The ability to affordably treat brackish groundwater would provide a sustainable solution for many rural communities.

Desalination is a range of processes which are used to reduce the level of dissolved solids in water. Reverse osmosis RO membranes desalination is the process of choice for brackish groundwater desalination due to size or capacity flexibility, and suitability for a wide range of feedwater qualities, which is usually encountered in brackish waters. However, like any other desalination process, it creates a concentrate or brine stream containing the rejected salt at much higher concentrations, that must be handled properly to avoid many environmental problems. Management of brine from brackish groundwater desalination is usually a significant issue, especially when such plants are located away from the coast or public channel, i.e. inland desalination plants. So brine management is very critical for brackish groundwater desalination. Where brine management is a challenge, the ideal solution is Zero Liquid Discharge (ZLD) where brine is treated to produce more product water and almost dry salts, and hence there is no discharge of liquid waste from the desalination plant.

In this chapter we will explore water resources with a focus on groundwater quantity and quality, desalination technologies particularly membrane desalination and RO desalination, brine disposal methods and the factors led to the need for developing ZLD desalination as well as the recent developments in ZLD desalination technologies and challenges faced.

2.1 Water Resources.

Water is considered the most valuable natural resource and an indispensable commodity, due to the fact that it is essential for life, for human health, and for the preservation of the environment. Furthermore, water is also considered the most abundant compound on Earth's surface, covering around 70% of the total surface (USGS, 2011). Water exists in nature in all the three physical states liquid, solid i.e. ice, and in gaseous i.e. water vapor, however, due to its unique structure, it is mainly present in the liquid state.

Water resources are the different sources of water present in the environment that are useful for human activities such as agricultural, industrial, and household. Water resources can generally be divided to freshwaters and saline waters according to their content of dissolved salts. Table 2.1 present recent information on the amount of different water resources.

Table 2.1 Estimates of major water resources on Earth (Gleeson, Wada, Bierkens, & van Beek, 2012; Gleick, 2001, 2006).

Water Resource	**Volume, (10^3 km^3)**	**Percent of total water**	**Percent of total fresh water**
Saline water:			
Oceans/seas	1,338,000	96.54	-
Saline/brackish groundwater	12,870	0.93	-
Saltwater lakes	85	0.006	-
Freshwater:			
Glaciers and permanent snow covers	24,064	1.74	68.70
Fresh groundwater	10,530	0.76	30.06
Fresh lakes	91	0.007	0.26
Wetlands	11.5	0.001	0.03
Rivers	2.12	0.0001	0.006

Freshwater is the water present on Earth's surface and in underground aquifers, which is characterized by low content of dissolved salts, and usually considered as a renewable resource due to the natural water cycle. Surface freshwater is the water present in rivers, fresh lakes, and streams, which results mainly from natural precipitation of rains, snow….etc. Surface water has a low salinity usually below 500 mg/l. Although surface water is very common, it presents only 0.27% of the total available freshwater on Earth (Gleick, 2006).

Fresh groundwater is the groundwater present under the Earth's surface in aquifers located below the water table. Fresh groundwater is characterized by higher salinity when compared to surface water with salinity up to 2,000 mg/l (Mickley, 2006). Fresh groundwater constitutes about 0.76% of total water present on Earth, and 30% of total available freshwater (Gleick, 2006).

Saline water is the water with a reasonable content of dissolved salts as found in oceans, seas, and brackish groundwater. Saline water represents the majority of water on Earth in terms of volume by about 97.5% of the total water (Gleick, 2006). Saline water present in oceans and seas mainly characterized by its high salinity. Brackish groundwater is characterized by high salinity compared to fresh groundwater, with a salinity of about 2,000-10,000 mg/l or higher (Mickley, 2006), and usually present in deeper aquifers, and it accounts for about 0.93% of the total water on Earth, and present in a comparable quantity to that of fresh groundwater (Gleick, 2006).

Figure 2.1 shows the worldwide groundwater resources map; the map indicates that about 35% of the continental areas, excluding the Antarctic, is underlined by homogenous aquifers, with about 18% endowed with groundwater. The map shows as well that most of the areas facing water stresses and water scarcity in arid and semi-arid areas, due absence of surface water resources as in the Middle East and North Africa i.e. MENA area, and Central Asia, have good access to groundwater resources, and hence the increase rely on groundwater resources in such regions.

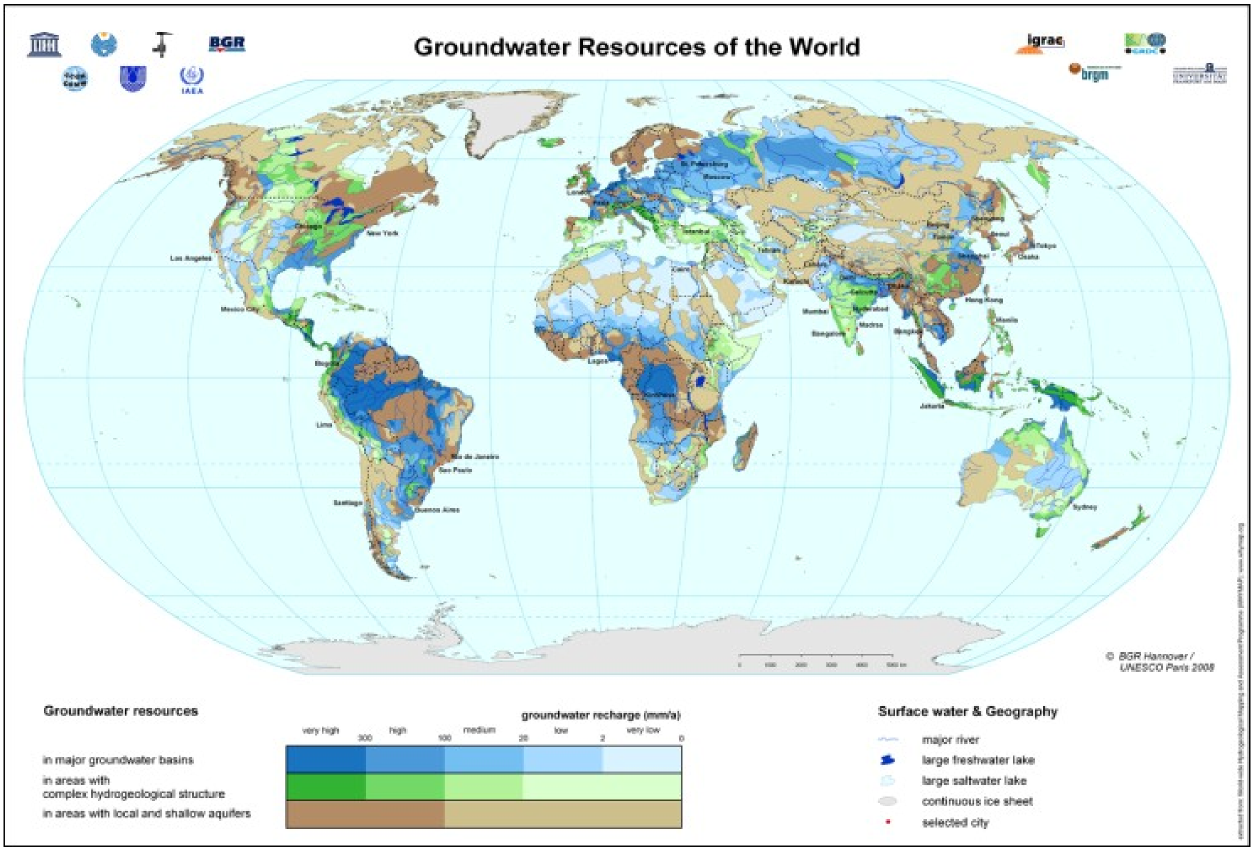


Figure 2.1 Worldwide groundwater resources map (Institute for Geosciences and Natural Resources, 2012).

2.2 Groundwater Quality.

Water quality is the different characteristics of water, mainly biological, physical, and chemical characteristics, and it generally helps to compare the different water sources to each other and to water standards. A water molecule is very simple and of unique structure, as it contains two hydrogen atoms bonded to one oxygen atom; however, such structure leads to many distinguished physicochemical properties. Due to its unique chemical structure, water is considered a universal solvent, hence it is able to dissolve and ionize many natural and synthetic, inorganic and organic compounds, as well as ability to suspend solids, thus it is very hard to be present naturally in pure form (Delleur, 2007; Gleick, 2006). The water quality is mainly characterized by its content of dissolved solids, dissolved gasses, suspended solids, and biological matter present.

Biological characteristics of water are related to the biological matter found in water, basically bacteria, fungi, algae, and viruses. Generally speaking, groundwater is free of microbes and biological matter due to natural filtration and absence of oxygen in underground aquifers (Reynolds & Richards P. A., 1996).

The physical characteristics of water are those related to dissolved solids, suspended solids, turbidity, taste, odor, and color. As groundwater undergoes natural filtration while flowing through soil formations, it has very low suspended solids and turbidity, clear color, low odor, and pleasant taste. However, while water is traveling through the rock formation, some of its content dissolves, thus water may contains high dissolved solids content, which varies depending on rock formation composition, flow velocity, and contact time (Delleur, 2007).

Chemical characteristics of water are mainly pH value, the chemical composition of dissolved solids, alkalinity, acidity, hardness, dissolved gasses, and other pollutants that might be present. The pH values range from 5 to 8.5 for natural water, which is generally acceptable; and for groundwater, it is mainly in the range of 7 to 8 (Gleick, 2006). The chemical composition of the dissolved solids found in groundwater depends mainly on the slow dissolving action of soils, rock formations and minerals and its type. Groundwater generally has higher hardness, which is basically due to the dissolution of dolomite and limestone formations that increase the concentration of calcium and magnesium in the groundwater (Delleur, 2007).

Generally speaking, groundwater has higher quality compared to surface water, which is quite uniform making it easier to treat. However, the main disadvantage is the higher content of dissolved salts that makes it brackish and therefore requires desalination to overcome such problem and to provide the water supply to the underserved community where groundwater makes up for water shortage and stress (Reynolds & Richards P. A., 1996).

Technical and economic evaluation of brackish groundwater desalination has begun since the early 1960s. The early brackish groundwater desalination plants were commissioned in Florida, US, in the mid-1970s, utilizing Reverse Osmosis RO with a capacity of 1,900 m^3/d (Bart Weiss, 2002). Field investigations along with model simulations were used to assess the technical and economic feasibility of large-scale RO desalination utilizing highly brackish groundwater as feed in many countries around the world showing its high feasibility (Al-Zubari, 2003; Hadi, 2002; Sherif, Mohamed, Kacimov, & Shetty, 2011).

The major misconception of considering groundwater has stable salinity, is very serious for RO desalination plant design, as the salinity of groundwater tends to increase over time i.e. in years, thus initial and projected future groundwater qualities; more specifically salinity should be considered (Missimer, 1994; NRS Consulting Engineers, 2008). The deterioration of groundwater quality is mainly due to different human activities such as over abstraction of groundwater resources combined with low groundwater aquifer recharge, in addition to seawater intrusion, more particularly in coastal zones. The seawater intrusion is a common problem in coastal areas, in which saline seawater moves into the fresh groundwater in coastal aquifers, mainly attributed to the density difference between fresh groundwater and seawater and to tidal effects, and found to be the major cause for the increased salinity of coastal aquifers worldwide (Amer, Al-muraikhi, & Rashid, 2008; Sherif et al., 2011).

2.3 Desalination Processes.

Desalination describes a range of technologies or processes that are used to reduce the total dissolved solids TDS or salts present in water. Desalination of seawater and brackish water is currently considered as a reliable method for water supply worldwide and had been practiced for decades with obvious technical and economic feasibility. The worldwide desalination capacity has increased significantly from 35 million cubic meter MCM/d in 2005 (Gleick, 2006) to about 86.8 MCM/d by June 2015, with the largest desalination plant of about 1 MCM/d at Shoaiba III plant in Saudi Arabia. By June 2015 there were 18,426 desalination plants online, in around 150 countries worldwide (IDA, 2015).

Desalination can generally be classified with respect to the feedwater source into two classes, seawater, and brackish water desalination. In 2006 seawater desalination accounts for around 56% of the world’s desalination capacity, while brackish water desalination accounts for 24% (Gleick, 2006). Gulf Cooperation Council (GCC) countries, United States (US), Spain, and Japan are the main countries utilizing desalination with capacity over 1 MCM/d, with Middle East countries holding more than 50% of the global water desalination capacity (IDA, 2008).

According to desalination technology, desalination processes are many and can be mainly divided into thermal desalination, membrane desalination, in addition to some other desalination processes which have not been fully developed at the commercial level yet.

The selection of desalination process, however, depends on several factors, with energy cost, feedwater type or quality, and fouling propensity are the salient ones. Table 2.2 shows the distribution of worldwide, US, and GCC desalination capacity according to desalination process.

Table 2.2 Desalination capacity percentage distribution by process type (Gleick, 2006).

Process Type	Worldwide	United States	GCC Countries
RO	46	69	28
MSF	36	1	54
ED	5	9	-
VC	5	3	-
MED	3	1	9
NF	-	15	-
Others	5	2	9
Total	100	100	100

The quality of produced water differs from one desalination process to another. Thermal desalination produces a very high quality water with salinity below 10 mg/l regardless of the feedwater quality (Gabbrielli, 1981; Khawaji & Wie, 1994), while product water from membrane desalination has a variable quality depending on many factors such as the feedwater quality or salinity (i.e. seawater or brackish water), design recovery, membrane characteristics, in addition to other operating conditions, but generally will have higher salinity compared to that produced from thermal desalination (D. Li & Wang, 2010).

The quality required for final product water depends mainly on the purpose the water will be used for, as it ranges widely from medium for drinking and agriculture applications, to very high quality for industrial and medical applications. Large desalination plants are usually designed to meet drinking water requirements, and further polishing to improve water quality can be applied at later stages to meet specific water requirements (Gabbrielli, 1981).

The drinking water guidelines or standards vary from one country to another according to the local environmental and health regulations. The drinking water standards of the US Environmental Protection Agency, USEPA are incorporated and widely accepted worldwide with 500 mg/l for total dissolved solids (USEPA, 2016). On the other hand, the World Health Organization WHO, considers water with salinity up to 1,000 mg/l is generally acceptable (Gorchev & Ozolins, 2011). Food and Agriculture Organization FAO considers water with salinity up to 2,000 mg/l is generally suitable for irrigation purposes with consideration given to other parameters such as sodium adsorption ratio, SAR (Ayers & Westcot, 1994; Bellows, 2004; FAO, 2011).

2.3.1 Thermal Desalination Processes.

Thermal desalination processes used to be the most viable process for a long time, with multi-stage flash distillation, MSF, and multiple-effect distillation, MED, as the main processes. Thermal desalination has provided a major portion of the world's desalination capacity for a long time till the recent developments in membrane desalination (Miller, 2003). Thermal processes are applied for high salinity feedwater i.e. seawater, specifically in GCC area as seawater can reach salinity of 45,000 mg/l relative to the standard seawater salinity of 32,000 mg/l (about 1.5 folds the salinity), high recoveries, feedwater with high temperature, and more important low energy cost, given the extensive energy consumption (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009).

Thermal desalination is phase-change desalination; which mimics the natural water cycle where thermal energy, in the form of solar energy, evaporates water into vapor, which condenses back into liquid, and hence phase changes from liquid to vapor and then back to liquid. In thermal desalination, heat, from burning fuel, is utilized to drive evaporation in evaporators or distillers.

2.3.2 Membrane Desalination Processes.

Due to the massive increase in energy cost, along with the developments in membrane science, membrane desalination, and specifically commercial RO have overtaken thermal desalination and became the leading desalination technology of today, mainly due to their favorable low energy consumption, along with recent technical developments.

RO desalination was first applied to brackish groundwater with first large-scale plants built in the late 1960s to mid-1970s. Further RO membrane development results in utilizing such membranes for seawater desalination, becoming a strong competitor to thermal desalination by 1980s (Van der Bruggen & Vandecasteele, 2002), and hence membrane desalination market expanded water sources by utilizing both brackish water and seawater.

Reverse osmosis membranes have experienced major development, enabling massive water production at moderate cost and energy consumption, helping to provide flexible solutions to wide different necessities within the different water supply fields such as domestic, industry, and agriculture. Such developments results in lower energy consumption, lower membrane cost, better membrane material, and longer lifetime (Sandia National Laboratories, 2009).

In membrane processes, a semi-permeable membrane is used, which allow water to pass but not salt ions to a different extent under certain hydraulic pressures as driving forces. The membrane processes differ depending on the degree of salt ion passage or rejection and driving force. The main membrane processes are reverse osmosis RO, nanofiltration NF, and forward osmosis FO.

Reverse Osmosis RO:

Osmosis is a natural phenomenon, in which solvent component, water in case of desalination, pass through a solvent semi-permeable membrane, i.e. impermeable to solute but permeable to solvent, from lower salt concentration i.e. higher water concentration, to higher salt concentration i.e. lower water concentration, as shown in figure 2.2, thus creating a kind of differential pressure across the membrane called osmotic pressure (El-Dessouky & H. M. Ettouney, 2002).

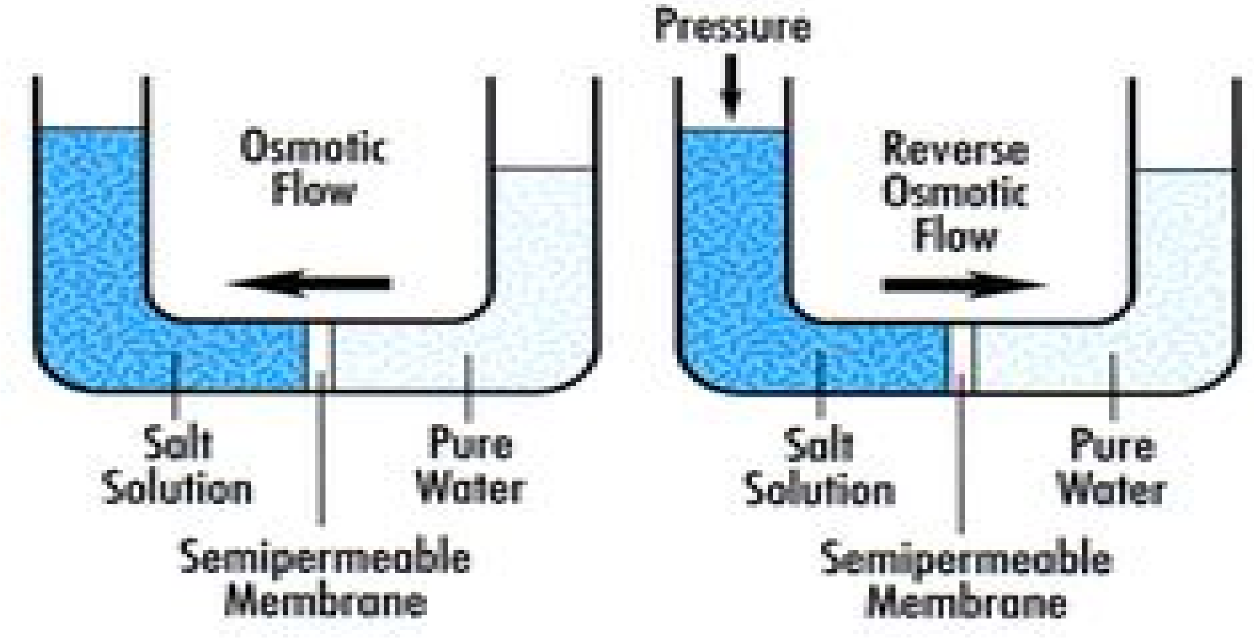


Figure 2.2 Osmosis and reverse osmosis phenomena.

Osmotic pressure depends on the concentration of solute, temperature, and nature of solute i.e. organic, inorganic, monovalent or divalent ions. The osmosis process continues to the point at which the hydraulic pressure difference across the membrane due to the liquid column balances the osmotic pressure difference between the two solutions on the membrane sides. In RO desalination, hydraulic pressure higher than that of osmotic pressure difference is applied to the high salinity i.e. seawater or brackish water, thus reversing the natural osmosis process, results in net water flow from the high salinity side to the dilute solution i.e. product water (Fritzmann, Löwenberg, Wintgens, & Melin, 2007).

RO membranes consist of a polymeric material of a layered, web-like structure, which is characterized by very impermeability or high rejection to salts present in water, with the typical rejection of about 99.4 - 99.8% (Greenlee et al., 2009; Lee, Arnot, & Mattia, 2011). The driving force for RO process is the applied hydraulic pressure, which is to overcome the osmotic pressure of the concentrated water, thus it varies considerably from 15-25 bar for brackish water to 60-80 bar for seawater (Fritzmann et al., 2007).

Nanofiltration NF:

Nanofiltration membrane was first developed by FilmTech in the early 1980s for RO membranes that allow selectively certain ionic solutes or compounds to pass through the membrane. The membrane's selectivity of the developed membrane was towards solutes of 1 nm cutoff, and hence comes the name Nano (Fritzmann et al., 2007). Nanofiltration is an intermediate membrane process between RO membranes and ultrafiltration UF membranes (Eriksson, 1988).

NF membranes generally have higher permeability toward monovalent ions compared to multivalent ions and organics with MWCO around 300 (Rautenbach & Groschl, 1990). NF membranes were widely applied for removal of hardness and natural organic matter for the pretreatment in seawater desalination (Matallah Al-Shammiri, Ahmed, & Al-Rageeb, 2004; Hassan, 1998), and for improving groundwater quality (Saitua, Gil, & Padilla, 2011; Tahaikt et al., 2007; Van Der Bruggen, Lejon, & Vandecasteele, 2003; Walha, Amar, Firdaous, Qumneur, & Jaouen, 2007). NF membrane operates in a similar fashion to that of RO membranes; however the applied hydraulic pressure is much lower; and hence lower energy consumption, but this is accompanied by lower product water quality (Schaep et al., 1998).

Electrodialysis/ Electrodialysis Reversal ED/EDR:

Electrodialysis ED is one of the old developed membrane desalination processes since the 1950s. In ED electrochemical separation is the phenomenon encountered through the application of electrical energy as a driving force to separate ions from water through specific-ions permeable membranes (Gleick, 2001). In typical ED cell, an alternating series of anion- and cation- permeable membranes are arranged between two electrodes cathode and anode, and hence ions concentration increase/decrease in alternating compartments of the cell (Walha et al., 2007), ED has been successfully applied for brackish water (Adhikary, Narayanan, Thampy, & Dave, 1991; Brown, 1981; Harkare, Adhikary, Narayanan, & Govinda, 1982; Walha et al., 2007), and seawater (Sadrzadeh & Mohammadi, 2008; Seto, Ehara, Komori, Yamaguchi, & Miwa, 1978; Yang, Gao, Fan, Fu, & Gao, 2014).

Electrodialysis reversal EDR, as major development in ED process that has been introduced in the 1970s, which operates on the same principle as ED, but with reversible electrode polarities at specific time intervals, hence there comes the term reversal, which results in ions attraction in the opposite direction, and hence the product and brine are alternated (Katz, 1979). EDR process has many features over conventional ED, such as ability to treat lower quality feedwater i.e. higher suspended and dissolved content, higher scale resistance so it operates at high saturation levels, being tolerant to scaling by non-ionic species such as silica, high chlorine tolerance, ease of cleaning, higher recovery, lower pretreatment requirements, and durability, however, the main disadvantages was the high energy consumption associated with electrical energy utilized in such systems (Fubao, 1985; Katz, 1982; Sadrzadeh & Mohammadi, 2008; Valcour, 1985).

Forward Osmosis FO:

Although RO membrane is currently the main membrane desalination process, energy and membrane costs are a major concern, so lower energy and lower fouling propensity membranes are being researched. Forward osmosis FO, or direct osmosis DO, utilizes the natural osmosis phenomenon (Cath, Childress, & Elimelech, 2006; Chung, Zhang, Wang, Su, & Ling, 2011).

In FO, the natural tendency of solvent i.e. water to pass through the semi-permeable membrane from the lower salinity to higher salinity is utilized. The higher salinity solution or usually called draw solution has a significant higher osmotic pressure than the lower salinity water i.e. seawater or brackish water in case of desalination, thus it improves the water flux through the membrane. Different draw solutions have been tested for FO operation, ranging from gasses or volatile solute, so it can be stripped out, to perceptible salts such as aluminum sulfate or alum (Cath et al., 2006; Chung et al., 2011).

Recently, a mixture of carbon dioxide-ammonia has been tested as a draw solution, with main advantages of high solubility of carbon dioxide and ammonia gasses in water, along with the high osmotic pressure of the formed solution of ammonium bicarbonate, enabling higher recovery, followed by easy recovery of gases from product water by moderate heating (McCutcheon, McGinnis, & Elimelech, 2005, 2006).

FO process does not require hydraulic pressure, unlike other membrane processes, so less energy is required, which results in lower operating and capital costs, in addition, to the lower fouling propensity. Nevertheless, the main challenge hindering the full-scale development of FO systems is the water extraction from draw solution and regeneration of draw solution to be recycled in the process (Chekli et al., 2012; Valladares Linares et al., 2014; William A. Phillip, 2010).

2.4 Challenges in Desalination Processes.

Desalination has been practiced intensively over the past few decades; due to the great developments that have led to wide application worldwide, specifically in arid areas. Although most desalination processes are currently well established, further developments are required to resolve various operational and technical issues, which represent the crucial keys for efficient desalination. These issues include fouling and scaling propensity, brine disposal, integration of different desalination processes, energy consumption, and desalination economics (Raphael Semiat & Hasson, 2012; R. Sheikholeslami, 2009).

2.4.1 Process Improvement.

Desalination plants used to employ one process type i.e. MSF, MED, or RO only; however, more attention has recently given to combining different desalination processes at one site, aiming to maximize overall system recovery and minimize brine discharge, energy required, and cost through the integration of multi desalination processes.

Different membrane processes have been integrated successfully, such as NF with RO, mainly for pretreatment of seawater resulting in improvement of RO performance (Matallah Al-Shammiri et al., 2004; Hassan, 1998). Similarly ED/EDR with RO (Oren et al., 2010), as well as FO with RO as well (Y. J. Choi et al., 2009; Martinetti, Childress, & Cath, 2009; Tang & Ng, 2008). Combining membrane and thermal processes such as NF/RO/MSF (Tang & Ng, 2008), FO and membrane distillation MD to RO (Martinetti et al., 2009) was found to be successful as well.

For thermal desalination processes, development of better corrosion resistance material believed to improve the process from early used carbon steel to stainless steel and then duplex steel. In addition, better antiscalants had a significant effect that led to much better scaling resistance enabling working at higher temperatures that result in increasing the water recovery, reducing the shutdown time-frequency and duration, and hence improving the process performance (Khawaji, Kutubkhanah, & Wie, 2008).

For membrane processes, advancement in membrane science for developing better membrane material that tolerates wide pH range, higher chlorine resistivity, with higher mechanical strength to enable utilization of higher hydraulic pressures, as membrane strength to hydraulic pressure was found to be the main recovery limiting seawater desalination, higher salt rejection, and higher fouling resistivity are considered very crucial, which to enable higher recoveries at lower energy consumption and cost (Cath et al., 2006; D. Li & Wang, 2010).

Pretreatment is considered one of the key issues for successful desalination process. During pretreatment many chemicals are added such as antiscalants, dispersants, coagulants, corrosion inhibitors…etc., which contribute to overall process performance as well as the operational cost, and hence any developments in these key chemicals will positively affect the desalination process (Greenlee et al., 2009; Llenas, Martinez-Llado, Yaroshchuk, Rovira, & de Pablo, 2011; Van der Hoek, Hofman, Bonne, Nederlof, & Vrouwenvelder, 2000).

2.4.2 Energy Consumption.

Desalination, in general, is well-known for high energy consumption, particularly thermal desalination, and hence energy consumption is the highest costly component in any desalination process. The energy consumption depends on the type of desalination process employed i.e. membrane or thermal, and the type of the process itself i.e. MSF, MED, RO...etc., water quality depending on the source i.e. brackish water or seawater, system recovery, plant capacity, system design, and energy source i.e. conventional or renewable, and hence energy consumption is usually case specific (Raphael Semiat, 2008).

Energy requirement is reported as specific energy consumptions, or simply energy consumed per unit of product water, in kWh/m^3, with literature reporting wide-range values for specific energy as it is very case or site specific. The energy consumed is also process specific, and of different nature, for example, thermal desalination requires two types of energy i.e. thermal and electrical. However, membrane desalination requires one type of energy i.e. electrical energy (Ghalavand, Hatamipour, & Rahimi, 2015).

MSF thermal desalination requires about 25–120 kWh/m^3 as thermal energy in addition to 2-5 kWh/m^3 as electrical energy with combined equivalent energy of 10–58 kWhe/m^3, however MED thermal desalination requires about 30–120 kWh/m^3 as thermal energy in addition to 2–2.5 kWh/m^3 as electrical energy with combined equivalent energy of 5–58 kWhe/m^3 (Ghalavand et al., 2015; Raphael Semiat, 2008).

Energy requirements for membrane desalination differ, mainly depending on the feedwater sources i.e. brackish water or seawater. Energy requirements for RO seawater desalination is usually higher as it operates at higher pressures above 60 bars, and hence the energy consumption is about 4-7.5 kWh/m^3 , however, for brackish water desalination it is about 2–5 kWh/m^3 (Ghalavand et al., 2015; Raphael Semiat, 2008).

In RO process, energy is consumed to deliver the required feed pressure, which should be in excess to that of osmotic pressure. However, most of this pressure energy is stored in the high-pressure brine. Energy recovery devices ERD, have been developed specifically to recover major part of this energy before brine being discharged (Greenlee et al., 2009).

Desalination plants are usually co-sited with power plants, which is called cogeneration, and most commonly with thermal desalination so it can utilize single energy source i.e. fuel, for multi purposes i.e. power and water production, offering a more effective energy utilization. Power plants utilize high-pressure steam for power generation; then the steam comes out as lower-pressure, which can be utilized further to drive thermal desalination processes (Gleick, 2001).

Renewable energy as sources for energy to drive desalination processes offers a good development opportunity, particularly for membrane processes, as it requires less energy relative to thermal desalination, and importantly in the case of rural communities as desalination systems are of smaller capacity, with non-continuous operation nature, thus it can utilize renewable energy sources. Recent work on utilizing different renewable energy sources, mainly solar (photovoltaic and thermal), wind, and geothermal (A. Al-Karaghouli, Renne, & Kazmerski, 2009, 2010; Ali Al-Karaghouli & Kazmerski, 2013; Mathioulakis, Belessiotis, & Delyannis, 2007) indicated the high feasibility of such option, but this still under development, and mainly applied at very low capacity.

2.4.3 Desalination Economics.

Economic feasibility is a very crucial and has to be considered carefully to evaluate desalination processes. It is very hard to standardize the economics of desalination processes, similarly to energy consumption. Desalination cost is case specific. Factors affecting the desalination cost are mainly feedwater source or quality i.e. brackish water vs. seawater, plant size i.e. small, medium, or large, desalination process in use i.e. membrane vs. thermal, energy source i.e. traditional vs. renewable, and finally plant size (Dore, 2005; Karagiannis & Soldatos, 2008).

Water source, and hence the quality and salinity of feedwater plays a crucial role in determining operating and capital costs, and hence the overall desalination cost. Brackish water has lower salinity relative to seawater, so its capital and product water costs are usually less. Recent estimates for average investment costs for desalination of brackish water are about \$200-450/ (m^3/d), along with product water cost in the range of \$0.25-0.75/m^3 for RO desalination, which dominates brackish water desalination (Vince, Marechal, Aoustin, & Bréant, 2008; Yun, Gabelich, Cox, Mofidi, & Lesan, 2006). On the other hand seawater desalination, has higher investment cost in the range of \$400-1000/ (m^3/d) for RO, \$850/ (m^3/d) for MED, and \$900-1500/ (m^3/d) for MSF, with product water cost of less than \$1/m^3, \$0.55/ m^{3,} \$0.55-0.7/m^3 respectively (American Membrane Technology Association, 2012; Karagiannis & Soldatos, 2008; Reddy & Ghaffour, 2007; Sauvet-Goichon, 2007).

Desalination cost was found to vary significantly for the same water sources or type, depending on its salinity for the same desalination process. The product water cost for low salinity brackish water of about 3,000 mg/l was around \$0.32/m^3, however for highly brackish water at about

10,000 mg/l salinity, the cost was \$0.54 /m^3 (Karagiannis & Soldatos, 2008), similarly for seawater desalination cost ranges from about \$0.54 /m^3 for Mediterranean, to about \$0.87/m^3 for high salinity sweater of Arabian Gulf seawater, of about 45,000 mg/l (Greenlee et al., 2009).

The energy sources to drive desalination processes can generally be divided into two categories, conventional and renewable sources. Desalination cost using renewable energy is currently higher than that using conventional energy sources in terms of capital cost. Renewable energy source like wind, solar i.e. photovoltaic or solar collector and geothermal are the main sources used so far (Karagiannis & Soldatos, 2008).

Capacity or plant size greatly affects the product water cost. It was generally concluded that as the plant size increases the product water cost decreases (i.e. scale effect), Table 2.3 below shows a comprehensive summary of desalination cost of different desalination processes.

Table 2.3 Average desalination cost of main thermal and membrane processes (Ali Al-Karaghouli & Kazmerski, 2013; Ghalavand et al., 2015).

Feedwater	**Plant size (m^3 / d)**	**Feedwater**	**Cost (US\$ / m^3)**
MSF	23,000 - 528,000	Seawater	0.56 – 1.75
MED	91,000 – 320,000		0.52 – 1.01
	12,000 - 55,000		0.95 – 1.5
	≤100		2.0 – 8.0
VC	30,000		0.87 – 0.95
	1000		2.0 – 2.6
RO	100,000 - 320,000		0.45 – 0.66
	15,000 - 60,000		0.48 – 1.62
	1,000 - 4,800		0.7 – 1.72
	40,000	Brackish water	0.26 – 0.54
	20 – 1,200		0.78 – 1.33
	≤20		0.56 – 12.99
ED	Large		0.6
	Small		1.05

2.5 Scaling and Fouling in Desalination Processes.

Fouling or scaling is a phenomenon that outbreaks the desalination unit operation, due to the deposition of foulants or scales on the mass or heat transfer areas, in membrane and thermal desalination processes respectively. This, in turn, reduces the water productivity and quality, and usually combined with increased energy consumption to maintain water productivity, till unit is cleaned during periodic shutdown (Hamrouni & Dhahbi, 2001b; R. Sheikholeslami, 2004).

In membrane desalination, fouling can be due to any of the retained constituents on feed/brine side of the membrane, and generally classified to (Fritzmann et al., 2007):

1) Chemical fouling or scaling: which is due to deposition of sparingly soluble inorganic salts when it exceeds normal saturation limits,
2) Physical or colloidal fouling: which is due to suspended particulate matter,
3) Biological fouling or biofouling: which is due to the deposition and formation of biofilms from biological matter, and
4) Organic fouling: which is due to deposition of natural organic matter NOM.

Although the main goal for desalination processes is to maximize the water recovery and hence reduce the brine disposed of, water recovery is usually limited by fouling (R. Semiat, Hasson, Zelmanov, & Hemo, 2004).

Scaling or fouling due to deposition of sparingly soluble salts is usually mitigated by estimating the saturation levels according to feedwater quality, along with system design recovery and other operating conditions such as temperature and pH, and to operate at condition in which scale formation is unlikely to occur (R. Sheikholeslami, 2004). Extensive work on determination of the saturation levels of common scale-forming sparingly soluble salts with a focus on calcium salts specifically calcium sulfate and carbonate, and silica is available in literature (S. He, Oddo, & Tomson, 1994; Marshall & Slusher, 1966; R. Sheikholeslami, 2003; R. Sheikholeslami, Al-Mutaz, Koo, & Young, 2001; R. Sheikholeslami & Bright, 2002; R Sheikholeslami, 2003).

In seawater desalination, scaling due to deposition of calcium carbonate and calcium sulfate is the common fouling type in thermal desalination due to the high temperatures encountered; however, for membrane desalination, it is mainly biofouling (Al-Ahmad & Abdil Aleem, 1993).

In membrane desalination of seawater, scaling by sparingly soluble salts is less likely, mainly due to the relative lower recovery, higher ionic strength, and lower bicarbonate and sulfate concentrations present in seawater (Reverter, Talo, & Alday, 2001).

Brackish groundwater has mainly higher quality in terms of lower dissolved and suspended solids hence lower chemical and physical fouling is expected, in addition, due to the low bacterial count and low content of organic matter biofouling and organic fouling is absent. However, due to the higher calcium, carbonate, sulfate, and silica concentrations in brackish groundwater, scaling by sparingly soluble inorganic salts is more likely to occur. The high concentration of such scale-forming constituent is mainly due to chemical weathering or dissolution of rock formations i.e. minerals upon contact of groundwater with the calcite and gypsum rocks forming the aquifer (Faust & Aly, 1998), as a result scaling due to calcium carbonate and sulfate has been extensively studied for brackish groundwater desalination (Rahardianto, Mccool, & Cohen, 2008; R. Sheikholeslami, 2003; Roya Sheikholeslami, 2003).

Silica present in groundwater is due to dissolution of amorphous or crystalline SiO_2 and the major clay minerals such as feldspar (Faust & Aly, 1998). Silica in the form of sand is the most abundant mineral on Earth’s surface, crystalline silica or colloidal silica that results from the condensation polymerization of silicic acid has a very low water solubility. On the other hand, amorphous silica that monomers and low polymers of silicic acid, can have a water solubility of about 100-140 mg/l at a natural pH value of 7, increasing to 889 mg/l at pH value of 10 (Hamrouni & Dhahbi, 2001a; R Sheikholeslami & Tan, 1999). Silica present in water can be classified into reactive silica that is able to react with ammonium molybdate within 10 minutes, and non-reactive silica which is not able to react (Hamrouni & Dhahbi, 2001a). Scaling due to silica has been studied extensively as one of the major foulants in membrane desalination (M. Al-Shammiri, Safar, & Al-Dawas, 2000; Freeman & Majerle, 1995; Neofotistou & Demadis, 2004; Ning, 2003; Raphael Semiat, Sutzkover, & Hasson, 2003; R. Sheikholeslami et al., 2001).

Proper pretreatment of feedwater for desalination is very crucial for successful desalination operation as its primary goal is to lower the fouling and scaling propensity (Neofotistou & Demadis, 2004). Scale inhibitors or antiscalants are added to feedwater during pretreatment to inhibit scale formation of crystalline mineral precipitates such as calcium carbonate, sulfate, fluoride, but not silica due to its amorphous nature (Freeman & Majerle, 1995).

2.6 Sparingly Soluble Salts.

During water desalination, the concentration of different constituents, and ions, are increased, mainly due to the decrease solvent amount i.e. water present, and this increase is directly proportional to the system recovery, i.e. recovery of 50%, which means almost doubling the salt concentration, while that of 75% represents a four-fold increase. This is usually represented as concentration factor CF, present in equation 2-1 (Wilf, 2007):

$$CF = 1/(1-R) \qquad 2\text{-}1$$

Where:

CF = Concentration factor, dimensionless

R = System recovery as fraction, dimensionless

Upon concentration of some constituents naturally present in water, it starts to precipitate, as their ion activity product exceeds the solubility product for such salts. In general, for salt ions or electrolytes present in water it dissolves according to the following dissolution reaction (Stumm & Morgan, 1996):

$$A_m B_n(s) \Leftrightarrow mA^{n+}(aq) + nB^{m-}(aq) \qquad 2\text{-}2$$

Equilibrium conditions can be represented by:

$$\left\{A_m B_n(s)\right\} = \left\{A^{n+}(aq)\right\}^m \left\{B^{m-}(aq)\right\}^n \qquad 2\text{-}3$$

The conventional solubility expression or solubility product can be represented by:

$$K_{s0} = \left\{A^{n+}(aq)\right\}^m \left\{B^{m-}(aq)\right\}^n \qquad 2\text{-}4$$

In order to test if a solution is oversaturated or undersaturated with respect to certain mineral or solid phase, and hence will precipitate or dissolve, respectively, we should check for the value of free energy of dissolution i.e. positive, zero, or negative, as presented by equation 2-5, and can be represented by saturation index of equation 2-6:

$$\Delta G = RT\ln\frac{\left\{A^{n+}\right\}_{act}\left\{B^{m-}\right\}_{act}}{\left\{A^{n+}\right\}_{eq}\left\{B^{m-}\right\}_{eq}} = RT\ln\frac{IAP}{K_{s0}} \qquad 2\text{-}5$$

$$SI = EXP(\Delta G / RT) = \frac{IAP}{K_{s0}} \qquad 2\text{-}6$$

Where:

$\left\{A_m B_n(s)\right\}$ = concentration of solid present in water

$\left\{A^{n+}(aq)\right\}$ = Aqueous concentration of A, with valence of (+n)

$\left\{B^{m-}(aq)\right\}$ = Aqueous concentration of B, with valence (-m)

K_{s0} = solubility product, or equilibrium constant of dissolution/precipitation reactions.

ΔG = free energy of dissolution

$IAP = \left\{A^{n+}\right\}_{act}\left\{B^{m-}\right\}_{act}$ = Ion Activity Product

SI = Saturation index

The result of such equation indicates one state of three, summarized as:

i- Oversaturated/precipitates: IAP $> K_{S0}$ and SI > 1,
ii- Saturated/equilibrium: IAP $= K_{S0}$ and SI = 1,
iii- Undersaturated/dissolves: IAP $< K_{S0}$ and SI < 1,

Literature contains massive data on solubility and solubility products of different sparingly soluble salts present in desalination system such as calcium carbonate (Greenlee, Testa, Lawler, Freeman, & Moulin, 2010; Pervov, 2015; R Sheikholeslami, 2003), calcium sulfate (Azimi, Papangelakis, & Dutrizac, 2007; Dydo, Turek, & Ciba, 2003; Marshall & Slusher, 1966; R Sheikholeslami, 2003; Zarga, Ben Boubaker, Ghaffour, & Elfil, 2013), and silica (Carroll, Mroczek, Alai, & Ebert, 1998; Fournier & Marshall, 1983; Freeman & Majerle, 1995; Okamoto, Okura, & Goto, 1957). More compiled data for solubility products of different solids at different conditions are available in the literature (Stumm & Morgan, 1996).

2.7 Brine Disposal and Management for Inland Desalination.

Concentrate, brine, or reject are different names for the retentate feed after water extraction in the desalination process. Desalination produces two streams; high-quality product water, and brine that contains the retained dissolved salts were initially present in the feedwater stream, along with different chemicals added during desalination process.

In order to lower required energy, cleaning time and cost, and loss of production, it is very crucial to avoid fouling. The approach followed is to study feedwater characteristics and operating condition combined and to operate at levels where the feed/brine is stable, thus fouling tendency is minimum. On the other hand, working at lower recoveries to mitigate fouling increases the flow of brine stream generated and hence is the main operation trade-off (Hadi, 2002; McCool et al., 2010).

Brine stream usually has 2 or 4-5 folds the feedwater salinity for seawater desalination at 50% recovery, or brackish water desalination at 75-80% recovery, respectively. This is also in addition to different chemicals added during the pretreatment such as biocides, acids, coagulants, scaling and corrosion inhibitors, and other cleaning chemicals. Moreover, in thermal desalination, the brine will be at much higher temperature compare to the feedwater (Ahmed, Shayya, Hoey, & Al-Handaly, 2002). Brine discharge for seawater and brackish water desalination is completely different, as for seawater desalination, brine is usually discharged back to the sea, given that brine will be only 2-fold the salinity of the feedwater i.e. seawater, and the mixing effect as it is discharged to large water body i.e. seas or oceans (Khawaji et al., 2008).

Brine management for brackish desalination plants is usually a critical problem as such plants are usually placed far from the coast i.e. inland desalination, or public water channel where the brine can be discharged. Hence, the options for brine disposal from inland desalination plants are limited. Traditional methods are evaporation ponds, deep-well injection, irrigation of plants tolerant to high salinities, and disposal to surface water bodies or municipal sewers if available (Ahuja & Howe, 2005; Fitzpatrick, Squire, Murrerl, & Holden, 1997; Mickley, 2006).

Brine disposal cost is a major cost component of any desalination process, and present about 5-33% of the total desalination cost, with main factors influencing the choice of brine disposal method are (Ahmed et al., 2000):

1) The quantity or volume of brine stream,
2) The composition or quality and constituents present in the brine,
3) Physical and geographical considerations of the desalination plant site,
4) Capital and operational costs of each discharge method,

The method of brine disposal should be considered carefully after performing the necessary efforts and investigations to minimize the volume of the brine stream, thus reducing the brine disposal cost. This can be achieved through proper feedwater pretreatment, and proper choice of desalination process, thus maximizing the water recovery.

2.7.1 Disposal to Evaporation Ponds.

In this method, brine is sent to a pond of large surface area, in which water is evaporated naturally. That is mainly practiced in arid areas due to the high evaporation rate. Disposal to evaporation ponds is considered the most commonly used method for brine disposal from inland desalination (Glater & Cohen, 2003).

Evaporation ponds are easy to construct at low operational and maintenance cost, with no need for equipment, specifically mechanical equipment (Ahmed et al., 2000). In addition, evaporation ponds can be used for cultivation of brine shrimps, and some other aquatics, as it provides a natural monoculture environment with the absence of predators or food competitors (Ahmed, Shayya, Hoey, & Al-Handaly, 2001).

On the other hand, there are some concerns related to the application of evaporation ponds, such as leakage of brine through soil that can result in groundwater contamination and increased salinity of the groundwater aquifer (Ahmed et al., 2001; Al-Faifi et al., 2010; Mohamed, Maraqa, & Al Handhaly, 2005). Lining with polymeric sheets has been applied recently for leakage prevention, in addition to proper pond monitoring (Mickley, 2006).

Although evaporation ponds have low operational and maintenance costs, its implementation requires large land areas to accommodate for brine volume, along with high pond construction costs due to lining requirements. Hence, proper evaporation ponds are costly and impractical for large inland desalination plants. Furthermore, water evaporated is considered a lost resource (US Department of the Interior Bureau of Reclamation, 2000).

2.7.2 Deep-Well Injection.

In deep-well injection, the brine from desalination process is injected back deep underground, primary deeper than groundwater abstraction level. Considerations for brine disposal through deep well injection include permitting considerations, which identify proper geologic formations to avoid upward flow from injection area to groundwater aquifer area. Design considerations, which look to the tubing and packing installed in the finally cemented casing of the injection well, as well as compatibility of the brine to be injected with the tubing material, concentrate flow, and finally monitoring and leak detection systems (Muniz & Skehan, 1990).

Depleted gas and oil well fields offer a very good option for brine disposal by deep well injection, with advantages such as utilization of the readily available gas or oil wells, in addition to the long experience gained from the long operation of such wells (Nicot & Chowdhury, 2005).

Selection of proper site for installation of wells for the deep-well injection, is very critical as many hydrological and geological characteristics of the site are to be considered (Ahmed et al., 2000). Although of many advantages of deep-well injection for brine disposal, there are some critical disadvantages are encountered and can be summarized as follows (Mickley, 2006):

1) Complex process of site selection, due to the need for geological and hydrological studies,
2) Possible corrosion of well-casing , and subsequent leakage,
3) Seismic activity which might cause the well, and subsequent leakage,
4) Well life uncertainty,
5) Contamination of groundwater due to upward migration of brine.

2.7.3 Disposal to Surface Water Bodies and Sewer Systems.

Brine disposal to surface water bodies or sewer systems presents a ready brine disposal option, if available, but brine stream should be well diluted by mixing. However there are some problems that might be associated with such option as the salinity of the receiving body can increases due to the high salinity of brine stream, and hence the self-purification capacity of the intended receiving water should be carefully considered (Ahmed et al., 2000).

Disposal of brine to the sewer system, usually considered in the case of small membrane desalination plants, is another viable option, as it utilizes the readily available and installed sewage infrastructure, in addition to lowering the biological oxygen demand BOD of sewage wastewater. However, disposal to sewer systems should be considered very carefully as it might result in increased salinity of sewage wastewater, which in turn might affect the wastewater treatment plant, specifically biological treatment units, as well as rendering treated sewage unsuitable for irrigation purposes (Ahmed et al., 2002; Glater & Cohen, 2003).

2.8 Inland Desalination with Zero Liquid Discharge.

Given the disadvantages and concerns associated with different brine disposal methods, especially the negative environmental impacts, along with the importance of providing a proper brine disposal and management, developing a Zero Liquid Discharge ZLD process for inland desalination of brackish groundwater is much desired. In ZLD, brine stream to be further processed to extract more product water, and essentially dry salts; thus there is no brine to be discharged from the desalination site. Currently employed ZLD processes are mainly for industrial wastewater, utilizing thermal and/or membrane processes (Koppol, Bagajewicz, Dericks, & Savelski, 2004; Yao, Wen, Shen, & Wang, 2016).

Thermal processes work in a fashion similar to that of thermal desalination processes which are a mature technology that produces high-quality water, but it is also very energy-intensive with high capital and operating costs. Additionally, membrane processes also have some limitation concerning maximum applicable pressure and fouling tendency, and cannot provide complete ZLD solution independently.

Development of cost efficient ZLD process will be of remarkable benefit and will provide an effective solution to water supply challenges to rural communities worldwide. In addition, inland desalination with ZLD represents the ultimate solution for the brine management challenge. The advantages imposed by inland desalination with ZLD are:

1) Water recovery maximization, as it approaches 99-100% recovery, relative to 70-85% for conventional brackish groundwater desalination.
2) Preserving the groundwater resources both quantitatively and qualitatively.
3) Beneficial use of byproduct salts, being considered as added-value products.
4) Ease of integrability, as it can be easily integrated into current brackish groundwater desalination plants regardless of plant size and site location.

2.8.1 Current Zero Liquid Discharge Schemes.

The literature contains few schemes for inland desalination with ZLD; however, three schemes are recognized, which are explained as follow:

1) Application of thermal processes for brine concentration, followed by drying or crystallization to obtain final salt (Mickley, 2006).
2) Application of chemical treatment to the brine, followed by further membrane desalination for further extraction of water, followed by final drying or crystallization to obtain final salt (Bond & Veerapaneni, 2008; C. J. Gabelich, Rahardianto, Northrup, Yun, & Cohen, 2011; C. J. Gabelich, Williams, Rahardianto, Franklin, & Cohen, 2007; C. Gabelich, Yun, Green, Suffet, & Chen, 2002).
3) Application of ED/EDR process to brine, followed by drying or crystallization to obtain final salt (Greenlee et al., 2009; Hanrahan, Karimi, Ghassemi, & Sharbat, 2015; Oren et al., 2010; Zhang, Ghyselbrecht, Meesschaert, Pinoy, & Van der Bruggen, 2011).

All three schemes have some similarity, specifically in terms of the final brine concentration step and final salt production, but differs in brine treatment for further water extraction, which aims at significantly reducing the final brine volume to undergo final brine concentration. Different integration options, aiming to maximize recovery and minimize cost should be considered for process optimization (D. H. Kim, 2011).

Current brackish groundwater desalination systems achieve high recovery of about 70-85% in single desalination step, which is usually limited due to scaling by sparingly soluble salts such as calcium carbonate and sulfate, and silica (Freeman & Majerle, 1995; Hater et al., 2011; Koo, Lee, & Sheikholeslami, 2001).

The first scheme which employs a thermal process for brine concentration and further recovery of product water, followed by drying or crystallization to obtain dry salts. The thermal process employed is highly energy-intensive and high in both capital and operating costs, just as conventional thermal desalination processes. It is hard to be implemented in remote site of inland desalination plants, as well as size or capacity limitation, due to the low capacity of such inland desalination plants (Mickley, 2006).

The second scheme, employ a chemical treatment of brine stream that aims at efficiently remove scale-forming constituents, making the treated brine suitable for further processing in membrane desalination to recover more product water. The chemical treatment of brine is considered to be a cheap process. It utilizes cheap chemical reagents, hence reducing the overall cost, therefore drawing more attention compared to other ZLD schemes (C. J. Gabelich et al., 2011; McCool, Rahardianto, Faria, & Cohen, 2013; Rahardianto, Gao, Gabelich, Williams, & Cohen, 2007; Shane Walker, Kim, & Lawler, 2014).

In the third scheme, the brine is subject to further desalination using desalination process that can operate at high saturation levels, and hence is less sensible to scaling by common scale-forming constituents, thus ED/EDR is usually the process of choice in this case (Hanrahan et al., 2015; Oren et al., 2010).

2.8.2 Precipitative Softening for Chemical Treatment of Brine.

The key element for successful ZLD desalination when employing the second scheme is the chemical treatment of brine stream; with the main objective of removing scale-forming constituents such as calcium, carbonate, sulfate to minimize scaling resulting from calcium carbonate and sulfate, in addition to silica. Very few chemical treatments are found to remove all these constituents, however achieving reasonable removal efficiency that is enough to mitigate scaling by such sparingly soluble salts to a reasonable extent should be acceptable.

Precipitative softening is a widely used water treatment process aims at removal of hardness, i.e. calcium and magnesium, along with alkalinity in water treatment plants. Calcium is mainly removed by precipitation as calcium carbonate and magnesium as magnesium hydroxide by the addition of strong alkalies such as calcium hydroxide i.e. lime or calcium hydroxide i.e. slaked lime in lime softening, and sodium carbonate if required, followed by coagulation/sedimentation to remove precipitated solids (Reynolds & Richards P. A., 1996).

Removal of calcium present one of the key objectives of brine chemical treatment, as brine is mainly supersaturated with respect to calcium sulfate and carbonate (Rahardianto et al., 2008; R. Sheikholeslami, 2003; Roya Sheikholeslami, 2003).

Removal of silica during the precipitative softening has been extensively studied and found to occur mainly through by co-precipitation with metal hydroxide, or by precipitation as magnesium silicate or calcium silicate (Latour, Miranda, & Blanco, 2014; R. Sheikholeslami & Bright, 2002). Caustic softening, in which sodium hydroxide is used instead of lime, was found to be more effective for silica removal over lime softening (Al-Rehaili, 2003; R. Sheikholeslami & Bright, 2002). Furthermore, the addition of aluminum salts was found to improve silica removal by co-precipitation with aluminum hydroxide (Cheng, Chen, & Yang, 2009; Lindsay & Ryznar, 1939).

Some advancement of softening processes was introduced in compact accelerated precipitation softening process CAPS, in which water flows through a bed of calcium carbonate to improve crystal growth and approach chemical equilibrium, however this was applied mainly for feed pretreatment rather than brine treatment, leading to desupersaturation of feed with respect to calcium carbonate (Gilron, Chaikin, & Daltrophe, 2000; Gilron, Daltrophe, Waissman, & Oren, 2005; Masarwa, Meyerstein, Daltrophe, & Kedem, 1997; Oren, Katz, & Daltrophe, 2001; Zalmonb, 1997).

Precipitative softening has efficiently applied for removal of calcium and silica, in addition to heavy metals during pretreatment for RO desalination (Al-Rehaili, 2003; Lindsay & Ryznar, 1939; R. Sheikholeslami & Bright, 2002), and is very promising for chemical treatment of brine, achieving high calcium and silica removals, and enabling higher recovery (C. J. Gabelich et al., 2011, 2007; Ning & Troyer, 2009).

Sulfate is usually present in RO brine at high concentrations and hence scaling by calcium sulfate as gypsum is very likely to occur (Rahardianto et al., 2008; R. Sheikholeslami, 2003; Roya Sheikholeslami, 2003). However precipitative softening was not found to be effective for high sulfate removal. Sulfate removal from industrial wastewaters of paper mills, mining, and fertilizers industries using a membrane and thermal processes was studied (Ericsson & Hallmans, 1996). Furthermore, removal of sulfate by precipitation and crystallization as calcium sulfate i.e. gypsum, by the addition of calcium mainly as lime (Tait, Clarke, Keller, & Batstone, 2009) or calcium chloride (Benatti, Tavares, & Lenzi, 2009) were found to be highly efficient.

However, removal of sulfate below 1300 mg/l, as solubility limit when saturated with respect to calcium sulfate, is very hard due to the solubility of calcium sulfate. The addition of aluminum ions from different salts such as aluminum sulfate or alum, aluminum chloride, aluminum nitrate (Christoe, 1976), was found to improve the removal of sulfate from industrial wastewaters, more specifically cooling water, through the formation of more complex solids such as $3CaO.Al_2O_3.3CaSO_4.31H_2O$ which has very low solubility relative to the solubility of calcium sulfate (Ahmed Abdel-Wahab & Batchelor, 2006; Batchelor, B.; McDevitt, M.; Chan, 1985; Batchelor & Mcdevitt, 1984; Christoe, 1976); however such cooling waters had different aqueous chemistry and ionic strength compared to brine.

2.8.3 Secondary Brine Concentration and Salt Production.

Final brine from secondary desalination process, i.e. thermal or membrane, has to be further concentrated to reach the complete zero liquid discharge ZLD; however, complete ZLD and dry salts cannot be achieved by membrane desalination as it is not a multi-phase process, hence thermal process has to be employed, followed by drying or crystallization (Mickley, 2009).

The final thermal process has a dual purpose, first to recover water and second to concentrate brine up to 250,000 mg/l, while final salt can be obtained through final drying or crystallization (Mickley, 2006).

Solids produced during the intermediate chemical treatment of brine should be considered as a byproduct or added value product, rather than solid waste. The precipitated solids resulted from these chemical treatments are very rich in calcium, magnesium, carbonate, sulfate, silicates, in addition to other added components as reagents during the chemical treatment. This mixture can be utilized in many applications such as an additive in cement industry or for road pavement.

2.8.4 Cost of Zero Liquid Discharge Systems.

Achieving inland desalination with zero liquid discharge should be carefully be evaluated at technical and economic levels. While ZLD could be achieved technically, the costs associated with any proposed ZLD system should be cautiously assessed. In the second scheme discussed above in 2.8.1, it is easily noticed that employing membrane desalination helps reduce both operational and capital costs compared to any thermal ZLD scheme, due to the massively reduced final brine quantity to be thermally treated.

Inland desalination with ZLD is expected to have a higher product water cost, as many units have been added including chemical treatment, secondary desalination, final brine concentration, and drying or crystallization for final salt production, which are utilized to recover the last portion of water. This, in turn, increases both capital, operating, and hence overall cost relative to conventional brackish groundwater desalination (Greenlee et al., 2009). However, given the stringent regulations on brine disposal using conventional methods, an environmental awareness, and ongoing efforts for preserving natural resources such as groundwater, more driving force toward ZLD processes is highly encouraged (Mickley, 2006).

2.9 Conclusions.

While groundwater is the major water source in the absence of surface water, as encountered in many arid areas, the quality of such groundwater resources is deteriorating, more specifically its salinity, which led to the use of desalination to obtain water suitable for domestic and irrigation purposes.

The use of RO membrane desalination for brackish groundwater desalination is very beneficial due to its several advantages of capacity or size flexibility, lower energy consumption, and lower cost. However, the brine stream generated from such desalination process present the main concern as it has to be disposed and managed properly. Current methods of brine disposal have many disadvantages either environmentally or cost prohibitive. Thus it is crucial to develop zero liquid discharge for inland desalination of brackish groundwater to manage the brine generated in environmentally benign approach at an affordable cost.

III. RESEARCH METHODOLOGY AND APPROACH

This chapter explains in detail the research methodologies and approaches followed to achieve work's objectives. The chapter describes first the preliminary process analysis that is performed to analyze the major groundwater quality parameters that are considered for the different uses of groundwater, namely drinking and irrigation purposes. It also covers the preliminary analysis of brackish groundwater membrane desalination process, determining the key elements limiting the desalination system recovery in different membrane system at different operating conditions, that helps to estimate the critical components which have to be removed during the chemical treatment of brine stream, produced in primary or 1st stage RO unit to eliminate the scaling tendency and make the stream suitable for further water extraction in secondary or 2nd stage RO.

The chapter then describes the experimental and analytical procedures developed and used during the bench-scale experiments to evaluate the effectiveness of the proposed chemical treatment for removal of such scale-forming constituents. It also explains the procedures used to develop the equilibrium modeling of the advanced softening processes for the chemical treatment of brine using equilibrium software packages of OLI stream analyzer.

In this chapter also we will tackle the procedure utilized for the characterization of solids produced during the advanced lime softening processes, which helps identify beneficial uses for byproduct solids rather than having it as solid waste. Finally, the chapter explains the procedure used for the development of improved membrane separation model, along with the overall process model in details to study the effect of various process variables on overall process performance.

3.1 Preliminary Process Analysis of Major Groundwater Quality Parameters.

Groundwater is the main water resource in arid and semi-arid zones worldwide due to the absence of surface water sources such as rivers and lakes. Fresh groundwater represents about 30% of the total fresh water, and about 0.76% of the total water available globally, while saline/brackish groundwater accounts for about 0.93% of the total water available globally, compared to 0.007% for rivers and lakes, and 96.54% for seawater (Gleick, 2001).

Middle East region, or sometimes referred to as the Middle East and North Africa MENA, or West Asia and North Africa, are one of the world's largest arid zones. In MENA region there are more than 22 countries, covering more than 13 million square kilometers (more than 5 million square miles), rich in natural resources such as oil and gas. However, it has very limited water resources. Surface water in the form of rivers and lakes is only available in few countries, namely Egypt, Sudan, Iraq, and Syria, with some other smaller rivers. As a result groundwater resources and desalinated water are the most common water resources in the absence of surface water, with the former mainly for agriculture and drinking purposes, more specifically in rural communities.

The GCC countries, in particular, are a good example of an arid area with harsh clime and very limited surface water resources, as it is situated in extremely arid zones with a very low endowment of renewable water resources. The region is mostly a desert with few exceptions in some mountain ranges and coastal areas. The average annual rainfall ranges from 70 to 130 mm except in the coastal zone. The annual evaporation rate reaches up to 4,500 mm in KSA, down to ranges from 2,500 mm in the coastal areas (Abulrazzak, 1995; Al-Rashed & Sherif, 2000).

Due to such limited freshwater resources, GCC countries depend heavily on groundwater supplies for the agriculture sector and domestic water supply for rural communities, and on seawater desalination for domestic water supply in large coastal cities and for industrial purposes (Al-Rashed & Sherif, 2000). In addition, groundwater resources receive higher attention from GCC countries as the main water supply in case of emergency i.e. water security, and to provide water supply during the off-time of major desalination plants in case of emergency. The GCC countries have been listed among the top 15 nations with groundwater having the largest share in the total annual freshwater worldwide, which is mainly used for irrigation purposes with a share of about 84–97% (National Groundwater Association, 2013).

Groundwater quality in general, and salinity, in particular, is very site-specific in nature and varies significantly from one country to another, and even within the same country depending on the utilized aquifer, furthermore in many cases, it varies within the same groundwater aquifer (Gleeson et al., 2012). The State of Qatar, as many GCC states ,does not have surface water in the form of rivers, streams, nor lakes. It has one of the lowest precipitation rates worldwide, in addition to being highly erratic in time and space, variable, and unpredictable (Ministry of Environment MoE, 2013). The average annual rainfall during the last 20 years is 82 mm, with value as low as

24 mm in 2012 compared to 3240 for Colombia, 715 for the USA, and 534 for Canada with a very high annual evaporation rate of about 2200 mm (The World Bank, 2015).

Groundwater abstractions are dominated by abstraction for agriculture purposes with 230 MCM (million cubic meters) in 2012 (92% of all groundwater abstractions). The main two groundwater aquifers are the Northern and Southern Groundwater Basins, as shown in the State of Qatar's map figure 3.1, both rely on rainfall for replenishment. The Northern Groundwater Basin is an important source of water of acceptable quality, with groundwater salinity in the range of 300–3,000 mg/l. The Southern Groundwater Basin has a higher water salinity with water salinity in the range of 3,000-6,000 mg/l making it not fully suitable for irrigation purposes (Amer, 2008).

Groundwater resources in Qatar are facing unique challenges relative to other GCC countries. The first challenge that Qatar is located in the heart of GCC arid area with very low fresh or renewable water resources due to low precipitation, along with high evaporation rate, so groundwater aquifer recharge is minimal. Secondly, Qatar occupies a small peninsula in the Arabian Gulf (with an area about 11, 500 Km^2 or 4,500 square miles), and hence seawater intrusion to groundwater aquifers increases as groundwater abstraction continues, with high salinity seawater of 45-50 g/l, about 1.5 the standard seawater salinity.

Due to all the aforementioned facts, the State of Qatar was chosen as a specific case study for detailed analysis of groundwater resources available there face formidable challenges such as low groundwater aquifer recharge rate, increased salinity, and higher scaling tendency of its water.

The state of Qatar has a continuous groundwater quality monitoring programme, administrated by Ministry of Environment's Water Department since 1996, monitoring a total of 344 wells spanning all over the country, in which samples from 100 different sites are analyzed biannually. The data collected for the quality of different groundwater resources from groundwater monitoring program was used for preliminary process analysis (Ministry of Environment MoE, 2013).

The data collected from 49 groundwater wells in at different operational farms mainly for agriculture purposes, containing the detailed analysis of the main quality parameters, namely pH and electrical conductivity, along with analysis for the major cations: sodium Na^+, potassium K^+, Calcium Ca^{++}, and magnesium Mg^{++}; anions: chloride Cl^{-}, bicarbonate $HCO3^{-}$, and sulfate SO_4^{--}, in addition to silica SiO_2.

The quantitative assessment is concerned mainly about the water balance, or simply the rates at which the groundwater resources are recharged or abstracted over time. The groundwater aquifer recharge takes place basically either naturally through runoff water from rainfall and irrigation; or artificially through artificial aquifer recharge. The groundwater abstraction is mainly for agriculture purposes, or for drinking purpose in case of rural communities.

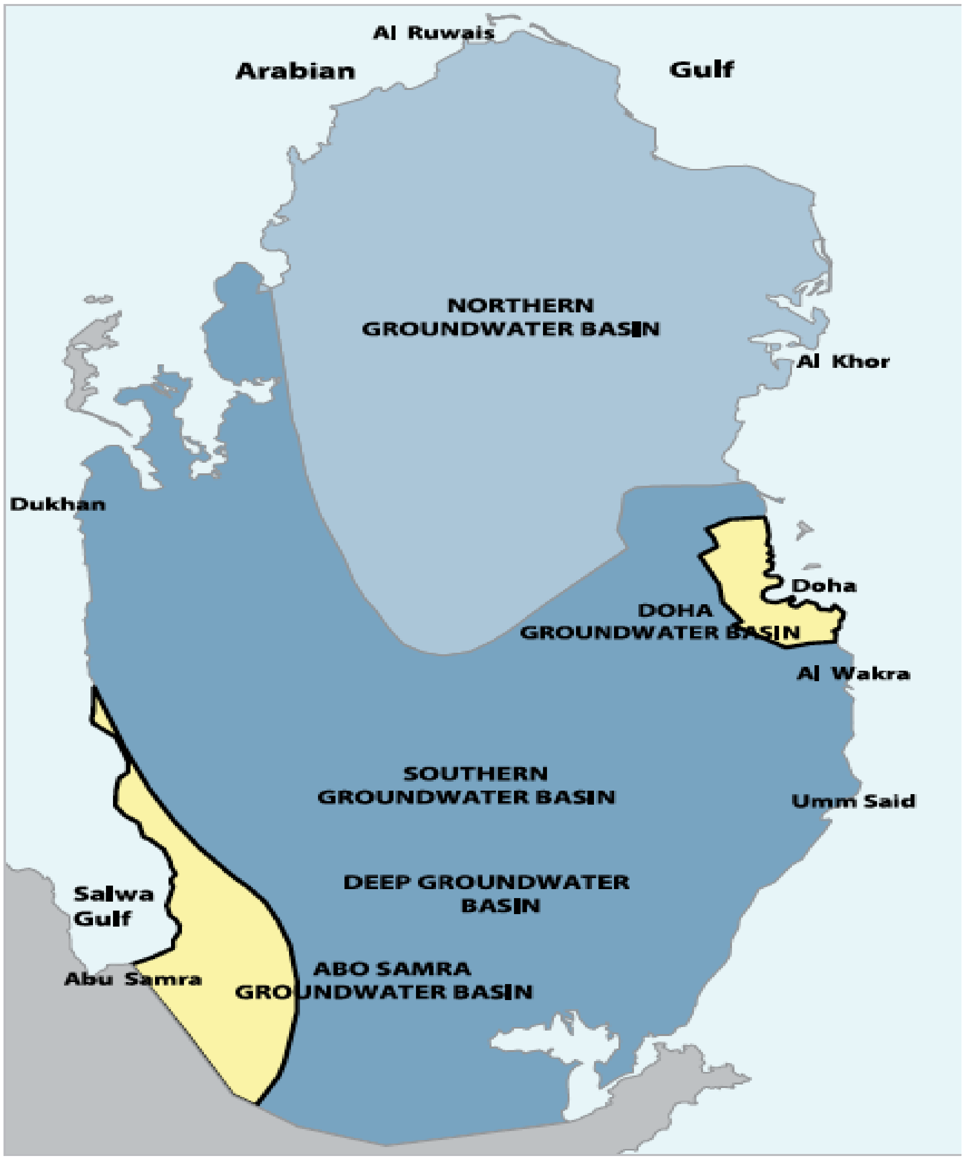


Fig. 3.1 Map of State of Qatar showing the main groundwater aquifers.

The qualitative assessment is concerned mainly about the major groundwater quality parameters that are to be considered for the use of water for certain purposes. The main quality parameters to be considered for utilizing groundwater for drinking purposes are per United States Environment Protection Agency USEPA guidelines given in table 3.1. The main quality parameters to be considered for utilizing groundwater for agriculture or irrigation purposes are as per Food and Agriculture Organization FAO guidelines are given in table 3.2. Both USEPA and FAO standards for drinking water and irrigation water, respectively, are used for the assessment of groundwater as being accepted worldwide.

Table 3.1 USEPA Major drinking water quality parameters (USEPA, 2016).

Quality parameter	**Acceptable value**	**Noticeable effect**
Total Dissolved Solids, TDS	500 mg/l	Hardness, colored water, deposits, staining, and salty taste.
pH	6.5 – 8.5	Low pH: Corrosive and bitter metallic taste. High pH: Soda taste, slippery feel, and deposits.
Chloride, Cl^-	7 meq/L or 250 mg/l	Salty taste.
Sulfate, SO_4^{--}	5 meq/L or 250 mg/l	

Table 3.2 FAO Major irrigation water quality parameters(Ayers & Westcot, 1994; Bellows, 2004; FAO, 2011).

Quality parameter	**Acceptable value**
Electrical Conductivity, EC_w	3 dS/m
Total Dissolved Solids, TDS	2000 mg/l
pH	6.0 – 8.5
Calcium, Ca^{++}	20 meq/l or 400 mg/l
Magnesium, Mg^{++}	5 meq/l or 60 mg/l
Sodium, Na^+	40 meq/l or 920 mg/l
Chloride, Cl^-	30 meq/l or 1065 mg/l
Sulphate, SO_4^{--}	20 meq/l or 960 mg/l
Sodium Adsorption Ratio, SAR	15 meq/l

3.2 Preliminary Process Analysis of Brackish Groundwater Desalination.

The analysis of brackish groundwater desalination process is mainly concerned with determining the maximum achievable recovery for a given feedwater quality, along with the quality of the produced water and brine streams. In most cases of brackish groundwater desalination, recovery is controlled by scaling with sparingly soluble salts usually present in groundwater feed. This is in contrast to seawater desalination, where recovery is usually limited by the maximum applied pressure that membrane can withstand without damage, as these systems usually operate at high pressures of 50 – 68 bars, with new membranes up to 80 bars.

The supersaturation of key salts such as $CaCO_3$, $CaSO_4$, and SiO_2 in brackish groundwater as feed to RO and concentrate streams has to be quantified in order to identify the key components that limit recovery due to scale formation. Supersaturation of some other sparingly soluble salts such as $BaSO_4$, $SrSO_4$, CaF_2, and $Mg(OH)_2$ are usually present as well. However due to the low concentrations of F^-, Ba^{2+}, Sr^{2+} relative to other components, in addition, that $Mg(OH)_2$ scaling require very high pH, these salts are not of major concern relative to the former salts that will result in more scales to be formed. Furthermore, the antiscalant addition can mitigate the formation of such minor scales to much higher saturation index relative to the major scale salts. For example, Vitec 3000® by Avista Technology, which is a broad spectrum antiscalant, can be used with supersaturation limits up to $3.5K_{sp}$, $20K_{sp}$, $105K_{sp}$, and $1000K_{sp}$ for $CaSO_4$, $SrSO_4$, $BaSO_4$, and CaF_2 respectively (Avista Technology, 2016).

The literature contains massive work on the supersaturation of such sparingly soluble salts as the main scaling components in so many applications such as desalination and steam generation. There are well-established correlations that account for the different water qualities, temperature, pH….etc. (Abdel-Aal, Rashad, & El-Shall, 2004; Alimi & Gadri, 2004; Klepetsanis, Dalas, & Koutsoukos, 1999; Raphael Semiat et al., 2003; Roya Sheikholeslami, 2003; Zarga et al., 2013). This literature work has been utilized in the membrane desalination field by membrane manufacturer as well as antiscalant formulators to develop software packages to quantify the supersaturation of these compounds at different conditions for the feed and brine streams.

Antiscalant manufacturers and formulators have developed some guidelines for the antiscalant doses to be used with membrane desalination systems, and more advancement has resulted in developing some software. In this study, Avista Advisor developed by Avista Technologies (Avista Technologies, 2013), has been used, which can project the doses of different chemicals such as biocide, coagulant, pH modifiers and more importantly antiscalant for membrane systems. Antiscalant dosing software has been used to assess the supersaturation of different sparingly soluble salts present in groundwater in this study.

3.3 Kinetics and Equilibrium Study of Scale-forming Constituents Removal during Softening Processes.

The proposed chemical treatment process is the key component for the proposed zero liquid discharge process, hence extensive attention is given to investigate its efficiency. Given the novel application of ultra-high lime with alumina UHLA process as an advanced lime softening for the intermediate chemical treatment of brine from primary RO unit, it is very important to study the kinetics and equilibrium of such process for removing the target scale-forming constituent, namely sulfate and silica at bench scale first.

Three-part bench scale experimental plan has been set to study the kinetics and equilibrium of scale-forming constituents’ removals during the advanced softening process using high lime doses with sodium aluminate at bench scale level. A conventional softening process utilizing lime and soda ash is a very well-established process, which can be adequately modeled using different equilibrium modeling software such as OLI (OLI Systems, 2016). However, the situation is different in the case of advanced softening processes which requires experimental investigation with the support of utilizing equilibrium modeling packages.

The first part is to study the removal of sulfate from water i.e. water contains sulfate salt only, in the advanced softening process, in which sets of experiments to study the kinetics and equilibrium of sulfate removal from synthetic solutions containing representative concentrations of sulfate present in brine stream from inland desalination. The first set is kinetic experiments, with the main purpose of obtaining the time needed to reach equilibrium or quasi-equilibrium state for sulfate removal. Then different sets of equilibrium experiments to evaluate the extent of sulfate removal as affected by lime and other chemical reagents doses, initial sulfate concentration, temperature, and pH value. The second part is to study the kinetics and equilibrium of silica removal from water that contains only silica, during the chemical treatment process and was performed in a fashion similar to that of sulfate removal.

The third part is devoted to studying the kinetic and equilibrium of chemical treatment of synthetic or model brine to mimic the treatment of actual brine stream from 1st stage RO unit. The experiments were performed in a fashion similar to those of first and second parts. The main objective of this part is to study the interaction of different water constituents during the chemical treatment and its effect on the removal efficiency of scale-forming constituents and the overall water quality of the treated brine.

3.3.1 Chemicals and Reagents.

The chemicals used for bench scale experiments were all of analytical grade: calcium hydroxide (Fisher Scientific), sodium aluminate (Fisher Scientific), sodium chloride (VWR), sodium sulfate (EMD), sodium silicate (Fisher Scientific), magnesium chloride (VWR), calcium chloride (VWR), and sodium bicarbonate (VWR).

All synthetic solutions were prepared using deionized water (DI water) from a Millipore system to at 18 MΩ. The working solutions of sodium sulfate, sodium silicate, sodium chloride, and model brine were prepared weekly. All primary standard solutions (calcium, magnesium, silicon, sodium, aluminum, chloride, and sulfate) were of the appropriate grade. Required secondary standards for instruments calibration were freshly prepared daily from the primary standard solutions.

3.3.2 Bench Scale Experimental Procedure.

High-density polyethylene (HDPE) bottles (125 ml) were utilized as well-mixed batch reactors. All the kinetic and equilibrium experiments were carried out in duplicates. After addition of an appropriate dose of chemical reagents in solid form to the solution of sulfate, silica, and model brine. Bottles were rapidly and tightly closed, well-mixed by shaking at room temperature in an orbital shaker.

Kinetic experiments were carried out at different reaction times up to 24 hours. Equilibrium experiments were performed at 6 hrs for sulfate and model brine, and for 2 hrs for silica removals.

NaCl was added at 150 mM to investigate the effect of NaCl usually present in actual brine streams on the removals of sulfate and silica.

At the end of each time intervals, HDPE bottles were removed from the shaker, then the pH and electrical conductivity were immediately measured before filtration. 5-ml samples were taken with a plastic syringe and filtered through 0.2 μm Whatman® membrane filters (VWR). Filtered samples were acidified to $pH \leq 2$ and stored in the refrigerator till performing the required water analyses.

3.3.3 Analytical Procedures.

All analytical procedures followed the Standard Methods for The Examination of Water and Wastewater (APHA, 1998). Sulfate $SO4^{2-}$ was analyzed by Dionex ICS2000. While Aluminum Al, Calcium Ca, Magnesium Mg, and Silicon Si were analyzed by Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) iCAP 6500 from Thermo Scientific.

pH and electrical conductivity were measured using a multimeter (SympHony B30PCI, VWR). pH probe with gel-filled combination electrode standardized with pH 4.00, 7.00, pH 10.01 and pH 12.45 buffers (VWR), while electrical conductivity probe was calibrated using 1000, 1470, 10,000, 20,000, and 100,000 μS/cm.

3.3.4 Kinetic and Equilibrium of Sulfate Removal:

A set of kinetic experiment was performed to study the kinetics of sulfate removal, i.e. time for the sulfate removal to reach stable or meta-stable conditions (at which there is no further significant removal). Two sub-sets of experiments were conducted with different initial sulfate concentrations; the first set had a 20 mM (1920 mg/l) of sulfate, while the second set had 40 mM (3840 mg/l) of sulfate. The reason for using two different initial concentrations was to investigate the effect of the initial sulfate concentration on the kinetics of the removal reactions at concentrations close to that normally found in RO brine stream. In order to investigate the effect of stirring on the removal efficiency, both sets were stirred at 275 rpm and 350 rpm.

To each reactor bottle, lime, $Ca(OH)_2$, and sodium aluminate, $NaAlO_2$, were added at a constant stoichiometric ratio of 200% and 100% to the initial sulfate concentration, respectively (i.e. molar ratio of Lime: Sodium Aluminate: Sulfate = 2 : 1: 1). This is performed to ensure that the reaction in each sample proceeds to completion, and not to be reactants-limited.

Another set of equilibrium experiments was conducted to study the effects of lime dose (of 0, 20, 40, 80 and 160 mM i.e. 0, 50, 100, 200, and 400% to initial sulfate) and sodium aluminate: lime was added at molar ratio of 1:2 at initial sulfate concentration of 40 mM.

In addition, a set of equilibrium experiments was conducted to explore the effect of initial sulfate concentration (10, 20, 30 and 40 mM) on sulfate removal. The ratio of lime dose and sodium aluminate doses to initial sulfate concentration were kept constant at 250% and 62.5%, respectively (i.e. calcium to aluminum ratio of 4:1, and lime to sulfate ratio of 2.5:1).

3.3.5 Kinetic and Equilibrium of Silica Removal:

A set of experiment was performed to study the kinetics of silica removal in a fashion similar to that of sulfate removal for initial silica concentration of 2.5 mM (150 mg/l). The concentration of 2.5 mM was chosen, being the maximum allowable silica concentration in RO brine streams as advised by membranes and antiscalant manufacturers, as well as being the solubility limit of silica at the normal pH. To each sample, lime, $Ca(OH)_2$, and sodium aluminate, $NaAlO_2$, were added at a constant stoichiometric ratio to the initial silica concentration of 400% i.e. 10 mM each.

Effects of lime and sodium aluminate doses on the equilibrium removals of silica studied in two sub-sets, with lime and sodium aluminate doses over the range of 0 - 7.5 mM. The effect of initial silica on silica removal was investigated by conducting a set of experiments at different initial silica concentrations of 1, 2, 3, 4 and 5 mM at lime and sodium aluminate dose to initial silica concentration molar ratio of 3:1, as concluded from equilibrium experiments that studied the effect of lime and aluminum doses on silica removal. The effect of temperature on silica removal was also investigated by conducting a set of experiments at various temperatures (30, 40 and 50 °C) for an initial silica concentration of 2.5 mM.

Effect of pH on silica removal as it is highly pH-dependent was studied at a range of pH values (10.5 to 13.01) was investigated at initial silica concentration of 2.5 mM. For each sample, the stoichiometric ratios of lime and sodium aluminate to initial silica concentration were kept constant at 3:1 (i.e. 7.5 mM each). After the addition of the aforementioned reagents, the initial pH of the sample is recorded, and then the pH was adjusted to the desired value using either sodium hydroxide, NaOH, to raise the pH or acetic acid, CH_3COOH, to lower the pH, with final pH of the sample is recorded.

3.3.6 Kinetic and Equilibrium of Combined Sulfate and Silica Removals:

A set of experiment was performed to study the kinetics and equilibrium of sulfate and silica removals from model brine solution, in a fashion similar to that of sulfate, and silica removal explained previously. The model brine solution had the concentrations of different constituents as outlined in table 3.3 below. These concentrations were based on projected quality of brine at the recovery of about 70-75%, in new large scale brackish groundwater desalination system at one of the under development farm in the State of Qatar.

First, a set of experiments was conducted to evaluate the removal of the different scale-forming constituents, by following the removal of SO_4^{2-}, and SiO_2. The experiments spanned over 18 hours at room temperature. To each sample, lime and sodium aluminate were added at a constant stoichiometric ratio to the initial sulfate concentration of 2:1, and 1:1 respectively i.e. 80 mM of lime and 40 mM of sodium aluminate.

Second a set of equilibrium experiments was conducted at room temperature for 2 hours, as concluded to be the equilibrium time from the kinetic experiments (by which more than 75% removal of sulfate was achieved), to evaluate the effects of lime doses and sodium aluminate at ratio varied up to 2:1, and 1:1 to initial sulfate concentration, respectively i.e. lime doses = 0–80 mM, and sodium aluminate doses = 0–40 mM.

3.4 Equilibrium Modelling of the Chemical Treatment Process:

Modeling of chemical treatment process presents an important task for the current study, as it helps to simulate the process performance under different conditions. Given the fact that brine from RO desalination of brackish groundwater will have a different composition as it is site-specific, and tends to change as well with time over the long operation, this model will be very crucial helping to design the ZLD desalination process that fits each inland desalination requirements.

Table 3.3 Composition model brine for brackish groundwater.

Constitute	**Model Brine**
Calcium Ca^{2+}, mM (mg/l)	20 (800)
Magnesium Mg^{2+}, mM (mg/l)	10 (240)
Sodium Na^{+}, mM (mg/l)	210 (4,830)
Bicarbonate HCO_3^-, mM (mg/l)	5 (305)
Chloride Cl^-, mM (mg/l)	180 (6,390)
Sulphate SO_4^{2-}, mM (mg/l)	40 (3,840)
Silica SiO_2,mM (mg/l)	2 (120)
Electrical Conductivity EC, mS/cm	22.51
Total Dissolved Solids TDS, mg/l	16,065
pH	7.91
Langelier Saturation Index, LSI	-
Stiff & Davis Saturation Index, SDSI	**0.85**
$CaSO_4$ Saturation Index	**1.03**
SiO_2 Saturation Index	**0.946**

The proposed chemical treatment process is based on treating the brine stream in an advanced lime softening. There is a wide range of softening processes that are specific to the quality of water to be used. Conventional lime-soda softening employs calcium hydroxide (as base for the raise of pH and as a source of hydroxide ion for the precipitation of magnesium as required), and soda ash or sodium carbonate, as a source of carbonate for low alkalinity water. The result is precipitation of calcium and alkalinity as calcium carbonate at pH 9.5-10, and magnesium as magnesium hydroxide at pH around 11, which requires higher lime dose (Hoover, 1937). Some modified softening processes utilize sodium hydroxide instead of calcium hydroxide in order to eliminate the addition of more calcium to the system.

Although conventional lime softening is very effective for removal of hardness i.e. calcium and alkalinity as carbonate in addition to efficient removal of silica, it has limited efficiency in sulfate removal. The treated water will be left saturated with respect to calcite or calcium carbonate and gypsum or calcium sulfate. In the proposed advanced softening processes, another reagent, i.e. sodium aluminate, is added which in turn present aluminum ions into the water. The objective of adding aluminum is to form more complex solids that have a much lower solubility, which in turn desupersaturates the treated water with respect to gypsum and calcite (Batchelor, B.; McDevitt, M.; Chan, 1985).

The ultimate objective of the chemical treatment process here is to convert the soluble ions into insoluble salts by modifying the medium pH, and/or introducing the counterpart ion of insoluble salt form. These removals reactions are widely dependent on the medium pH, and the chemical reagents used. Due to the presence of so many ions in the reaction medium i.e. brine, a wide range of reactions take place due to the interactions among different ions present. In general, the reactions taking place during the chemical treatment of brine can be categorized into two main categories, as outlined in sections 3.4.1 and 3.4.2.

Equilibrium modeling of the chemical reactions taking place during the chemical treatment process has been considered rather than kinetic modeling due to the fact that most of the ionic reaction proceeds at high reaction rate due to the high attraction forces encountered between positive and negative ions (Ahmed Abdel-Wahab, Batchelor, & Schwantes, 2005). Dissolution and precipitation for the transformation of components from the solid phase to soluble components in liquid phase and vice versa have been considered to be at equilibrium as well, as precipitation softening has been found to reach such solid-liquid equilibrium quickly (Stumm & Morgan, 1996). In addition, kinetic experiments have shown that the removal reactions are very fast and reach equilibrium within 2 hrs, and 6 hrs for silica and sulfate removals, respectively.

3.4.1 Dissolution of Chemical Reagents:

Chemical reagents added to the chemical treatment during the softening process are usually present in solid form and can be divided into two main categories:

i. pH raising reagents: which are bases added to raise the medium pH to value at which different solids become insoluble and their concentration to exceed their solubility limit i.e. ion activity product IAP is greater than the solubility product (as the solubility of most sparingly soluble salts decreases as pH increases i.e. in alkaline/basic medium). The main chemicals used for these purposes are calcium hydroxide, $Ca(OH)_2$ (slaked lime or just lime), and hence the process is called lime-softening, or sodium hydroxide, NaOH, therefore the process called soda-softening. The dissolution reactions for these chemicals can be outlined as follow:

$$Ca(OH)_2(s) + 2H^+ \leftrightarrow Ca^{2+} + 2H_2O \tag{3-1}$$

$$NaOH + H^+ \leftrightarrow Na^+ + H_2O \tag{3-2}$$

In the current study, calcium hydroxide has been used as pH raising reagent i.e. source of OH^-, as well as a source of Ca^{2+}.

ii. Specific softening reagents: which are specific reagents added to enhance the removal of specific ions present in water, for example, sodium carbonate (soda ash) is usually added in softening processes along with lime, and hence called lime-soda softening to introduce carbonate ion in carbonate-lean water to enhance the removal of calcium ion as calcium carbonate for hardness reduction (Hoover, 1937).

Multivalent ion salts such as aluminum salts and ferric salts, in addition to magnesium salts (in magnesium-lean water), are usually added to enhance the removal of silicate from silica-rich waters (Al-Mutaz & Al-Anezi, 2004). In this study, the focus will be on aluminum salts, namely sodium aluminate, as it provides a basic medium (in contradictory to aluminum sulfate, i.e. alum, which on dissolution in water decreases the pH of the medium), in addition, to showing some success in sulfate removal in industrial wastewaters (Batchelor, B.; McDevitt, M.; Chan, 1985). The dissolution reactions for these chemicals can be outlined as follow:

$$Na_2CO_3(s) \leftrightarrow 2Na^+ + CO_3^{2-} \tag{3-3}$$

$$NaAlO_2(s) + 2H_2O \leftrightarrow Na^+ + Al(OH)_4^- \tag{3-4}$$

3.4.2 Precipitation of Sparingly Soluble Salts:

Different solids can be precipitated during the chemical treatment process, as these solids become insoluble and their concentration to exceed their solubility limit i.e. ion activity product IAP is greater than the solubility product K_{sp}. The solids precipitated and precipitation extent mainly depending on the ions present in water, concentration of different ions, chemical reagents added (which might increase the concentration of ions already present in water such as Ca^{2+}, or add new ions to the water such as Al^{3+}), and finally medium pH that has a great effect. The solids precipitated during the chemical treatment can generally be divided as follow:

i. Carbonates of calcium and magnesium: As pH increases with the addition of lime, calcium, magnesium, and carbonate ions present in the water combine and precipitate as calcium carbonate completely at pH up to 10.5 as well as dolomite or calcium magnesium carbonate, according to the following reaction:

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(s) \qquad 3\text{-}5$$

$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \leftrightarrow CaMg(CO_3)_2(s) \qquad 3\text{-}6$$

ii. Magnesium Hydroxide: As pH increases with the addition of lime, magnesium ion present in water combine with hydroxide ion and precipitates as magnesium hydroxide completely at pH above 11 according to the following reaction:

$$Mg^{2+} + 2H_2O \leftrightarrow Mg(OH)_2(s) + 2H^+ \qquad 3\text{-}7$$

iii. Silicates of calcium and magnesium: Silica can also be removed at high pH values present during the softening process by adsorption to precipitates formed especially $Mg(OH)_2$, or by co-precipitation with it, or as calcium or magnesium silicate according to the following reactions:

$$Ca^{2+}/Mg^{2+} + H_2SiO_4^{2-} \leftrightarrow (Ca/Mg)H_2SiO_4(s) \qquad 3\text{-}8$$

Advanced softening processes where high lime doses and specific reagents such as aluminum, and ferric salts are applied can improve the removal of silica by forming very low solubility salts such as calcium aluminosilicate or ferrosilicate according to the following reaction:

$$2Ca^{2+} + 2\,Al/Fe(OH)_4^- + H_4SiO_4 + 2OH^- \leftrightarrow Ca_2(Al/Fe)Si(OH)_{14}(s) \quad 3\text{-}9$$

iv. Sulfate salts: Sulfate present in water can be removed during lime softening as calcium sulfate i.e. gypsum, according to the following reaction:

$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4(s) \qquad 3\text{-}10$$

In advanced softening processes improve the removal of sulfate by forming very low solubility salts such as calcium sulfoaluminate and calcium mono sulfoaluminate, depending on the concentration or reacting ions according to the following respectively:

$$6Ca^{2+} + 2\,Al(OH)_4^- + 3SO_4^{2-} + 4OH^- \leftrightarrow Ca_6Al_2(SO_4)_3(OH)_{12}(s) \qquad 3\text{-}11$$

$$4Ca^{2+} + 2\,Al(OH)_4^- + SO_4^{2-} + 4OH^- \leftrightarrow Ca_4Al_2(SO_4)(OH)_{12}(s) \qquad 3\text{-}12$$

Due to the variety of solids that can be formed during the chemical treatment, equilibrium modeling using mineral equilibrium package is paramount. The solids formed during the chemical treatment should be formed in the order from lower K_{sp} to the higher one i.e. from, the lower in solubility to the higher in solubility. Table 3.4 below shows the K_{sp} values for different solids expected to be formed during the advanced lime softening treatment of brine as compiled from different sources (Ahmed Abdel-Wahab & Batchelor, 2006; Batchelor, B.; McDevitt, M.; Chan, 1985; Batchelor & Mcdevitt, 1984; Parkhurst, 1999; Qing et al., 2007; Stumm & Morgan, 1996)

Table 3.4 K_{sp} values for different solids expected to be formed during the advanced softening treatment.

Solid	**Phase**	**Log K_{sp}**
Calcium Carbonate, $CaCO_3$	Calcite	-8.48
	Aragonite	-8.336
Calcium Magnesium Carbonate, $CaMg(CO_3)_2$	Dolomite-ordered	-17.09
	Dolomite-disordered	-16.54
Magnesium Hydroxide, $Mg(OH)_2$	Brucite	-10.744
Calcium Silicate, CaH_2SiO_4		-8.02
Magnesium Silicate, MgH_2SiO_4		-4.64
Calcium Aluminosilicate, $Ca_2(Al/Fe)Si(OH)_{14}$		-23.09
Calcium Sulfate	Anhydrite, $CaSO_4$	-4.36
	Gypsum, $CaSO_4.2H_2O$	-4.58
Calcium Sulfoaluminate, $Ca_6Al_2(SO_4)_3(OH)_{12}$	Ettringite	-44.56
Calcium mono Sulfoaluminate, $Ca_4Al_2(SO_4)(OH)_{12}$		-29.43

3.4.3 Equilibrium Modeling:

A basic model of the chemical reactions and processes taking place during the chemical treatment of the brine is to be developed in order to predict the concentrations of different constituents such as sulfate, silica, calcium,…etc. in the effluent stream i.e. treated brine, utilizing the information on the chemical reagents and doses, in addition to the quality i.e. composition of brine stream. Precipitation is to be assumed as the mechanism that controls the solubility of the species in the system. The experimental results data and conditions from the different experimental work are to be used to validate the developed equilibrium model.

Aqueous and electrolyte chemical equilibrium software are chemical equilibrium software packages used to calculate and draw the thermodynamic equilibrium concentration of species in complex chemical systems. The software packages used in this study is the OLI stream analyzer.

OLI Electrolyte Simulation (OLI Systems, 2016) is a basic electrolyte thermodynamic model, based on a true speciation model, and predictive Helgeson equation of state. OLI AQ model covers +80 elements and is based on published experimental data. The model uses data regression in addition to estimation and extrapolation where required.

OLI provides general simulation capability for aqueous systems, giving an accurate prediction for almost any water chemistry over wide ranges of temperatures, pressures, and ionic strength. OLI has been widely used for predicting the solubility and mineral equilibrium of a wide range of water chemistries (Azimi et al., 2007; J. S. Choi, Hwang, Lee, & Hong, 2009; McCool et al., 2013; Rahardianto, McCool, & Cohen, 2010).

3.5 Identification and Characterization of Precipitated Solids.

In order to develop a complete environmentally benign technology, all the process wastes should be handled environmentally, and as a result, it was paramount to look at the solid products from the proposed chemical treatment process. The main objective of the proposed technology is to approach a zero liquid discharge for inland desalination, although the solid waste is much less in terms of volume generated and ease of handling, it still has to be handled properly.

Two types of solids are produced from the proposed process. The first is the precipitated solids from chemical treatment of the primary brine stream, which differs in composition and quantity according to the chemical reagents used and the feedwater quality. This product is believed to be rich in certain components such as calcium, magnesium, aluminum, sulfate, silica, and carbonate. The second stream is the final salt that will be produced from the final evaporation of final brine stream in ideal zero liquid discharge process, which will be mainly salts of sodium and potassium chloride, in addition to some sodium and potassium sulfate salts. The solid products from the chemical treatment are the main concern in this study for identifying potential applications.

The first step to evaluate the opportunities of solids potential applications is to identify the compounds formed during the chemical treatment. In this regard, the equilibrium model to be developed will play an essential role in addition to the literature performed as they provide information about the different solid phases or minerals that result during precipitation softening. The solids formed are believed to be a combination of different calcium/magnesium with sulfate/ silica/ aluminate/ carbonate compounds.

The solids formed during the chemical treatment can be identified by two approaches:

i. Theoretical approach: in which the equilibrium modeling packages used in section 3.4, OLI stream analyzer, is utilized. The results obtained from running the equilibrium model contain saturation indices information, which provides information on which solid phases are oversaturated in the solution, and hence are expected to be present in the precipitated solids, OLI was found to provide the amount expected from such solids as well, by carrying out material balance calculations of the system at equilibrium conditions.
ii. Experimental approach: in which the solids formed during the chemical treatment are collected and analyzed using different solid characterization and analytical techniques utilizing X-ray.

In the second approach, solids produced from selected bench top experiments, as outlined in table 3.5 below and according to the protocol mentioned in 3.3.2, are collected by filtering the treated water through 0.2 µm filter paper, drying the filtered cake in an inert atmosphere at 105 ^{o}C for 12 hrs. The dried solids are then analyzed using X-ray techniques, namely, X-ray Diffraction using Rigaku, Ultima IV Multipurpose XRD with a scanning rate of 2θ/min and scanning range from $2\theta = 5 - 80$. The use of XRD helps determine the different qualitatively the solids present in the precipitate as well as the different phases of each solid.

In addition, the same samples to be analyzed using X-ray Fluorescence using Rigaku, ZSX Primus II Wavelength Dispersive XRF in both oxide and elemental modes, which helps to provide elemental analysis of the different elements present in the precipitate both qualitatively and quantitatively.

Table 3.5 Experimental conditions for solid characterization using X-ray techniques.

Medium	Lime dose, mM	Sodium Aluminate dose, mM	Symbol
Synesthetic (model) Brine SB	40	20	**SB-40-20**
	80	20	**SB-80-20**
	80	40	**SB-80-40**

3.6 Development of Complete Process Model.

Complete process model to be developed for the proposed ZLD technology that includes the different units involved such as membrane separation units i.e. primary RO and secondary RO, along with chemical treatment unit. The units have a great dependence on each other as the product from one unit is feed to the next, this complexity increases as the options of streams mixing (recycle/bypass). The model should predict the performance and effectiveness of the whole process under different input condition of feedwater quality and flowrate, and doses of chemical reagents to estimate the water productivity i.e. recovery, the amount of solids produced and composition.

The model will be utilizing the developed equilibrium model for the chemical treatment along with newly developed membrane separation models for membrane separation. Figure 3.2 shows a schematic for the complete process model incorporating different input and outputs.

3.6.1 Membrane Model Parameters.

Membrane separation models require the combination of mass and momentum transport equations through the membrane. Different reference works provide equations for modeling of RO membrane (Dow Water Solutions, 2013; Y. M. Kim et al., 2009; Oh, Hwang, & Lee, 2009; Sundaramoorthy, Srinivasan, & Murthy, 2011; Wilf, 2007), and main model parameters can be summarized as follow:

<u>Osmotic pressure Π:</u> Osmotic pressure is one of the main parameters that determine the performance of RO membranes. Osmotic pressure is the most important characteristic of saline solution, and can be indirectly measured by the level of solution salinity through the following simple equation for an ideal solution:

$$\Pi = \mathrm{RT}\sum m_i \qquad 3\text{-}13$$

Where:

Π = Osmotic pressure, bar R = universal gas constant (0.08314 bar.l/ mol.k)

T = Absolute temperature, K m_i = molar concentration of constitute i, mol/l

OLI (OLI Systems, 2016) calculates the osmotic pressure in more rigorous formula for calculating the osmotic pressure that incorporates the activity coefficient of the solution, which is of high importance for concentrated solutions, more specifically seawater desalination, as follow:

$$\Pi = -\left(\frac{\mathrm{RT}}{V_{H2O}}\right)\ln\sum a_{H2O} = -\left(\frac{\mathrm{RT}}{V_{H2O}}\right)\ln\sum x\gamma_{H2O} \qquad 3\text{-}14$$

Where:

V_{H2O} = partial molal volume of water, l/mol a_{H2O}= Activity of water

γ_{H2O}= activity coefficient of water x = mole fraction of solute

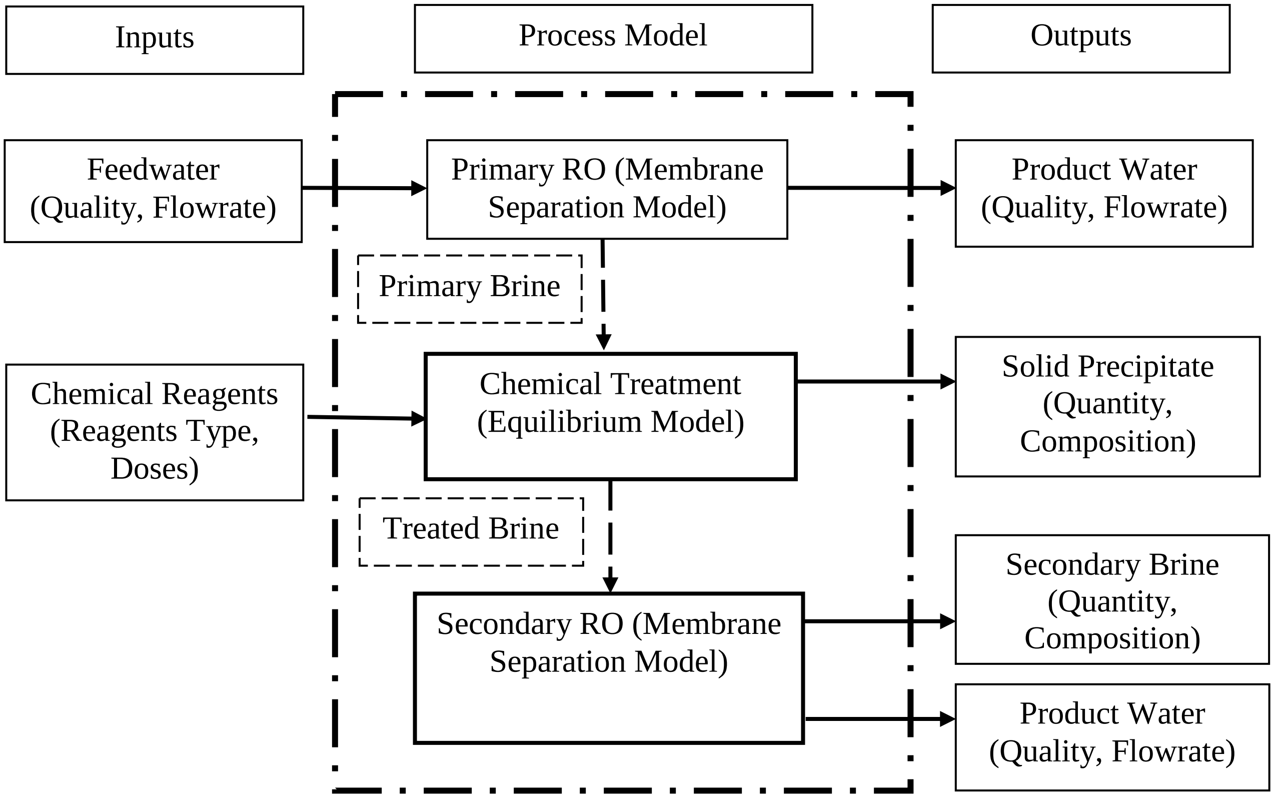


Figure 3.2 Schematic diagram for the complete process model.

System recovery R_P: System recovery is the fraction of water produced as permeate through the membrane relative to the feedwater flowrate. This is a very important parameter indicating the system performance. Usually, it is desired to maximize the recovery of the system at specific operating conditions, and the recovery is related to the system streams through the following equation, as indicated in figure 3.3:

$$R_P = Q_P/Q_F * 100\% = (C_C - C_F)/(C_C - C_P) * 100\% \qquad 3\text{-}15$$

Where:

R_P = Product recovery, %
Q_P = Product flowrate, m^3/hr
Q_F = Feed flowrate, m^3/hr
Q_B = Brine flowrate, m^3/hr
C_F = Feed salt concentration, g/m^3
C_B = Brine salt concentration, g/m^3
C_P = Product salt concentration, g/m^3

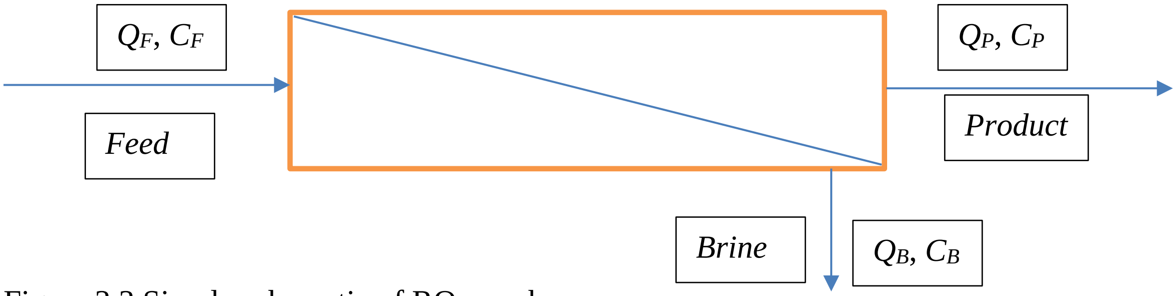


Figure 3.3 Simple schematic of RO membrane.

Net driving pressure NDP: Net driving pressure represents the difference between the applied pressures and the osmotic pressure on membrane feed/brine side, in addition to pressure losses. NDP can be simply defined as:

$$NDP = P_F - \Pi - P_P - o.5P_d \qquad 3\text{-}16$$

Where:

P_F = Feed pressure, bar
Π = Osmotic pressure, bar
P_P = Permeate pressure, bar
P_d = Pressure drop across RO element, bar

Water transport Q_P: Water transport represents the rate of water permeation or flow through the membrane under the effect of the applied driving force i.e. NDP and can be simply defined as:

$$Q_w \cong Q_P = A.S.NDP \qquad 3\text{-}17$$

Where:

Q_P = Water flow through membrane, m^3/hr S = membrane surface area, m^2

A= Permeability of water through the membrane (or Water transport coefficient), $m^3/m^2.hr.bar$

NDP = Net driving pressure, bar

Salt transport Q_s: Salt transport represents the rate of salt permeation or flow through the membrane under the effect of the applied driving force i.e. NDP can be simply defined as:

$$Q_s = B.S.\Delta C \qquad 3\text{-}18$$

Where:

Q_s = Salt flow through membrane, g/hr S = membrane surface area, m^2

B= Permeability of salt through membrane (or salt transport coefficient), $m^3/ m^2/hr$

ΔC= salt concentration difference across the membrane, g/ m^3

Product salinity C_P: Product water salinity can be then calculated using the water and salt transport values as follow:

$$C_P = Q_S/Q_P \qquad 3\text{-}19$$

Salt passage SP and salt rejection SR: Although the RO membranes are theoretically semi-permeable in principle, i.e. allows only water to pass through the membrane and reject salts or other ions, in practical, there is no RO with complete rejection to salt ions, and hence some of the ions are passing through the membrane. The salt passage can be easily defined as the ratio of salt in the product water or permeate i.e. concentration of salt in product water to the average concentration (as the concentration at the feed membrane side changes from C_F to C_B) of salt on the feed/brine side of the membrane, as defined in equation 3-20.

$$\mathrm{SP} = C_P/C_{Fm} * 100\% \qquad 3\text{-}20$$

Where: C_{Fm} = Feed average concentration, g/m^3

The rejection of RO membranes is the opposite of the salt passage i.e. the percentage of salt ions rejected by the membranes, as given by equation 3-21. RO membranes have a high rejection to divalent ions approaching 99.0-99.8%, and less rejection to monovalent ions of approximately 98–99% depending on the system operating conditions.

$$\mathrm{SR} = 100\% - \mathrm{SP} \qquad 3\text{-}21$$

Concentration Polarization CP: As water flows through the RO membrane, and salt ions are retained at the membrane surface, the concentration of salt ions becomes higher at the membrane surface relative to the bulk of the solution. This, in turn, forms a boundary layer at the surface causing concentration polarization CP at the membrane surface and affecting membrane performance. Effects of concentration polarization are (Wilf, 2007):

i- Increase the osmotic pressure at the membrane surface, due to the increased concentration of salts, and hence reducing the NDP.
ii- Reduce water transport through the membrane Q_p.
iii- Increase the salt transport through the membrane Q_s and hence the product salinity.
iv- Increase the scaling tendency of sparingly soluble salts at the membrane surface.

In brackish groundwater desalination, concentration polarization is usually neglected or assumed to be 1.1 due to the fact that brackish groundwater usually will have salinity below 10,000 mg/l, and system recovery is usually up to 80%. Concentration polarization factor CPF, defined as the ratio of salt concentration at membrane surface C_S to that of the bulk C_B in equation 3-22, is usually considered with value ranging from 1.05 to 1.2 as recommended by membrane manufacturers.

$$\mathrm{CPF} = C_S/C_B \qquad 3\text{-}22$$

Energy consumption E: In RO membrane desalination, the major energy consumption is for pumping and increasing the feed pressure to the required P_F value to maintain the needed NDP for the water production of Q_P. The energy consumed can be easily calculated using equation 3-23 neglecting energy losses, and other energy consumption components (Oh et al., 2009; Wilf, 2007). Specific energy consumption SE is defined as the energy consumed per unit product water, as defined in equation 3-24 is commonly used as well.

$$E = Q_F P_F / \eta_{pump} \quad 3\text{-}23$$

$$SE = Q_F P_F / Q_P \eta_{pump} = P_F / R_P \eta_{pump} \quad 3\text{-}24$$

Where:

η_{pump} = Pump combined hydraulic and electrical efficiency.

3.6.2 Development of Membrane Separation Model:

RO membranes are usually available in three basic modules, namely spiral-wound, hollow-fiber, and plate & frame, with the first being the widely used module due to many advantages such as the high packaging density, good fouling resistance, and lower operating and capital costs. Figure 3.4 below shows the schematic of spiral-wound membrane element, showing the different module components such as membrane sheet, support, feed and permeate spacers, and feed/concentrate and permeate channels.

The membrane envelope is made of two sheets, glued at the edges of the sheets. The permeate side of this envelope is fixed on a perforated inner support, where permeate transported through the membrane is collected. Multi-envelopes, separated by very thin spacers are tightly wrapped around the perforated inner tube that collects permeate from the permeate channels. The RO membrane elements have a varied element length of 12”, 14, 21, and 40. RO membrane elements vary diameter as well from 2.5”, 4”, and 8”. 40” length with 4” diameter elements are widely used for RO plants, with 8” diameter elements used for large seawater desalination applications.

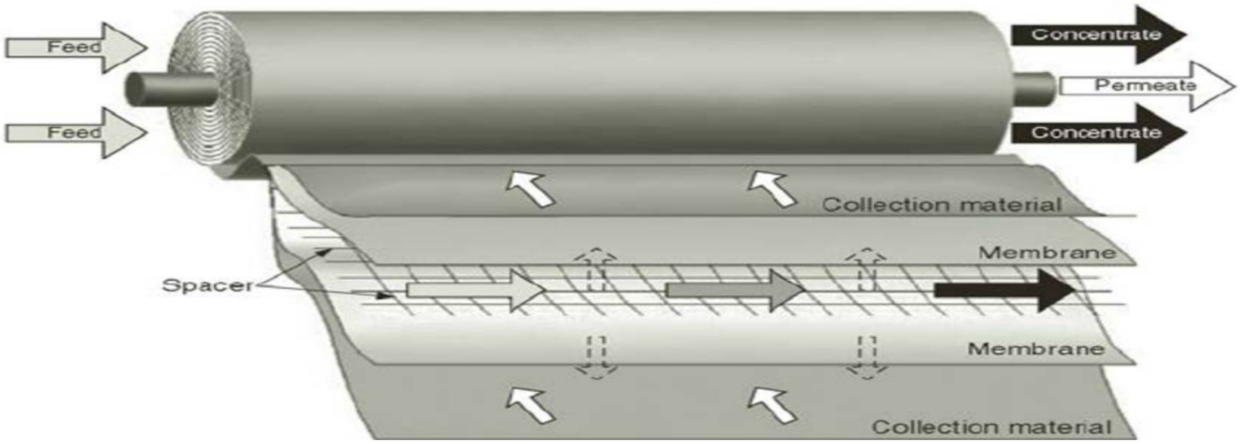


Figure 3.4 Spiral-wound membrane element.

A rigorous membrane model is to be built in Aspen Custom Modeler ACM V8.8 (Aspentech, 2016) environment, in order to utilize the different property packages to accurately estimate the system parameters and system performance. Furthermore, modeling the RO unit in ACM facilitates the integration of the chemical treatment unit. The chemical treatment will utilize the developed equilibrium model in OLI through OLI engine for Aspen V.9.2, to accurately predict the performance of the chemical treatment unit providing the effluent treated water quality.

The membrane separation model developed in this study has a distinct feature of treating salts present in water as dissociated ions rather than formed salts. This has the advantages of distinguishing the permeation of different ions according to their ionic nature i.e. mono-valent or di-valent, as the membrane generally reacts differently toward these ions i.e. different passage.

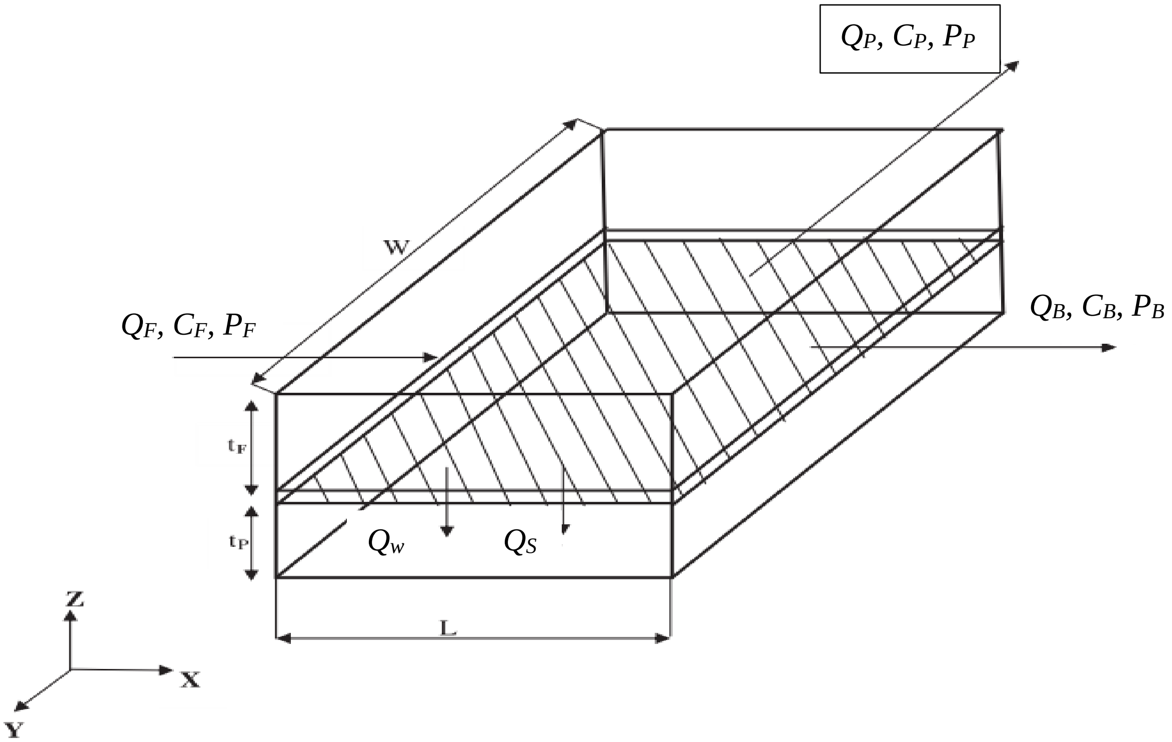


Fig. 3.5 Schematic for flattened spiral wound membrane element.

The essential advantages of building the model in ACM environment are (Aspentech, 2016):

i- Ease of model development for custom unit operation models.
ii- Running the models into complete simulation flowsheets.
iii- Quick execution of steady-state and dynamic simulations.

iv- Incorporating Aspen built-in models/units along with the developed model.

v- Readily incorporated solution methods as ACM uses advanced equation-based solution techniques to ensure a fast and reliable solution.

vi- ACM also utilizes Aspen Properties®, this allows ACM to access comprehensive property models available within Aspen Properties, and custom physical properties such as OLI in this study.

Once the RO model is built in ACM environment, it can be used for wide range of simulations, including:

i- Steady-state simulation for process design.

ii- Dynamic simulation to evaluate and understand the dynamic behavior.

iii- Dynamic/ steady-state parameters estimation to fit model parameters.

iv- Dynamic/ steady-state optimization to optimize of continuous processes.

Model assumptions:

i. Model components are true component ions, water, dissolved gasses, salts, and solids.

ii. The chemistry between components can be described by electrolyte NRTL model as well as model provided by OLI systems (OLI Systems, 2016).

iii. Negligible component of the brine and permeate velocities in radial and axial directions, respectively.

iv. Volumetric flow through the membrane is mainly solvent flux.

v. Mass transfer coefficient in channels equipped with spacers can be calculated by following relation $K=mt*\omega^{0.5}$ (Sundaramoorthy et al., 2011)

vi. The validity of Darcy's Law concerning pressure drops in a porous medium.

vii. Ions are classified based on electrical charge as monovalent or divalent.

<u>Material balance for ions</u>

- Brine side axial direction $$\frac{dF_i^B}{dx} = -J_i^m \cdot \Delta y \qquad \forall i \in I$$

- Brine side radial direction $$\frac{dF_i^B}{dy} = 0 \qquad \forall i \in I$$

- Permeate side axial direction $\frac{dF_i^P}{dx} = 0 \qquad \forall i \in I$
- Permeate side radial direction $\frac{dF_i^P}{dy} = J_i^m \cdot \Delta x \qquad \forall i \in I$

<u>Material balance for dissolved salts and solids</u>

- Brine side axial direction $\frac{dF_s^B}{dx} = -J_s^m \cdot \Delta y \qquad \forall s \in DS$
- Brine side radial direction $\frac{dF_s^B}{dy} = 0 \qquad \forall s \in DS$
- Permeate side axial direction $\frac{dF_s^P}{dx} = 0 \qquad \forall s \in DS$
- Permeate side radial direction $\frac{dF_s^P}{dy} = J_s^m \cdot \Delta x \qquad \forall s \in DS$

<u>Material balance for dissolved gases:</u>

- Brine side axial direction $\frac{dF_g^B}{dx} = -J_g^m \cdot \Delta y \qquad \forall g \in DG$
- Brine side radial direction $\frac{dF_g^B}{dy} = 0 \qquad \forall g \in DG$
- Permeate side axial direction $\frac{dF_g^P}{dx} = 0 \qquad \forall g \in DG$
- Permeate side radial direction $\frac{dF_g^P}{dy} = J_g^m \cdot \Delta x \qquad \forall g \in DG$

<u>Material balance for water</u>

- Brine side axial direction $\frac{dF_w^B}{dx} = -\bar{\rho}_w^B \cdot J_w^v \cdot \Delta y$
- Brine side radial direction $\frac{dF_w^B}{dy} = 0$
- Permeate side axial direction $\frac{dF_w^P}{dx} = 0$

- Permeate side radial direction $\dfrac{dF_w^P}{dy} = \overline{\rho}_w^P J_w^v \cdot \Delta x$

Momentum balance

- Brine side axial direction $\dfrac{dP^B}{dx} = -\mu^B \cdot K_B \cdot \omega^B$
- Brine side radial direction $\dfrac{dP^B}{dy} = 0$
- Permeate side axial direction $\dfrac{dP^P}{dx} = 0$
- Permeate side radial direction $\dfrac{dP^P}{dy} = -\mu^P \cdot K_P \cdot \omega^P$

Boundary conditions

$F_i^B\left(0, 0 \le y \le W\right) = F_{in,i}^B$ $\quad F_i^P\left(0 \le x \le L, 0\right) = 0$

$F_s^B\left(0, 0 \le y \le W\right) = F_{in,\mathrm{s}}^B$ $\quad F_s^P\left(0 \le x \le L, 0\right) = 0$

$F_g^B\left(0, 0 \le y \le W\right) = F_{in,\mathrm{g}}^B$ $\quad F_g^P\left(0 \le x \le L, 0\right) = 0$

$F_w^B\left(0, 0 \le y \le W\right) = F_{in,\mathrm{w}}^B$ $\quad F_w^P\left(0 \le x \le L, 0\right) = 0$

$P^B\left(0, 0 \le y \le W\right) = P_{in}^B$ $\quad P_w^P\left(0 \le x \le L, \mathrm{W}\right) = P_{out}$

Molar flux for ions

Monovalent ions $J_{imv}^m = B_{imv}\left(\rho^B \cdot Z_{imv}^B - \rho^P \cdot Z_{imv}^P\right) \cdot e^{\frac{J_w^v}{k}} \quad \forall imv \in IMV$

Divalent ions $J_{dmv}^m = B_{dmv}\left(\rho^B \cdot Z_{dmv}^B - \rho^P \cdot Z_{dmv}^P\right) \cdot e^{\frac{J_w^v}{k}} \quad \forall dmv \in DMV$

Molar flux for dissolved salts and solids $J_s^m = B_s\left(\rho^B \cdot Z_s^B - \rho^P \cdot Z_s^P\right) \cdot e^{\frac{J_w^v}{k}} \quad \forall s \in DS$

Molar flux for dissolved gasses $J_g^m = B_g\left(\rho^B \cdot Z_g^B - \rho^P \cdot Z_g^P\right) \cdot e^{\frac{J_w^v}{k}} \quad \forall g \in DG$

Volumetric flux of water $J_w^v = A\left(P^B - P^P - \Pi^S + \Pi^P\right)$

Ideal osmotic pressure at membrane surface $\Pi_{id}^{S} = 0.01\cdot R\cdot T\cdot \overline{\rho}_{w}^{S}\left(1-Z_{w}^{S}\right)$

Ideal osmotic pressure on permeate side surface $\Pi_{id}^{P} = 0.01\cdot R\cdot T\cdot \overline{\rho}_{w}^{P}\left(1-Z_{w}^{P}\right)$

Osmotic coefficient on the membrane surface $\Phi^{S} = -\dfrac{\ln\left(Z_{w}^{S}\cdot\gamma_{w}^{S}\right)}{1-Z_{w}^{S}}$

Osmotic coefficient on the permeate side $\Phi^{P} = -\dfrac{\ln\left(Z_{w}^{P}\cdot\gamma_{w}^{P}\right)}{1-Z_{w}^{P}}$

Osmotic pressure at membrane surface $\Pi^{S} = \Phi^{S}\cdot\Pi_{id}^{S}$

Osmotic pressure on permeate side surface $\Pi^{P} = \Phi^{P}\cdot\Pi_{id}^{P}$

Molar fraction at membrane surface for ions

$$\rho^{S}\cdot Z_{i}^{S} = \rho^{P}\cdot Z_{i}^{P} + \left(\rho^{B}\cdot Z_{i}^{B} - \rho^{P}\cdot Z_{i}^{P}\right)\cdot e^{\frac{J_{w}^{v}}{k}} \qquad \forall i \in I$$

Molar fraction of dissolved salts and solids

$$\rho^{S}\cdot Z_{s}^{S} = \rho^{P}\cdot Z_{s}^{P} + \left(\rho^{B}\cdot Z_{s}^{B} - \rho^{P}\cdot Z_{s}^{P}\right)\cdot e^{\frac{J_{w}^{v}}{k}} \qquad \forall s \in DS$$

Molar fraction of dissolved gasses and solids

$$\rho^{S}\cdot Z_{g}^{S} = \rho^{P}\cdot Z_{g}^{P} + \left(\rho^{B}\cdot Z_{g}^{B} - \rho^{P}\cdot Z_{g}^{P}\right)\cdot e^{\frac{J_{w}^{v}}{k}} \qquad \forall g \in DG$$

Molar fraction for water

$$\rho^{S}\cdot Z_{w}^{S} = \rho^{P}\cdot Z_{w}^{P} + \left(\rho^{B}\cdot Z_{w}^{B} - \rho^{P}\cdot Z_{w}^{P}\right)\cdot e^{\frac{J_{w}^{v}}{k}}$$

Mass transfer coefficient is defined $k = mt\cdot\sqrt{\omega^{B}}$

Constraints

The sum of mole fractions at membrane surface is equal unity: $\sum_{i=1}^{I} Z_{i}^{S} + \sum_{s=1}^{DS} Z_{s}^{S} + \sum_{g=1}^{DG} Z_{g}^{S} + Z_{w}^{S} = 1$

Electrical charge neutrality of ionic species on feed/brine side: $\sum_{imv}\delta_{imv}\cdot F_{imv}^{B} + \sum_{dmv}\delta_{dmv}\cdot F_{dmv}^{B} = 0$

Electrical charge neutrality of ionic species on permeate side: $\sum_{imv}\delta_{imv}\cdot F^{P}_{imv}+\sum_{dmv}\delta_{dmv}\cdot F^{P}_{dmv}=0$

Where:

Indices:

i: ions

i_{mv}: monovalent ions

i_{dv}: divalent ions

s: Dissolved salts and solids

g :Dissolved gases

w :Water

in :inlet

out :outlet

Sets

I: – set of ions

I_{MV}: set of monovalent ions

I_{DV}: – set of divalent ions

DS: – set of dissolved salts and solids

DG: – set of dissolved gasses

Parameters

δ Ions valence

R Universal gas constant, kJ/kmol/K

L Membrane module length, m

W Membrane module width, m

H_b Height of brine channel, m

H_p Height of permeate channel, m

A Permeability of water trough membrane, $m^3/m^2/bar/hr$

B Permeability of ions through membrane, $m^3/m^2/hr$

B_{idv} Permeability of divalent ions, $m^3/m^2/hr$

B_{imv} Permeability of monovalent ions, $m^3/m^2/hr$

B_s Permeability dissolved salts and solids, $m^3/m^2/hr$

B_g Permeability dissolved gasses, $m^3/m^2/hr$

k Mass transfer coefficient, m/hr

mt Parameter of Mass transfer coefficient (dimensionless)

K_B friction factor in brine channel, $1/m^2$

K_P friction factor in permeate channel, $1/m^2$

F^B Molar flowrate on the brine side, kmol/hr

F^P	Molar flowrate on the permeate side, kmol/hr
J^m	Molar flux of ions through membrane, kmol/m^2/hr
J^v	Volumetric flux of ions through membrane, m^3/m^2/hr
Z^B	Mole fraction on the brine side, kmol/kmol
Z^P	Mole fraction on the permeate side, kmol/kmol
Z^S	Mole fraction on the membrane surface, kmol/kmol
γ^S	Activity coefficient at membrane surface
ρ^B	Molar density of solution on the brine side, kmol/m^3
ρ^P	Molar density of solution on the brine side, kmol/m^3
ρ^S	Molar density of solution on the membrane surface, kmol/m^3
$\overline{\rho}$	Molar partial density, kmol/m^3
ω^B	Velocity of solution on the brine side, m/hr
ω^P	Velocity of solution on the permeate side, m/hr
T	Temperature of system, K
P^B	Pressure on the brine side, bar
P^P	Pressure on the permeate side, bar
Π^S	Osmotic pressure on the membrane surface, bar
Π^P	Osmotic pressure on the permeate side, bar
Π_{id}^S	Ideal osmotic pressure on the membrane surface, bar
Π_{id}^P	Ideal osmotic pressure on the permeate side, bar
Φ^S	Osmotic coefficient on the membrane surface
Φ^P	Osmotic coefficient on the permeate side
μ^B	Viscosity of solution on the brine side, bar.hr
μ^P	Viscosity of solution on the brine side, bar.hr
μ^S	Viscosity of solution on the membrane surface, bar.hr

Membrane system physical constrains:

In addition to the previous model constrains, the membrane module will have some additional constrains, which have to be considered while modeling the RO membrane system. Some of these constrains are related to the membrane characteristics, membrane type, and manufacturer, and usually obtained in the membrane datasheet as provided by the manufacturer. While other constrains are operating constrains, usually advised by RO membrane manufacturer, or antiscalant vendor, or as a result of pilot plant testing before the commission of RO plant. Table 3.6 shows the different constrains, with typical values for RO membrane for both brackish water and seawater RO membranes (Dow, 2013).

3.6.3 Model Parameters Estimation, Validation, and Sensitivity Analysis:

The developed RO membranes model has some parameters that need to be estimated in order to utilize the model for design purposes. Experimental data generated utilizing standard commercial small-scale RO unit (HP-UC35-235 from HP Water Makers, Milan, Italy), with one membrane element of 2.5” diameter and 40” length, and normal working pressure up to 60 bars has been utilized for this purpose.

The main membrane characteristic parameters are:

i- Water/solvent permeability coefficient through membrane A,

ii- Solute permeability coefficient through membrane B (B_{imv}, and B_{idv}) for monovalent and divalent respectively,

iii- The parameter of mass transfer coefficient, mt.

iv- Flow friction coefficient in brine and permeate channels K_b, and K_P respectively.

These parameters are to be estimated using ACM by feeding the ACM with experimental data provided by running the lab scale RO unit. Furthermore, appropriate sensitivity analysis with respect to parameter estimated to assess the variation in model outputs can be attributed to different input sources. Critical model inputs, such as parameters and operating conditions, to be identified, followed by quantifying how input uncertainties impact the model outputs (Marino, Hogue, Ray, & Kirschner, 2009).

Table 3.6 Typical RO Membrane characteristics and operating constrains.

Parameter	**Typical value for brackish water RO membranes (BW30-4040)**	**Typical value for seawater RO membranes (SW30-4040)**
Membrane element length, m (in)	1.016 (40.0)	
Membrane element diameter, m (in)	0.099 (3.9)	
Feed spacer, mm (mil)	0.8636 (34)	
Membrane active area, m^2 (ft^2)	7.2 (78)	7.4 (80)
Stabilized NaCl salt rejection, %	99.5	
Maximum operating temperature, °C (°F)	45 (113)	
Maximum operating pressure, bar (psi)	41 (600)	69 (1000)
Maximum pressure drop, bar (psi)	1 (15)	
Maximum feed flow, m^3/h (gpm)	3.6 (16)	
Maximum permeate flow, m^3/h (gpm)	0.30 (1.33)	
Minimum concentrate flow, m^3/h (gpm)	0.68 (3.0)	
Maximum element recovery, %	19	
pH range	2 - 11	
Maximum calcium carbonate saturation	LSI/SDSI ≤ 3.0	
Maximum calcium sulfate saturation	$SI_{CaSO4} \leq 3.5\ K_{sp}$	
Maximum silica concentration	≤ 120 mg/l	

IV. RESULTS AND DISCUSSION

In this chapter we discuss and explain the results obtained from the different work tasks performed to develop an environmentally benign inland desalination process, maximizing the desalination system productivity or recovery and minimizing the brine stream, in order to approach inland desalination with Zero Liquid Discharge ZLD.

Groundwater is the main water resource in arid areas worldwide due to the absence of surface water sources such as rivers and lakes. In the Middle East region, or sometimes referred to as MENA there are 22 countries where groundwater resources and desalinated water are the most common water resources, with groundwater used mainly for agriculture in general and domestic purposes in rural communities.

The GCC countries, in particular, are one of the extremely arid areas with harsh climatic conditions and very limited renewable water resources. The average annual rainfall ranges from 70 to 130 mm, with average annual evaporation rate, ranges from 2,500 to 4,500 mm (Abulrazzak, 1995; Al-Rashed & Sherif, 2000).

4.1 Preliminary Process Analysis of Major Groundwater Quality Parameters.

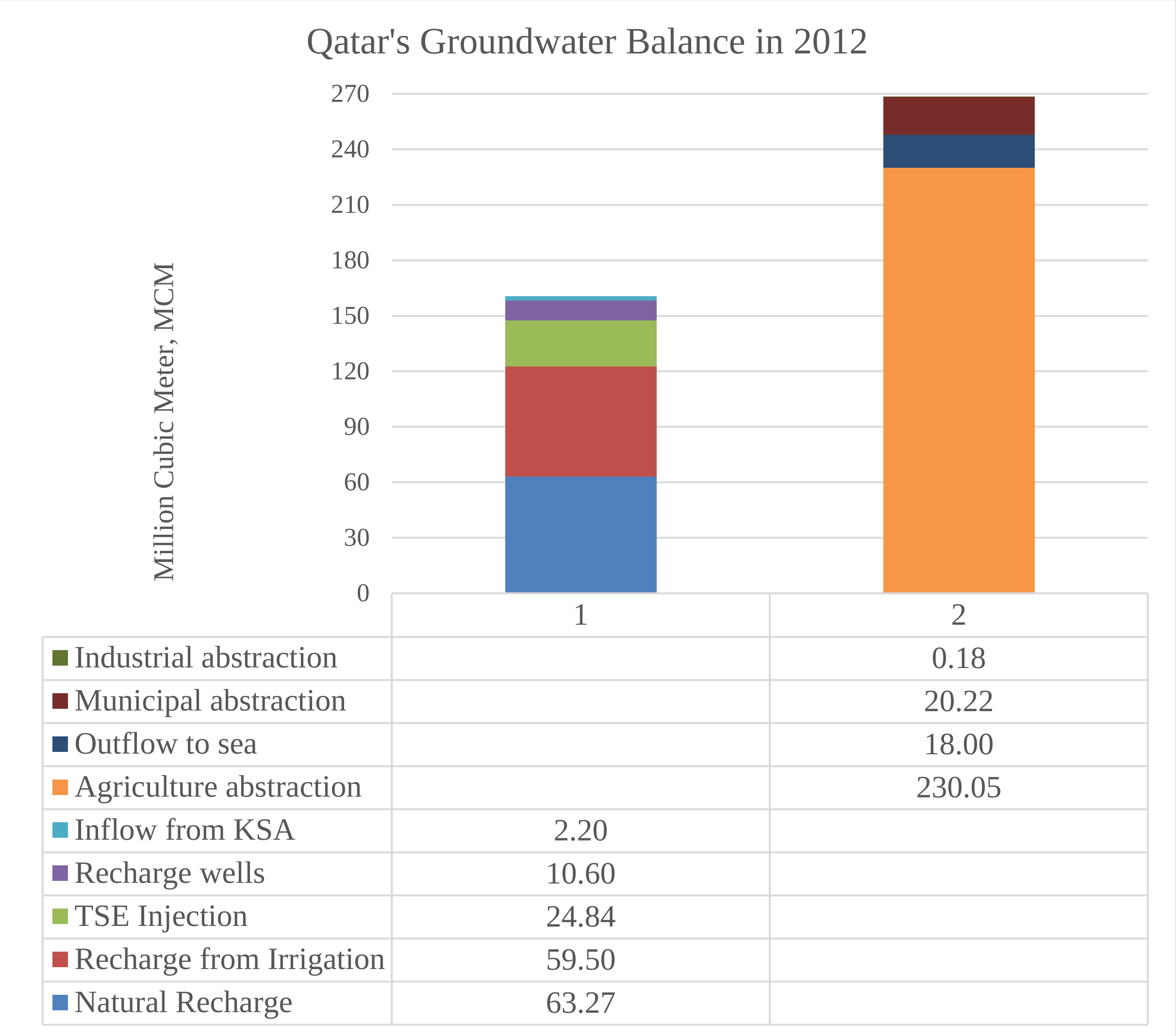
In this section, a quantitative and qualitative assessment of groundwater resources in the State of Qatar is the target of a specific case-study area is performed, in order to evaluate and determine the drivers behind the wide utilization of brackish groundwater desalination.

4.1.1 Quantitative Assessment of Groundwater Resources.

Quantitative assessment of groundwater resources is mainly concerned with groundwater balance. The amount of water stored in groundwater aquifer is variable and varies from time to another depending on relative rates of recharge i.e. increase of amount, which can be done naturally by rains, or artificially through artificial aquifer recharge with rain runoff or treated sewage effluent, TSE, or surplus water.

Figure 1 shows the most recent average annual groundwater balance (long-term annual average for natural and artificial water balance items in 2012). The long-term natural renewable water resources are about 65.5 million m^3/year or MCM. These natural recharges represent 40% of the annual additions to groundwater stocks. 60% of the annual additions to the groundwater stocks come from artificial recharges (recharge wells), injection of TSE, and irrigation returns, with total recharge, amounts to 160.4 MCM.

Agriculture accounts for most of the groundwater abstractions with 230 MCM (92% of all groundwater abstractions). Other abstractions from groundwater are meant for domestic / municipal uses (about 20.2 MCM), industrial uses (0.2 MCM), with total abstractions amounts to 268.5 MCM. The result is a deficit in groundwater balance of about 108.1 MCM in 2012.



	1	2
🟩 Industrial abstraction		0.18
🟥 Municipal abstraction		20.22
🟦 Outflow to sea		18.00
🟧 Agriculture abstraction		230.05
🟦 Inflow from KSA	2.20	
🟪 Recharge wells	10.60	
🟩 TSE Injection	24.84	
🟥 Recharge from Irrigation	59.50	
🟦 Natural Recharge	63.27	

Figure 4.1 Long-term annual average of groundwater balance in 2012 (*Environment Statistics Report, State of Qatar*, 2013).

The groundwater balance is a quantitative summing up of all inputs and outputs to and from the groundwater system. Input in the form of recharge by rainfall is weighed against outputs withdrawal and other losses. The water balance for groundwater resources in the State of Qatar has been carried out since 1971/1972 (and considered as the base year for the groundwater balance). Table 4.1, shows that groundwater abstraction is often greater than recharge, by a factor that ranges, at present, from four to five, except for a few years. Consequently, the mounted up groundwater deficit was estimated to be more than 2,180 MCM by the end of the year 2003/2004 and up to 3,210 MCM by 2011.

Table 4.1 Groundwater balance from 1971/1972 to 2011 (MCM) (Ministry of Environment MoE, 2013).

Year	**Groundwater Recharge from rain**	**Gross Consumption**	**Annual balance**	**Accumulated balance**
1971/1972	30.4	42.6	-19.6	-19.8
1975/1976	77.4	56.5	17.8	-87.1
1979/1980	40.7	68.5	-30.2	-206.2
1990/1991	22.5	145.0	-104.3	-688.4
1995/1996	161.9	237.0	-34.6	-1002.3
2000/2001	53.1	236.9	-143.2	-1710.2
2003/2004	30.5	220.8	-153.7	-2181.7
2005	60.1	248.0	-138.7	-2459.1
2010	21.1	248.2	-140.8	-3114.4
2011	65.6	249.5	-95.1	-3209.5

Table 4.2 shows the detailed groundwater balance over the years from 1990 to 2011. The table shows that annual aquifer recharge varies greatly from one year to another, from a minimum of 58.7 MCM in 1991 to a maximum of 220.46 MCM in 1996. Although rainfall is usually considered the major source of aquifer recharge, this source is found to be very variable and erratic over the years ranging from 20.6 in 2002 to 161.9 in 1996. In 2008 aquifer recharge with treated sewage effluent TSE and rain runoff water started with about 6.77 MCM reaching a value of 26.21 MCM in 2011 for TSE. The return from agriculture to the aquifer was assumed to be approximately at 25% of water consumed for agriculture irrigation. In addition, a fixed value of 2.2 MCM was considered for the Inflow to the aquifer across borders.

Currently, annual groundwater abstraction is fixed at about 250 MCM since 2005, with no intention to increase it in order to conserve groundwater resources. Table 4.2 shows clearly that the annual groundwater balance is always negative due to the higher abstraction rate compared to recharge rate from both natural i.e. rainfall, and artificial i.e. treated water injection. In addition, a fixed rate of 18 MCM of water distribution network leak loss is estimated annually.

Table 4.2 Detailed groundwater balance from 1990 – 2011(Ministry of Environment MoE, 2013).

Year	**Aquifer Recharge**			**Return to Aquifer**		**Total Aquifer Recharge**	**Total Consumption**	**Leak Loss**	**Annual Balance**	**Accumulated balance**
	Rainfall	**TSE**	**Rainfall wells**	**Wells**	**TSE**					
1990	**90.5**	**-**	**-**	**35.0**	**-**	**125.5**	**140.0**	**18.0**	**-30.3**	**-584.0**
1991	22.5	-	-	36.3	-	58.7	145.0	18.0	-102.1	-686.0
1992	46.0	-	-	40.0	-	86.0	158.0	18.0	-89.8	-776.0
1993	118.6	-	-	43.0	-	161.6	172.2	18.0	-26.3	-802.0
1994	26.8	-	-	46.4	-	73.2	187.8	18.0	-130.4	-933.0
1995	**160.0**	**-**	**-**	**55.2**	**-**	**215.2**	**223.3**	**18.0**	**-24.0**	**-957.0**
1996	161.9	-	-	58.6	-	220.5	237.0	18.0	-32.4	-989.0
1997	84.8	-	-	61.2	-	145.9	246.9	18.0	-116.8	-1106.0
1998	89.0	-	-	58.9	-	147.9	298.9	18.0	-161.8	-1268.0
1999	54.8	-	-	60.1	-	114.8	307.4	18.0	-208.4	-1476.0
2000	**14.5**	**-**	**-**	**61.8**	**-**	**76.3**	**304.4**	**18.0**	**-243.9**	**-1720.0**
2001	53.1	-	-	58.7	-	111.7	236.9	18.0	-141.0	-1861.0
2002	20.6	-	-	57.5	-	78.0	232.2	18.0	-170.0	-2031.0
2003	38.2	-	-	53.9	-	92.1	218.0	18.0	-141.7	-2173.0
2004	30.5	-	-	54.6	3.7	88.8	220.8	18.0	-147.8	-2320.0
2005	**60.1**	**-**	**-**	**56.5**	**8.5**	**125.2**	**248.0**	**18.0**	**-138.7**	**-2459.0**
2006	111.0	-	-	56.3	8.2	175.4	247.0	18.0	-87.4	-2547.0
2007	30.3	-	-	56.3	7.3	93.8	247.0	18.0	-169.0	-2716.0
2008	26.8	6.8	10.6	56.5	5.5	106.2	248.6	18.0	-158.2	-2874.0
2009	65.5	24.5	10.6	57.0	5.3	162.8	246.9	18.0	-99.9	-2974.0
2010	**21.1**	**26.2**	**10.6**	**57.2**	**8.1**	**123.2**	**248.2**	**18.0**	**-140.8**	**-3114.0**
2011	65.6	26.2	10.6	57.4	10.5	170.2	249.5	18.0	-95.1	-3210.0

One of the key concerns of water management in the State of Qatar is the ongoing depletion of its groundwater aquifers due to excessive abstraction and pollution. The Qatar National Development Strategy 2011-2016 (*Environment Statistics Report, State of Qatar*, 2013) addresses the need to monitor and conserve the quality and quantity of freshwater aquifers. The groundwater depletion can be monitored by changes in groundwater levels and changes of water quality.

4.1.2 Qualitative Assessment of Groundwater Resources.

Qualitative assessment of groundwater resources is mainly concerned with the salinity of such water as an overall measure of the quality. It goes into more details about the specific quality parameters such as the concentrations of major cations and anions. The importance of such assessment is to assess the suitability of water for certain purposes, which are mainly drinking and irrigation, and sometimes for industrial applications, mainly in food processing.

The groundwater resources are usually considered high-quality water resources, however in arid and semi-arid zones, such quality is deteriorating over time. This is mainly due to overexploitation of groundwater, which can lead to intrusion of seawater and saline deep groundwater into freshwater aquifers and thus increasing the salinity and concentration of dissolved substances (Zubari, Madany, Al-Junaid, & Al-Manaii, 1994). High concentrations of salinity and dissolved substances can make the water unusable for drinking and irrigation purposes.

The area of freshwater lens in the Northern Basin in Qatar has significantly declined, as in 1971 it underlay approximately 15% of the country, while in 2009 it underlay 2% only. The freshwater lens is currently is about 11% of its size in 1971. Figure 4. 2 shows the change in the freshwater lens between 1971 and 2009 (Amer et al., 2008), while figure 4.3 shows areas underlined by fresh and brackish groundwater in Northern Qatar, 1971-2008, which keep decreasing, indicating a continuous increase in groundwater salinity. The figure shows as well that groundwater suitable for irrigation purposes has dropped significantly from underlying an area of about 2370 km^2 in 1971 to only 1025 km^2 in 2008, constituting a 57% drop.

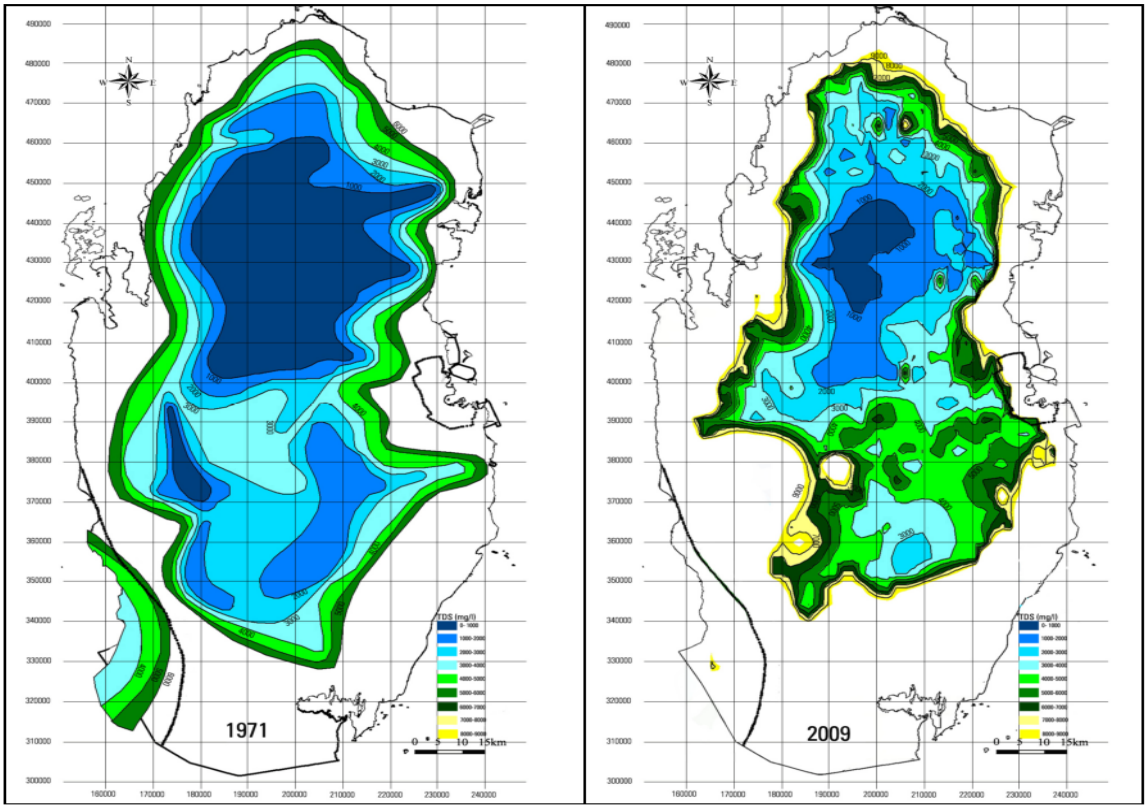


Figure 4.2. Change in the freshwater lens between 1971 and 2009 for the State of Qatar (Amer et al., 2008).

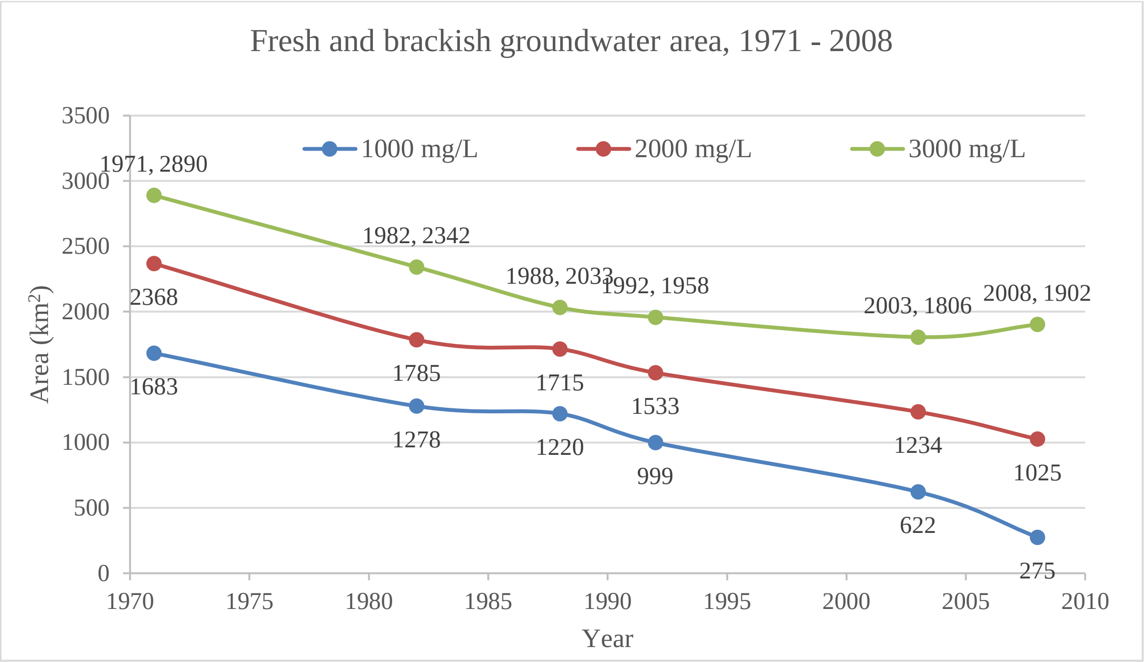


Figure 4.3. Areas underlined by fresh and brackish groundwater in Qatar, 1971-2008 (*Environment Statistics Report, State of Qatar*, 2013)

The detailed qualitative assessment is mainly concerned with the major groundwater quality parameters that are considered for typical water use. The main quality parameters to be considered for utilizing groundwater for drinking purposes follow the United States Environment Protection Agency USEPA guidelines (USEPA, 2016), whereas the Food and Agriculture Organization FAO guidelines (Ayers & Westcot, 1994; FAO, 2011) are adopted for agriculture or irrigation purposes and present in table 4.3.

Data from the groundwater quality program (Ministry of Environment MoE, 2013) collected in October 2012 was used for the qualitative assessment of groundwater quality. The program carries out two data collection cycles per year (one in October/November, and the other in April/May) from about 100 groundwater monitoring wells (out of total 344 monitoring wells). In this study, data related to 49 wells located in production farms spread over the country and utilized for both irrigation and drinking purposes are assessed for the major quality parameters; the detailed data are present in appendix B.

The bars shows the variation in the groundwater quality parameter over the years 2009-2013. These variation bars shows clearly the change of well salinity from one year to another over a short 5-years span of time indicating in most cases the increase in salinity in most of the wells, relative to the captured benchmark salinity survey of October 2012.

Table 4.3 Major drinking and irrigation water quality parameters.

Quality parameter	**Drinking water**	**Irrigation water**
Total Dissolved Solids, TDS **Or Electrical Conductivity, EC_w**	500 mg/l	2000 mg/l 3 dS/m
pH	6.5 – 8.5	6.0 – 8.5
Chloride, Cl^-	7 meq/L or 250 mg/l	30 meq/l or 1065 mg/l
Sulfate, SO_4^{-2}	5 meq/L or 250 mg/l	20 meq/l or 960 mg/l
Calcium, Ca^{+2}	-	20 meq/l or 400 mg/l
Magnesium, Mg^{+2}	-	5 meq/l or 60 mg/l
Sodium, Na^+	-	40 meq/l or 920 mg/l
Sodium Adsorption Ratio, SAR	-	15 meq/l

4.1.2.1 Assessment of Total Dissolved Solids TDS (or Salinity).

Figure 4.4 shows the salinity of groundwater wells considered in this study. It shows clearly that none of the wells have a groundwater quality suitable for drinking, i.e. salinity less than 500 mg/l, while only 5 wells have a salinity less than 2,000 mg/l representing only 10% of the total groundwater wells considered are of groundwater salinity suitable for irrigation purposes i.e. 2,000 mg/l, and mainly present in the southern groundwater basin. The figure also shows that about 8 out of 49 wells i.e. 16% have salinity more than 5,000 mg/l. The figure also indicates that the majority of groundwater wells have a salinity of about 2,000–5,000 mg/l representing 75% of total groundwater wells, which is to be considered in this study for assessing groundwater quality for desalination and chemical treatment of desalination brine.

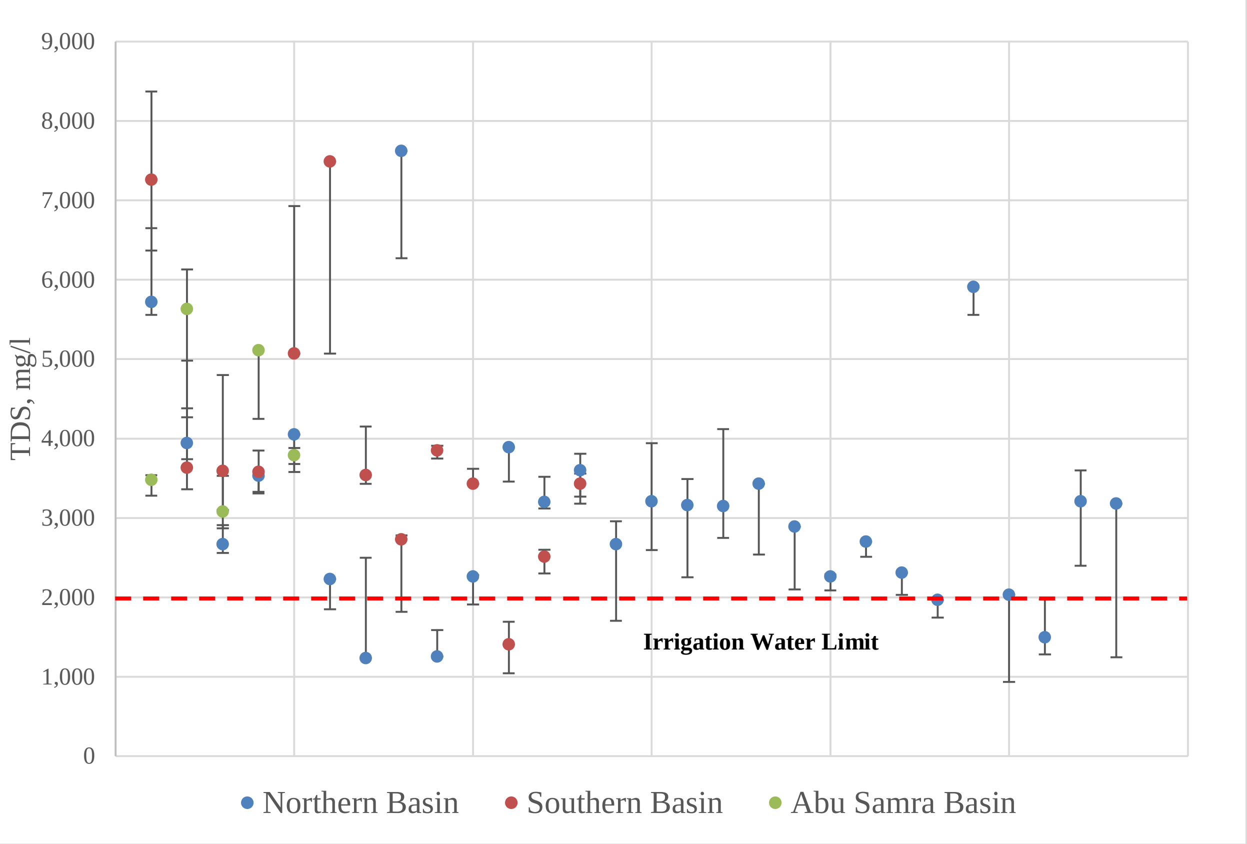


Figure 4.4 Salinity of groundwater wells in different groundwater aquifers.

4.1.2.2 Assessment of pH Value of Groundwater.

Figure 4.5 shows the pH value for groundwater wells studied. The figure shows clearly that almost all the groundwater pH values meeting the criteria for irrigation purpose i.e. 6 – 8.5, however for drinking water purposes about 25% of the wells do not meet the required criteria, i.e. 6.5 – 8, and seem to be more alkaline with values higher than 8.

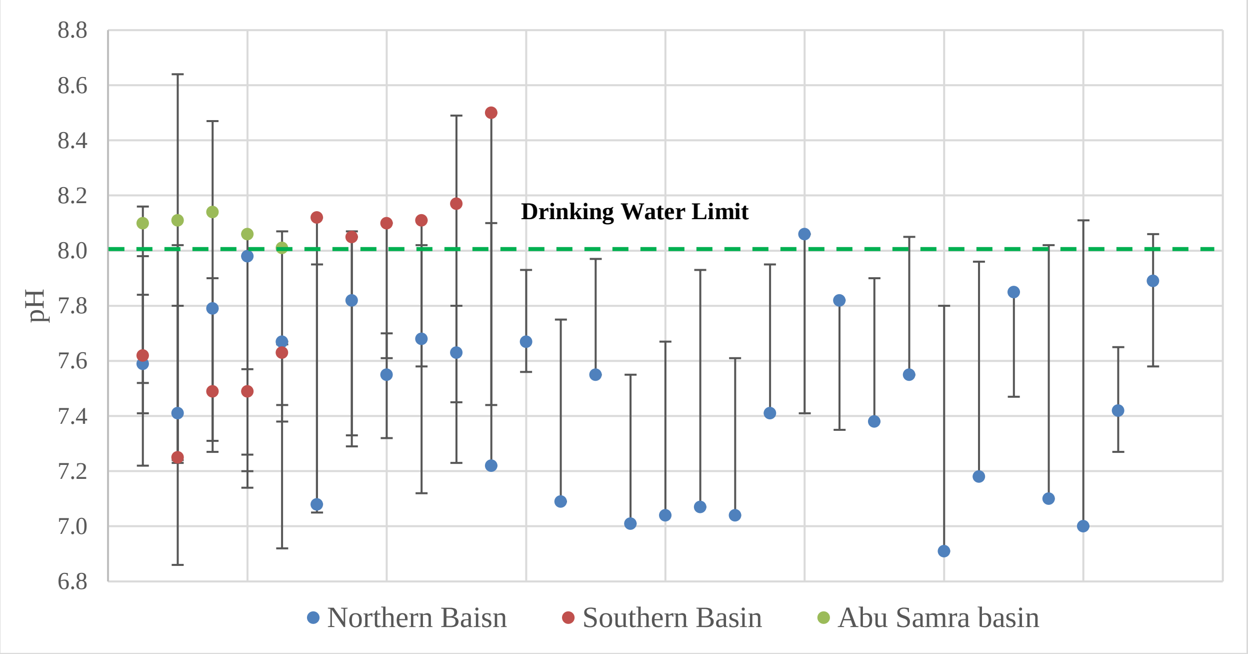


Figure 4.5 pH distribution of groundwater for different groundwater aquifers.

4.1.2.3 Assessment of Chloride and Sulfate Concentrations in Groundwater.

Figures 4.6 and 4.7 show the chloride and sulfate concentration for groundwater wells studied, respectively. The figure shows clearly that most of the wells, about 90%, has Cl^- and $SO4^{2-}$ concentrations higher than drinking water limit, and about 30% of wells have Cl^- concentrations higher than irrigation water limit, increasing to about 75% for $SO4^{--}$ concentration. The high concentration of $SO4^{2-}$ is mainly due to the contact with gypsum rock in the groundwater aquifer, which in turn increase the potential of scaling during groundwater desalination, and hence lower the maximum obtainable recovery. These results are well expected as the overall indicator for salt content in groundwater i.e. salinity, is already higher than the limits for both drinking and irrigation purposes for most cases.

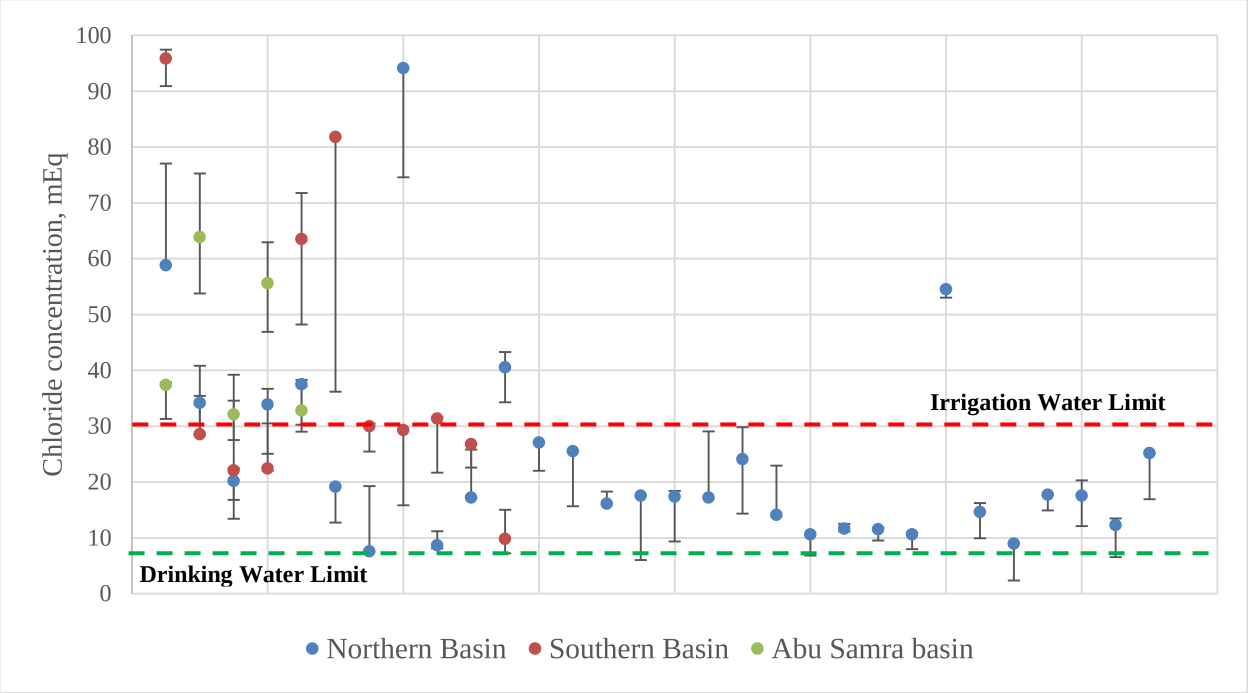


Figure 4.6 Chloride concentration distribution of groundwater for different groundwater aquifers.

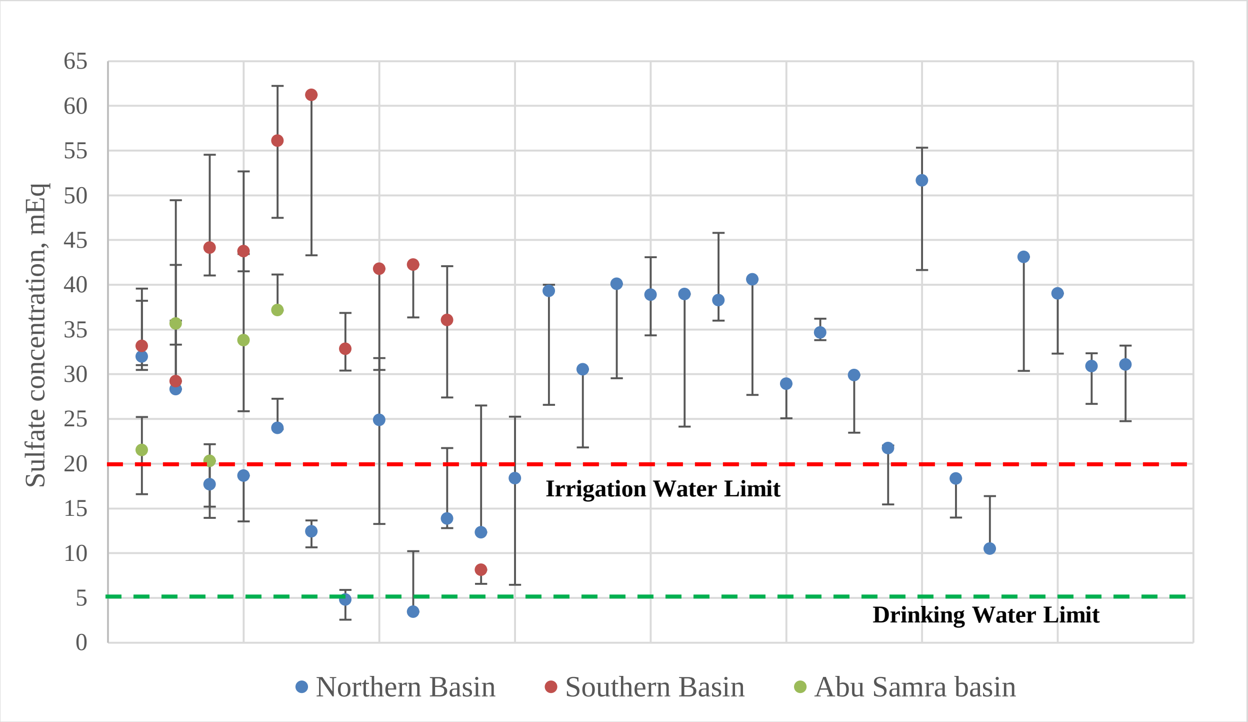


Figure 4.7 Sulfate concentration of groundwater for different groundwater aquifers.

4.1.2.4 Assessment of Calcium, Magnesium, and Sodium Concentrations in Groundwater.

Calcium, Magnesium, and Sodium concentration are of main importance for irrigation water, and regulated by FAO (Ayers & Westcot, 1994; FAO, 2011), however the concentrations of such components are not regulated for drinking water, as it is capped already by the salinity limit of 500 mg/l for drinking water. Figure 4.8 shows calcium, magnesium, and sodium concentrations in groundwater under this study. The figure shows that about 57% of the groundwater wells have Ca^{+2} concentration higher than the limit set by FAO for irrigation i.e. 20 mEq/l, however, this percentage increases to more than 90% for Mg^{+2} i.e. 5 mEq/l, and drops below 20% for Na^{+} which is 40 mEq/l. These three cations have an important effect on the suitability of water for irrigation purposes, so they are combined together in one parameter SAR, sodium adsorption ratio, which will be discussed later.

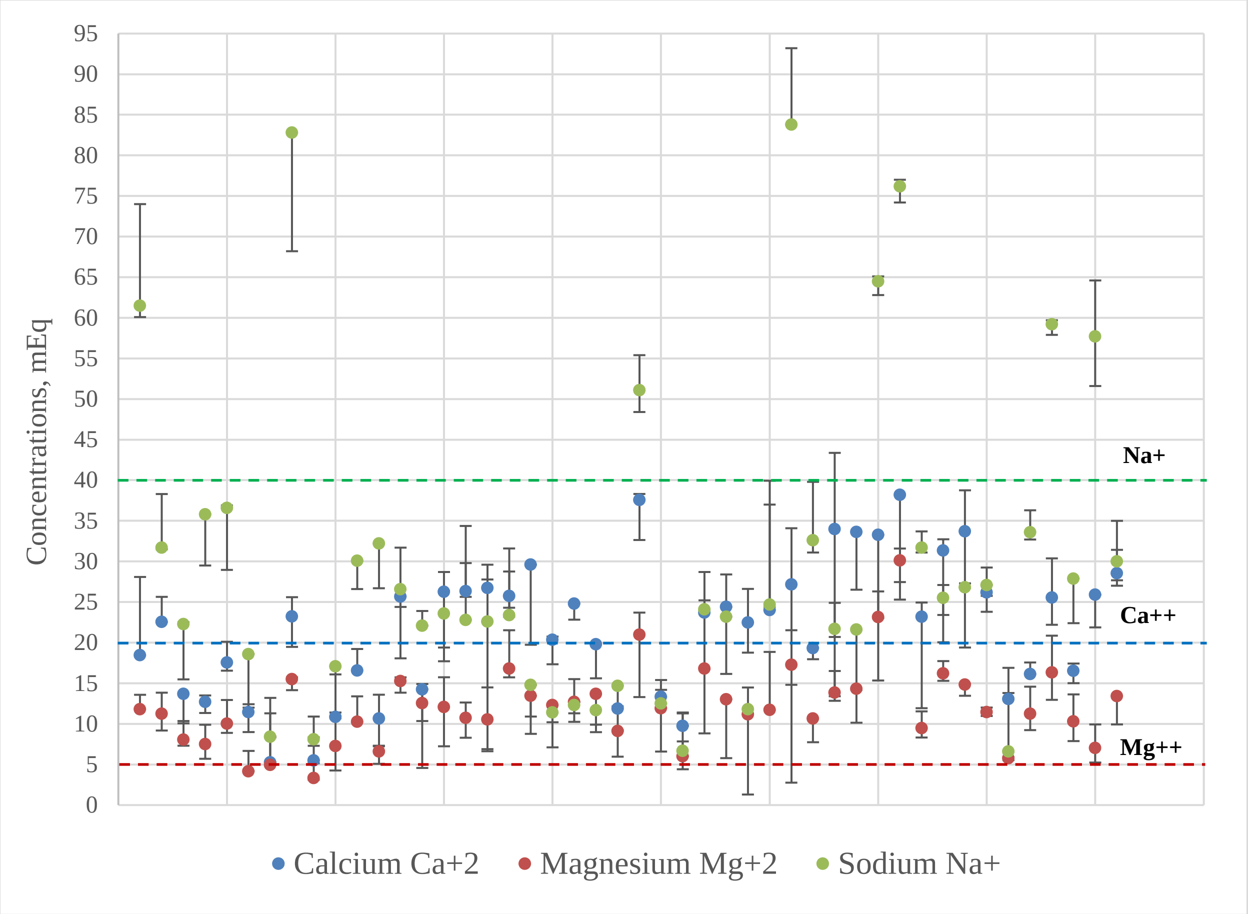


Figure 4.8 Concentration of calcium, magnesium, and sodium in groundwater.

4.1.2.5 Assessment of Sodium Adsorption Ratio SAR in groundwater.

Sodium Adsorption Ratio or SAR is one of the major parameters to assess the suitability of water for irrigation purposes (Ayers & Westcot, 1994; Bellows, 2004). High sodium concentration in irrigation water significantly affects the soil permeability causing some infiltration problems. Sodium in water is exchangeable and can replaces calcium and magnesium adsorbed on the soil causing dispersion of soil particles. Calcium and magnesium are the predominant cations adsorbed on the soil, making the soil tends to be easily cultivated with a permeable and granular structure. The dispersion due to sodium adsorption results in the breakdown of soil aggregates, in addition, the soil becomes harder and more compact when dry, hence reduces infiltration rates of water and air into the soil.

SAR values should be calculated and assessed along with the electrical conductivity data to assess the suitability of groundwater for irrigation purposes. The increase in salinity tends to mitigate the negative effect due to increase in SAR values; however, this should be still within the set electrical conductivity values for irrigation water, as indicated in table 4.4. SAR can be calculated for a given irrigation water quality, and more specifically, concentrations of Ca^{2+}, Mg^{2+}, and Na^{+} using equation 4-1, with concentrations in mEq/L (Ayers & Westcot, 1994; Lesch & Suarez, 2009).

$$SAR = Na/(\frac{Mg+Ca}{2})^{0.5} \qquad 4\text{-}1$$

Figure 4.9 shows the irrigation water classification diagram (Wilcox, 1955) which plots SAR and electrical conductivity EC for groundwater wells studied here. The figure is mainly divided into two axes with 4 regions for each; the horizontal access is for electrical conductivity divided into C1, C2, C3, and C4 regions (representing low, medium, high, and very high electrical conductivity values or salinity). While the vertical axis represents the SAR values divided into S1, S2, S3, and S4 (representing low, medium, high, and very high SAR values). The figure shows that most of the groundwater has a high to very high salinity combined with medium to very high SAR values, rendering the suitability of these waters for irrigation purposes.

Table 4.4 Salinity and SAR guidelines for irrigation water (Ayers & Westcot, 1994).

Potential Irrigation Problem			**Degree of Restriction on Use**		
			None	**Slight to Moderate**	**Severe**
Salinity EC_w, dS/m (TDS, mg/l)			< 0.7 (< 450)	0.7 – 3.0 (450 – 2000)	> 3.0 (> 2000)
Infiltration (Evaluate using EC_w and SAR together)					
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		> 2.9	2.9 – 1.3	< 1.3
	= 20 – 40		> 5.0	5.0 – 2.9	< 2.9

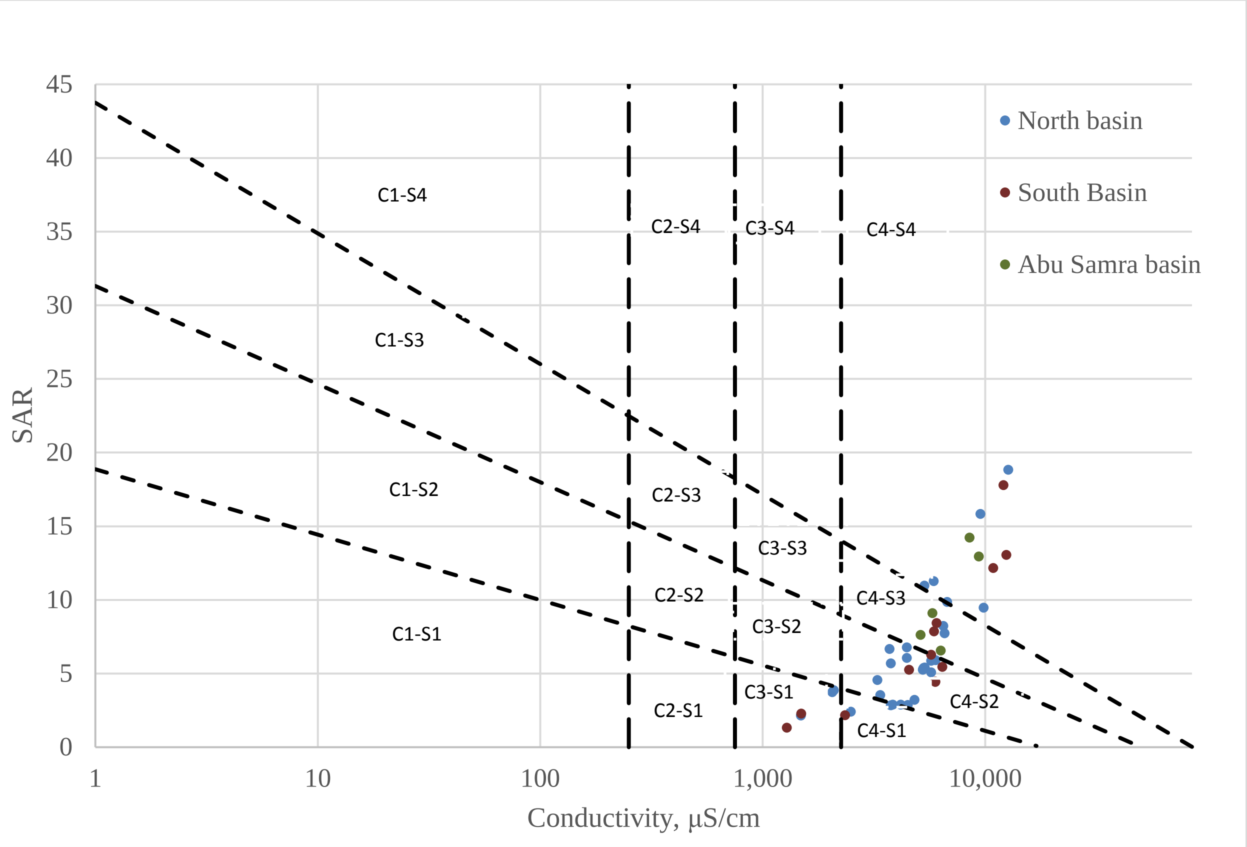


Figure 4.9 SAR and electrical conductivity distribution for different groundwater.

In conclusion, it was found that most of the groundwater wells under study have high salinity, making it unsuitable for drinking or irrigation purposes. The higher overall salinity results for most of the individual constituents concentrations such as sodium, calcium, chloride, and calcium were also high and did not meet the set criteria for drinking or irrigation waters as well. The groundwater was found to have high SAR values, making it harmful for irrigation purposes.

Groundwater was also found to have high variation in salinity and individual constituents. This is a direct effect of the erratic natural aquifer recharge over these years, with typical values of 26.8, 65.5, 21.1, and 65.6 MCM for 2008, 2009, 2010, and 2011 respectively, combined with constant abstraction rate of about 250 MCM over the same period, which in turn results in dramatic changes in groundwater overall salinity as well as individual constituent concentration.

4.2 Preliminary Process Analysis of Brackish Groundwater Desalination.

Due to the high salinity of groundwater, as concluded from section 4.1, showing that about 90% of groundwater has salinity higher than the limit for irrigation purposes, groundwater desalination has to be utilized to reduce such salinity to acceptable limit, preferably to 500 mg/l so that it meets the criteria for both drinking and irrigation purposes. In this section, the process of brackish groundwater desalination is to be assessed.

The main challenge encountered in brackish groundwater desalination, and hence limiting the recovery and performance of such system, is that although the relatively much lower salinity of groundwater, compared to seawater, groundwater usually becomes supersaturated with sparingly soluble salts upon concentration during RO desalination. The formed scales are then to block the RO membrane decreasing the system productivity and increasing the pressure drop, resulting in a complete system shutdown.

The conservative approach for long-term operation of RO is to utilize antiscalant, which helps reduce the deposition of supersaturated salts on membrane surface by inhibiting growth formation and crystallization of sparingly soluble salts and limit the recovery to a level that keeps the saturation levels of such salts below those recommended by antiscalant producers.

The supersaturation of key salts such as $CaCO_3$, $CaSO_4$, and SiO_2 in brackish groundwater as feed to RO and concentrate streams are to be quantified in order to identify the key components that limit recovery due to scale formation. In this section, we will discuss the results related to supersaturation of salts in waters with salinity higher than 1,000 mg/l, so it requires desalination to make it suitable for irrigation or drinking purposes.

4.2.1 Groundwater Saturation with Respect to Calcium Carbonate.

Calcium and carbonate/bicarbonate ions are dominant components in groundwater; this is mainly due to the contact of groundwater with carbonaceous rocks bearing calcium carbonate (limestone), which dissolve in water (Delleur, 2007). Carbonate system in water is highly pH dependent, and under normal pH of groundwater, bicarbonate will be the dominant anion.

Supersaturation of calcium carbonate $CaCO_3$ can be assessed through different indexes, however in desalination processes, calcium carbonate saturation is usually expressed as Langelier Saturation Index (LSI) as defined by equation 4-2 for waters with salinity less than 5,000 mg/l, or Stiff and Davis Saturation Index (SDSI) as defined by equation 4-3 for waters with salinity higher than 5,000 mg/l (Wilf, 2007). LSI and SDI calculations in this section have been performed using Advisor software package (Avista Technologies, 2013), and for both indices, positive values mean that water is supersaturated with respect to calcium carbonate (i.e. values higher than 0.2 - 0.5).

$$LSI = pH - pH_s \qquad 4\text{-}2$$

$$SDSI = pH - (9.3 + K - pCa - pAlk) \qquad 4\text{-}3$$

Where:

pH = actual pH value of water.

pH_s = pH that corresponds to saturation of ions forming calcium carbonate

K = constant obtained from monogram for the water system depending on the ionic strength.

$pCa = -\log[Ca^{2+}]$ $\qquad$ $pAlk = -\log[HCO_3^-]$

Figure 4.10 below shows that more than 75% of the groundwater is supersaturated with respect to calcium carbonate, and it becomes more supersaturated to limits exceeding those allowable upon use of proper antiscalant, which has a limit of about 2.5 to 3.0 for LSI (Avista Technology, 2016), which in turn limits the desalination system recovery. However, supersaturation with respect to calcium carbonate can be mitigated by the proper pretreatment of feedwater through acid addition, with acidification of the system, the equilibrium is shifted toward conversion of carbonate and bicarbonate to carbon dioxide gas, which is easily stripped out from the feedwater. However this, in turn, adds additional cost and can result in corrosion problems in the system (El-Manharawy & Hafez, 2000).

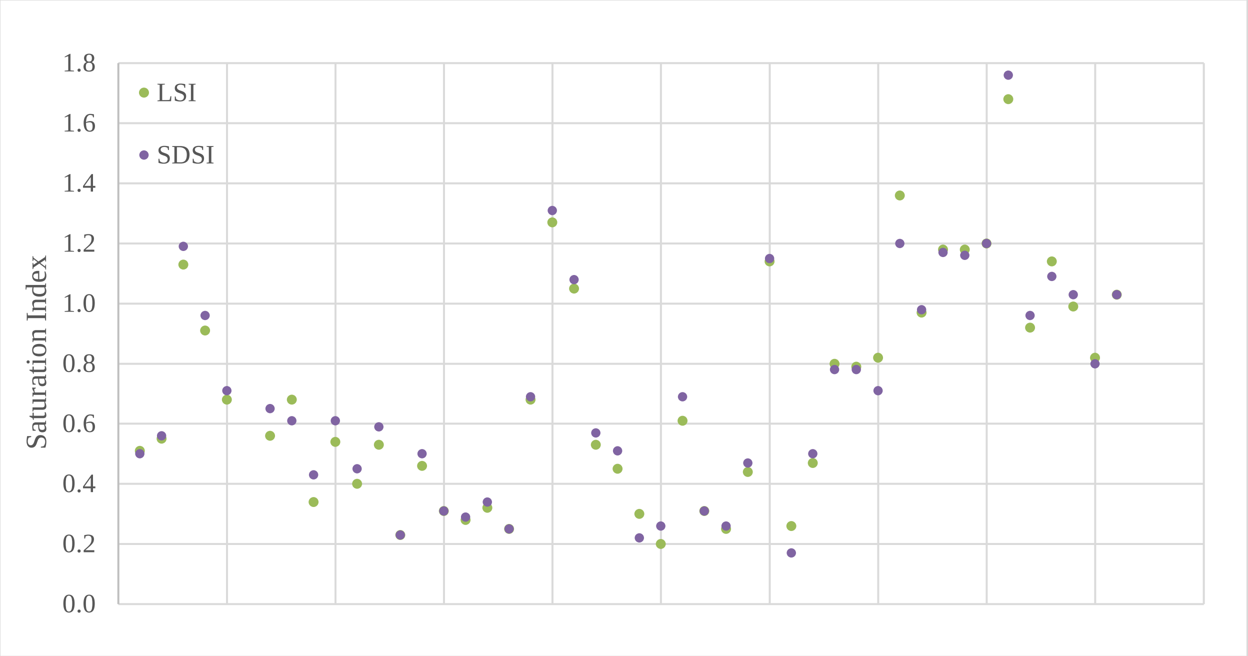


Figure 4.10 Saturation index for calcium carbonate in groundwater.

4.2.2 Groundwater Saturation with Respect to Calcium Sulfate (Gypsum).

Calcium and sulfate ions are dominant components in groundwater as well, which is mainly due to the contact of groundwater with gypsum rocks in the groundwater aquifer. In contrast to calcium carbonate, calcium sulfate is mainly pH independent, and precipitates as gypsum i.e. calcium sulfate dehydrate $CaSO_4.2H_2O$ at normal temperatures i.e. below 40 ^oC, which represents the transition point between gypsum and anhydrite $CaSO_4$ (Azimi et al., 2007).

Figure 4.11 below shows the saturation index of gypsum in groundwater under study. It was found that groundwater was already supersaturated with respect to gypsum in about 15% of the wells. However, upon assessing this groundwater for RO desalination, it was found that scaling due to calcium sulfate i.e. gypsum, is the main recovery limiting of the system reaching the set limit of 3.5 K_{sp} advised by antiscalant formulator, at the appropriate antiscalant dose.

This can be explained due to the fact that antiscalants added during feed pretreatment for desalination can mitigate the effect of scaling due to calcium carbonate to a higher level than mitigation of calcium sulfate or gypsum scaling. Moreover, calcium carbonate scaling can be significantly reduced by pH modification, which is not the case with gypsum.

Figure 4.12 below shows the maximum attainable recovery in brackish groundwater RO desalination systems, which was found to be in 90% of the cases limited by saturation due to supersaturation with respect to gypsum. As shown in the figure, the systems recovery ranges between 60 – 85%, leaving 15 – 40% of the water as brine needs to be properly managed.

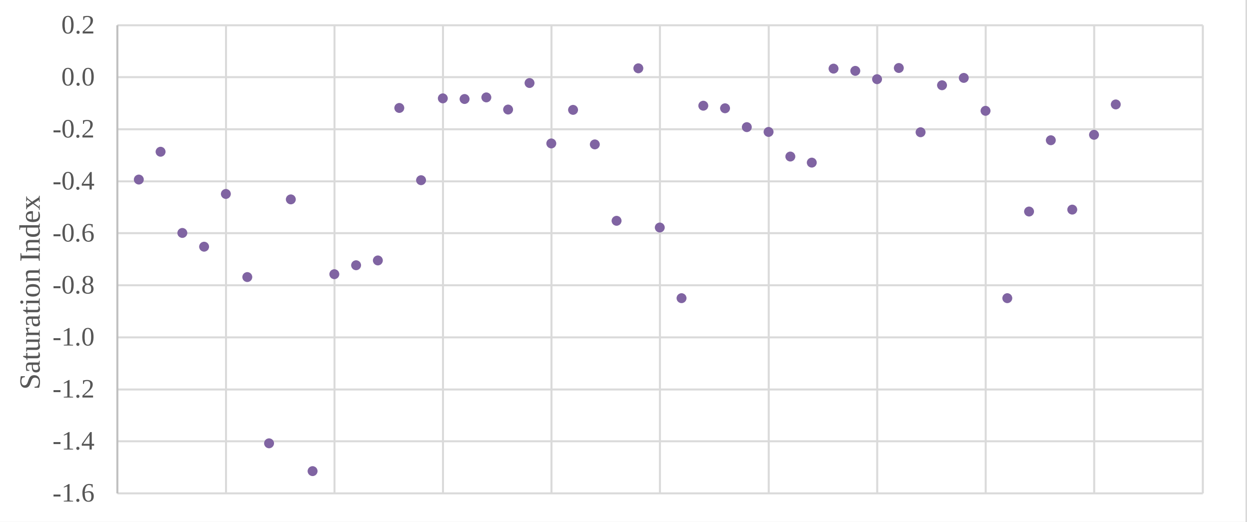


Figure 4.11 Saturation index for calcium sulfate or gypsum in groundwater.

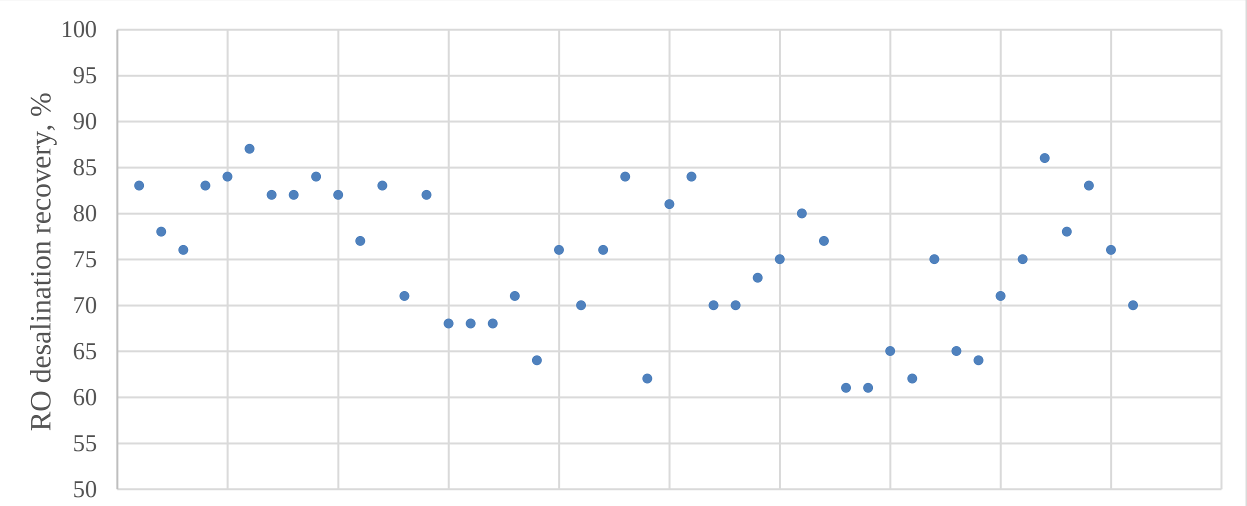


Figure 4.12 Maximum attainable recovery for brackish groundwater RO desalination.

4.2.3 Groundwater Saturation with Respect to Silica.

Amorphous silica present in groundwater is mainly due to contact with silicate rocks such as feldspar. Silica present in groundwater considered as a persistent problem in case deposition of silica occurs on the membrane surface, as it damages the membrane itself and it is very hard to clean during the chemical cleaning of the membrane system. As a result, it was set as desalination standard to limit the silica concentration in the brine of desalination systems to only 120 -150 mg/l (Avista Technology, 2016; Wilf, 2007).

Figure 4.13 shows that groundwater in this study is undersaturated with respect to silica with silica concentrations in the range of 14 – 33 mg/l. However, upon desalination, at the relative maximum attainable recovery for each groundwater, the brine will have high silica concentration, ranging from 50 to 150 mg/l, reaching close to the set limit for silica of 120 – 150 mg/l in about 25% of the groundwater.

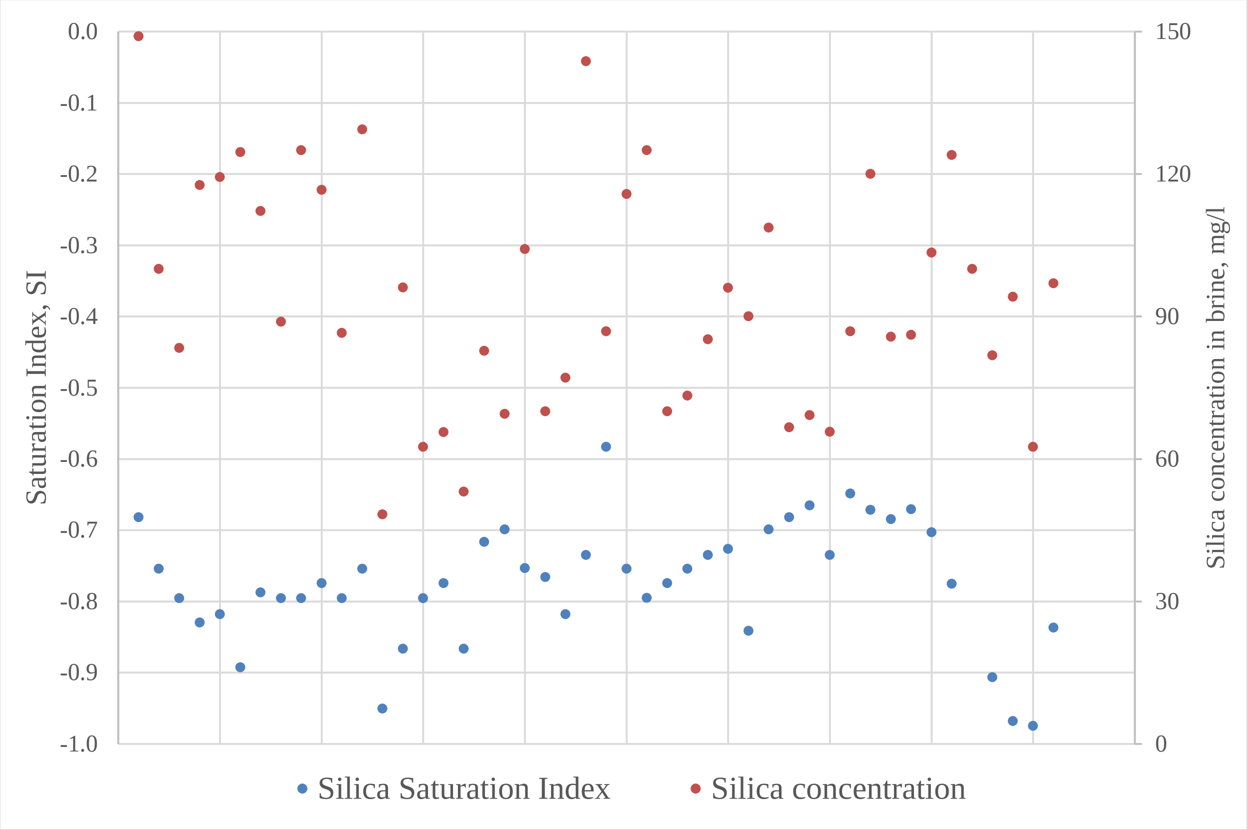


Figure 4.13 Saturation index of groundwater feed, and silica concentration in brine from brackish groundwater desalination.

In conclusion, supersaturation with respect to calcium sulfate or gypsum was found to be the main recovery limiting factor, followed by saturation with respect to silica. Although all groundwater was found to be saturated with respect to calcium carbonate, it was not the main recovery limiting factor as it can be well managed by lowering the feed pH. The results from brackish groundwater desalination assessment indicate that any chemical treatment process of brine should consider the removal of sulfate, calcium, and silica in order to have the brine suitable for further water extraction in RO desalination.

4.3. Kinetics and Equilibrium of Scale-forming Constituents Removal.

In conclusion from the assessment of groundwater desalination, it was found that calcium, carbonate, sulfate, and silica present in the brine stream making it supersaturated with calcium carbonate, gypsum, and silica are the main scale-forming constituents. Removal of such ions represents an ultimate objective to enable further desalination of brine, as it turns its chemistry to contain salts of sodium and potassium chlorides, which does not present any scaling propensity for RO desalination.

Lime softening is a well-known process for removal of hardness i.e. calcium and magnesium with calcium removed as calcium carbonate, so it represents a good process to reduce scaling due to calcium carbonate (Hoover, 1937; Suthaker, Smith, & Stanley, 1993). Several works indicated the removal of silica during lime softening due to coprecipitation as calcium/magnesium silicate, or due to adsorption mainly won magnesium hydroxide precipitated in lime softening (Al-Mutaz & Al-Anezi, 2004; Lindsay & Ryznar, 1939; Roalson, Kweon, Lawler, & Speitel, 2003).

Chemical treatment for removal of sulfate from industrial wastewaters has been studied extensively (Benatti et al., 2009; Christoe, 1976; Silva, Lima, & Leão, 2012; Tait et al., 2009). However, most of these removals were based on removal of high sulfate concentration waters through lime addition to supersaturate the waters with respect to gypsum, which is different from the current case as brine streams are already supersaturated with respect to sulfate, and it is required to de-supersaturate the solution further below the saturation limit for gypsum, in order to make the water suitable for further desalination.

In this part, a chemical treatment based on advanced lime-softening processes is studied to remove sulfate from brackish groundwater desalination brine, in addition to calcium, carbonate, and silica. The treatment is based on adding high lime doses along with aluminum source, at high pH values due to the high lime dose. Due to high concentrations of calcium, aluminum, sulfate, and silica more complex precipitates are expected to be formed. Due to the high ionic strength and richness of brine with different ions, high removal efficiency is expected for most of the scale-forming constituents as explained in section 3.4.2. The kinetics and equilibrium for removal of scale-forming constituents as explained in section 3.3 have been performed and results to be explained in this section

4.3.1 Kinetics and Equilibrium of Sulfate Removal:

A set of experiment was performed to study the kinetics of sulfate removal from sulfate-only solution, at two initial sulfate concentrations of 20 and 40 mM at two different shaking speeds of 350 and 275 rpm, according to protocol explained in 3.3.4, with results presented in figure 4.14.

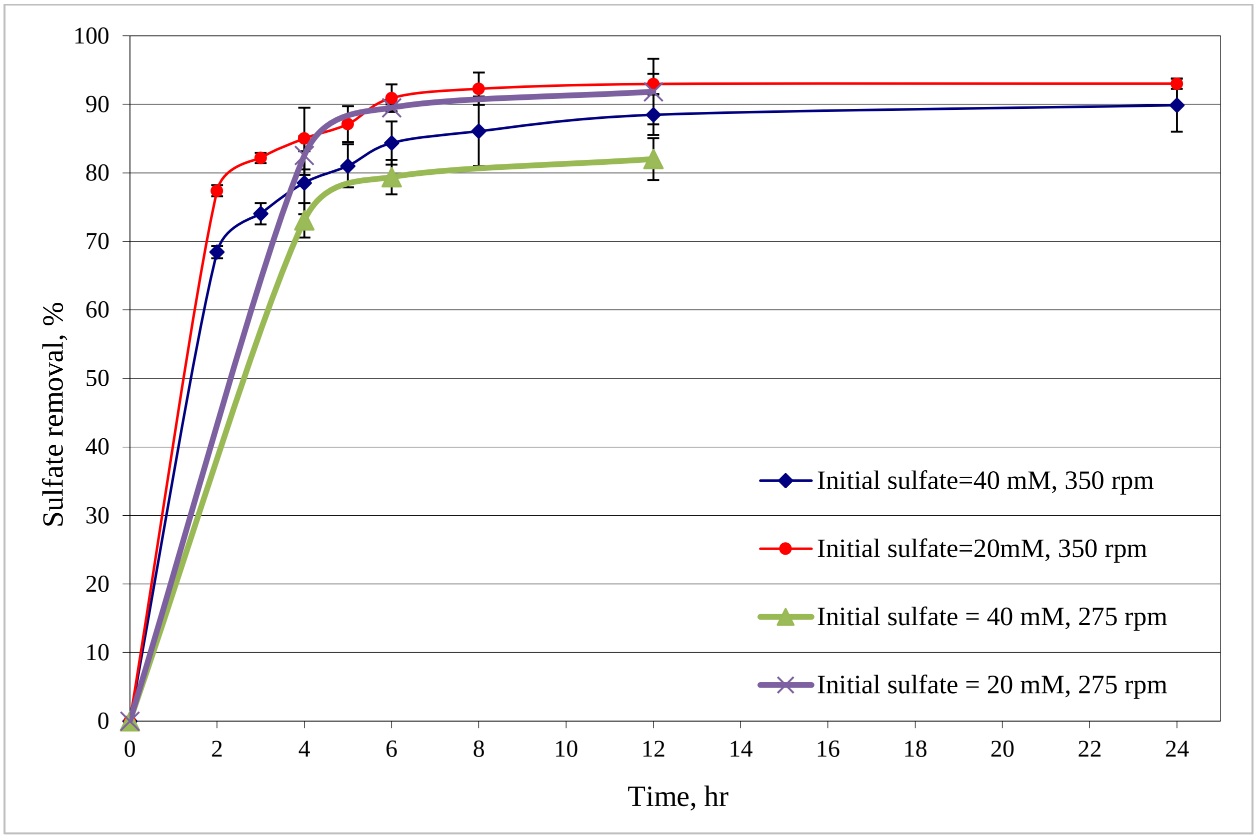


Figure 4.14 Kinetics of sulfate removal during advanced softening treatment.

Figure 4.16 above shows high removal efficiency of sulfate reaching about 70% and 80% within 2 hrs, and 85 and 90 after 6 hrs for initial sulfate concentration of 40 and 20 mM, respectively. The figure also shows that shaking speed had a little effect within 5% on the sulfate removal efficiency. The results obtained indicate that the kinetics of sulfate removal is fast enough to be applied for brine chemical treatment for removal of sulfate.

The results show that the removal kinetics for low initial concentration of 20 mM is faster than that of 40 mM. This is mainly due to the more time required to remove more sulfate moles from the 40 mM solution. Little effect was noticed for shaking speed indicating that well mixing was achieved at both speeds, with higher removal efficiency for the higher speed, due to the fact that lime and sodium aluminate reagents are added in solid form, hence require higher mixing to ensure dissolution of the reagents.

Another set of equilibrium experiments was conducted to evaluate the effects of lime and sodium aluminate doses on sulfate removal, for initial sulfate concentration of 40 mM. Figures 4.15 and 4.16 below show the results of the equilibrium experiments studying the effect of lime and sodium aluminate doses. It is well observed that the presence of 150 mM sodium chloride had no or little effect on the equilibrium removals of sulfate as both figures show very close removal values and similar removal behavior. In addition, both figures clearly indicate that neither addition of sodium aluminate nor lime alone resulted in any significant removal of sulfate.

The figures also show that the removal efficiency generally increases as the lime dose increases, however, for sodium aluminate dose there is an optimum dose, at which the highest removal of sulfate is achieved. It was found that the highest removal takes place at lime: sodium aluminate dose molar ratio of 4:1. Figure 4.17 shows the effect of lime to sulfate ratio, at fixed lime to sodium aluminate ration of 4:1 as concluded from previous experiments. It is shown that as lime to sulfate ratio increases, the removal of sulfate increases as well up to a molar ratio of 3:1.

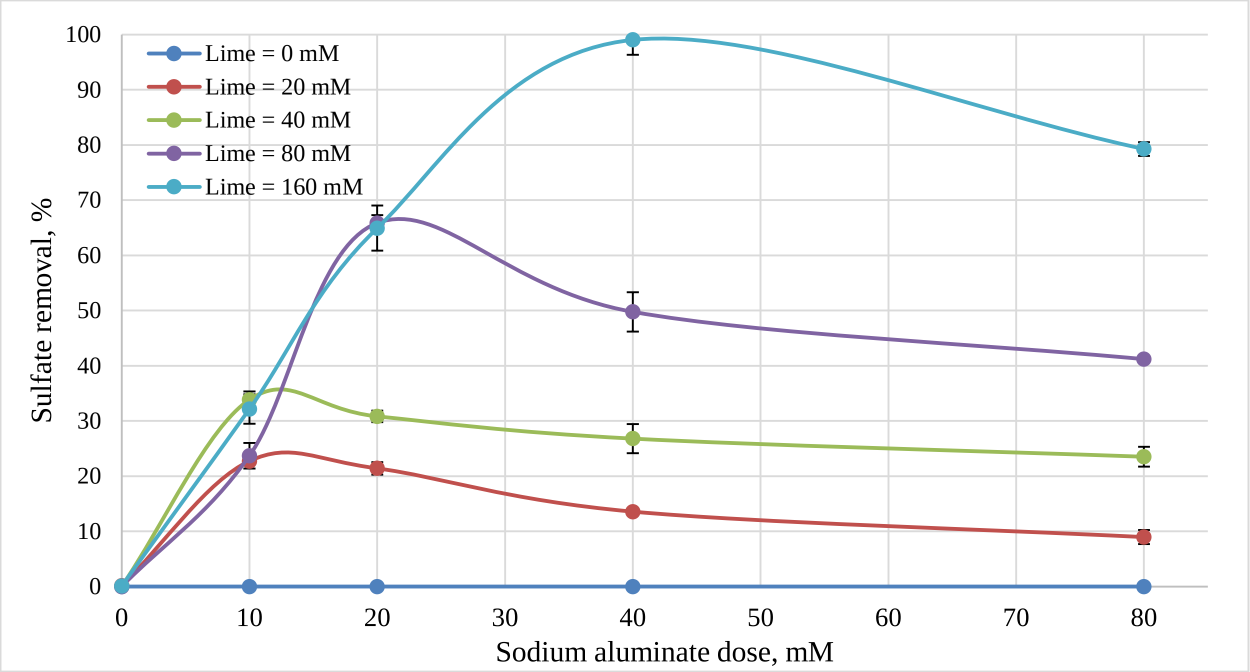


Figure 4.15 Effect of lime and sodium aluminate doses on equilibrium removal of sulfate for initial sulfate concentration of 40 mM.

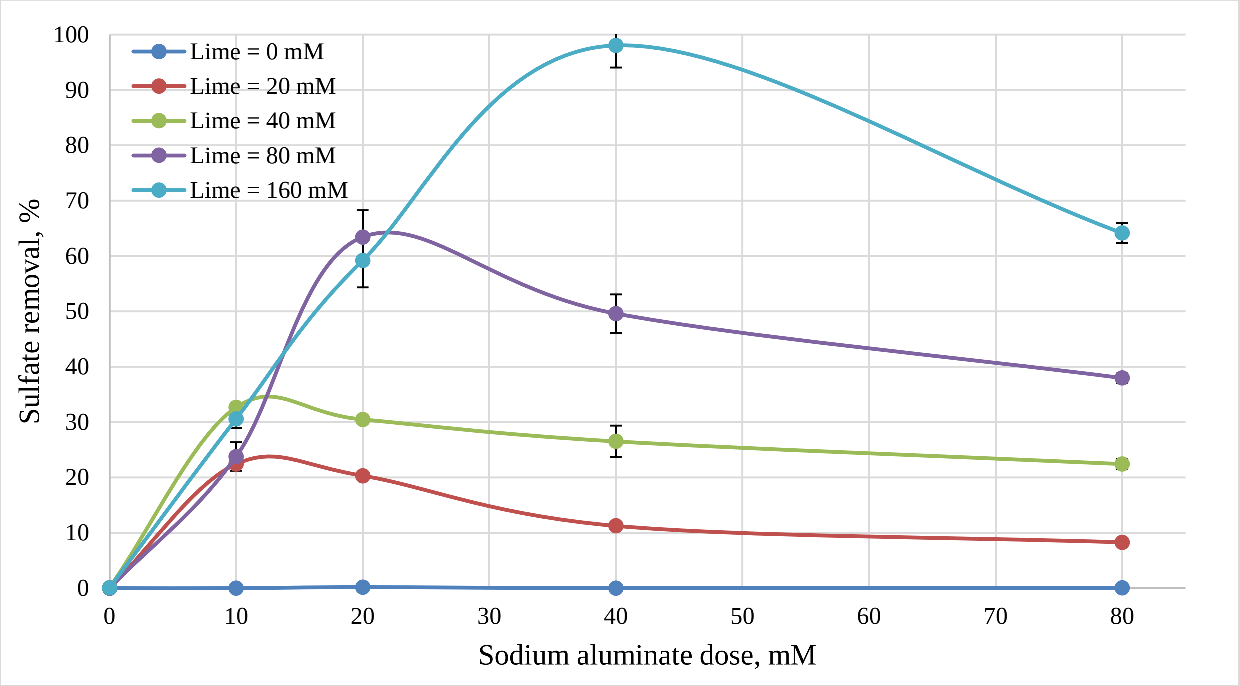


Figure 4.16 Effect of lime and sodium aluminate doses on equilibrium removal of sulfate during advanced softening treatment in the presence of 150 mM NaCl.

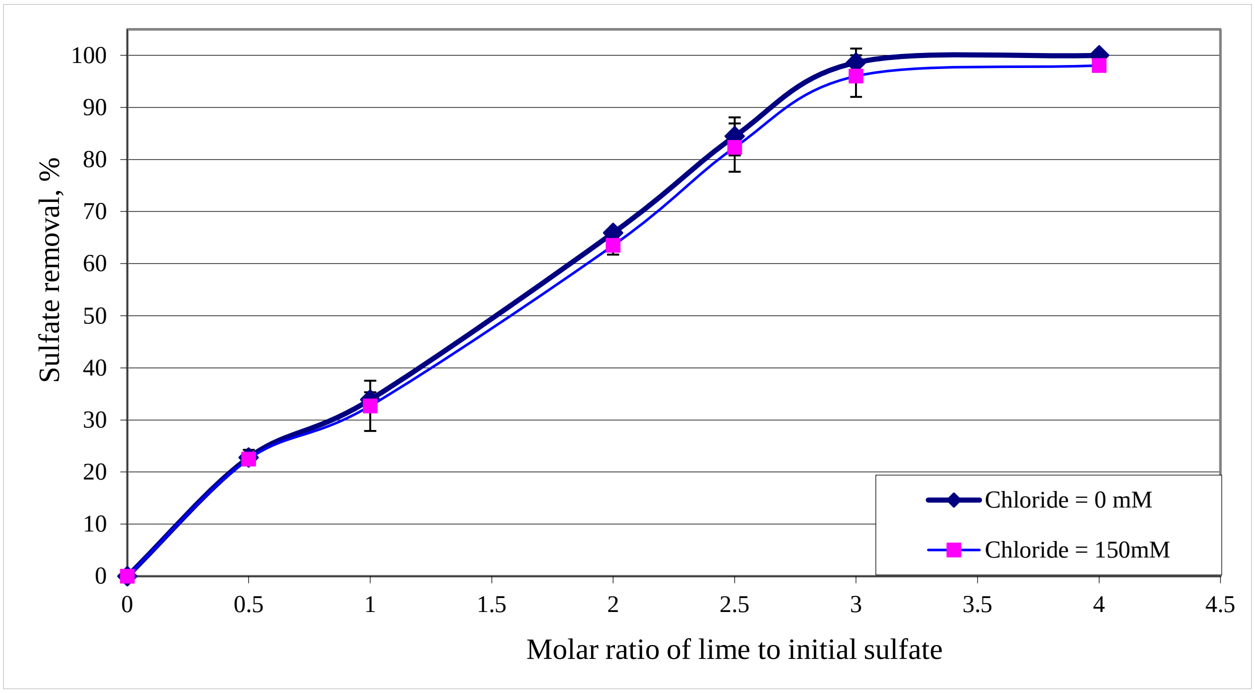


Figure 4.17 Effect of lime to sulfate ratio on equilibrium removal of sulfate at initial sulfate concentration of 40 mM at lime to sodium aluminate doses of 4:1.

In addition, a set of equilibrium experiments was conducted to study the effect of initial sulfate concentrations of 10, 20, 30, and 40 mM at lime to sodium aluminate ratio of 4:1, with lime to sulfate ratio of 3:1. Results show that the sulfate removal efficiency obtained at the different tested initial concentrations was high, obtaining more than 80% removal and that initial concentration has little effect on sulfate removal efficiency.

In conclusion, the proposed ultra-high lime with alumina UHLA process was found to be very effective for removal of sulfate at different experimental conditions. The removal was found to be fast reaching more than 80% within 2 hrs, with optimal removal at lime: sodium aluminate: initial sulfate molar ratio of 4:1:1. The addition of sodium aluminate as a source of aluminum was found to highly increase the removal efficiency at optimal dose molar ratio of 4:1 of lime to sodium aluminate. The high removal of sulfate, resulting in low residual concentration of sulfate far below 1,200 mg, as well as the increase of removal efficiency upon addition of sodium as sodium aluminate, highly suggest that more complex solids of calcium-aluminum-sulfate are formed mainly of mono sulfate and calcium sulfoaluminate (Batchelor, B.; McDevitt, M.; Chan, 1985; Christoe, 1976).

4.3.2 Kinetics and Equilibrium of Silica Removal:

A set of experiment was performed to study the kinetics of silica removal from a silica-only solution according to the procedure explained in section 3.3.5. Figure 4.18 below shows that the removal of silica was very high and fast, reaching more than 95% within 0.5 hr, which is very promising for the removal of silica from brine in advanced lime softening.

Effect of lime and sodium aluminate doses on silica removal was studied by performing another set of experiments. As shown in figure 4.19, the addition of lime alone was very effective in silica removal reaching about 70% for lime dose of 2.5 mM, and 93% at 5 mM, in contrast to addition of sodium aluminate alone, which had a little effect over the range from 0–7.5 mM; however, addition of sodium aluminate was found to improve the removal efficiency at all applied lime doses. Figure 4.20 shows that in the presence of NaCl, the removal efficiency decreased, although the same trend for the effect of lime and sodium aluminate doses was noticed. This, in turn, indicates a high interaction between chloride presence and silica removal which can be due to the formation of complex solids of the calcium-aluminum-chloride system such as Friedel's salt which is formed at such high pH conditions found in UHLA process (A. Abdel-Wahab & Batchelor, 2006).

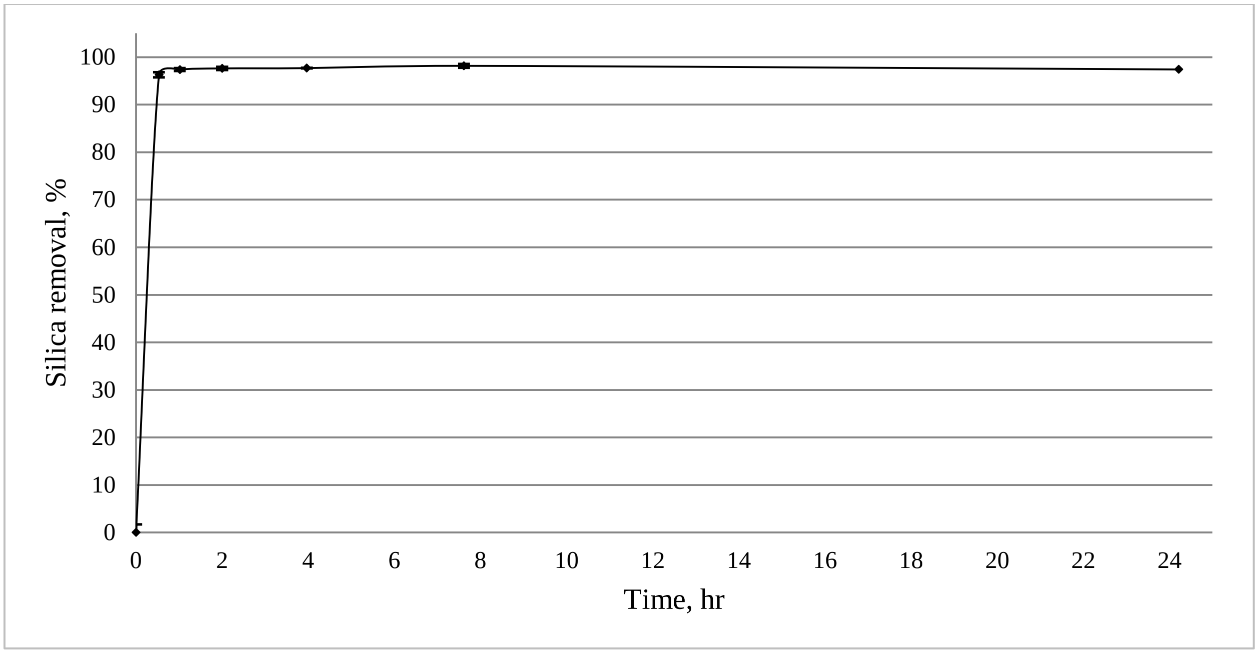


Figure 4.18 Kinetics of silica removal in advanced softening treatment.

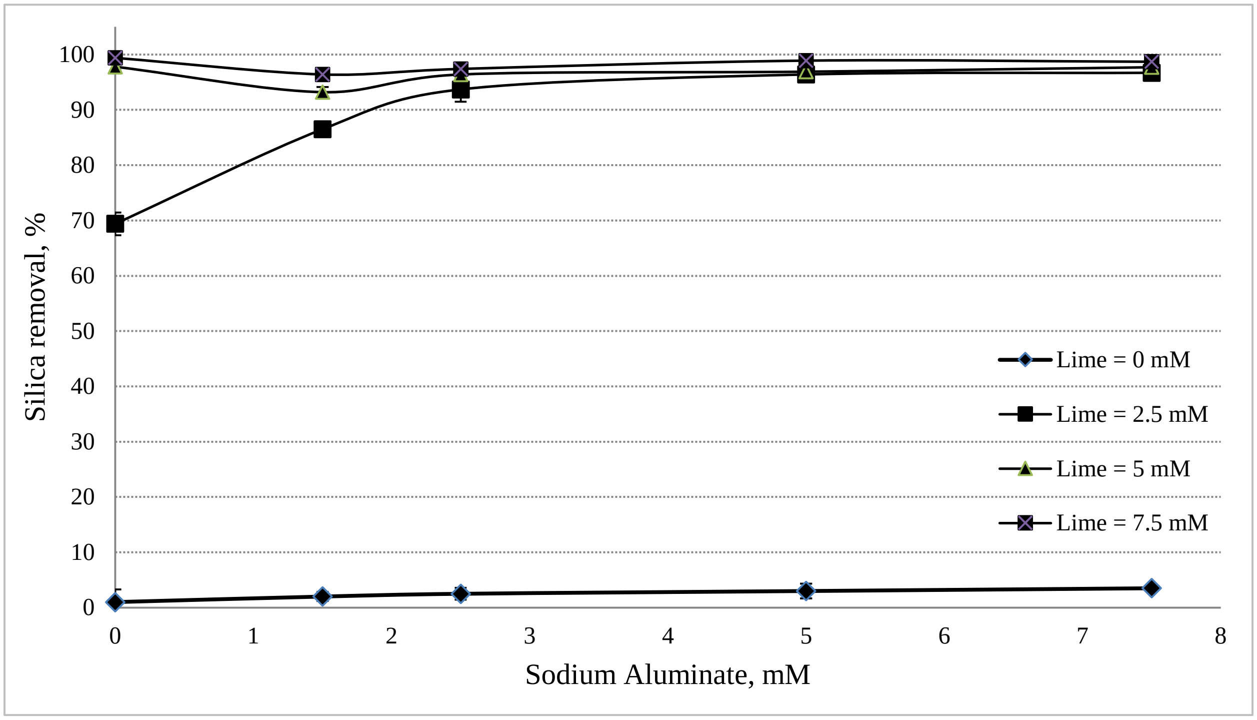


Figure 4.19 Effect of lime and sodium aluminate doses on equilibrium removal of silica in advanced softening treatment.

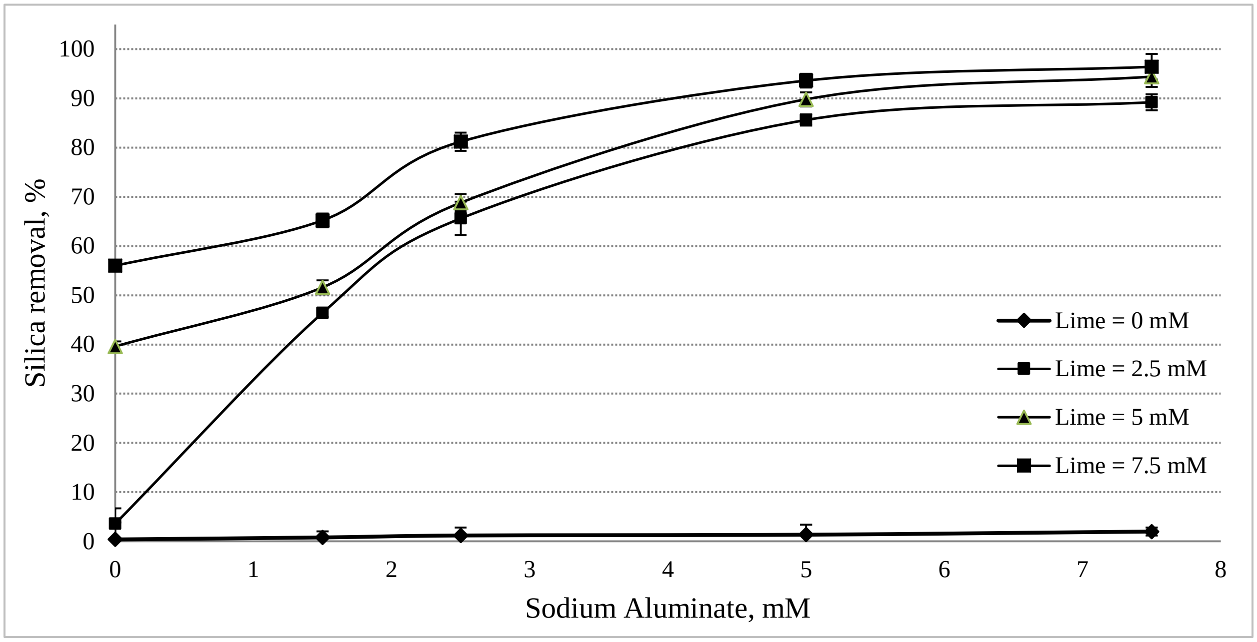


Figure 4.20 Effect of lime and sodium aluminate doses on equilibrium removal of silica in advanced softening treatment in the presence of 150 mM NaCl.

The effect of initial silica concentration on silica removal was investigated by conducting a set of experiments at initial silica concentrations of 1 - 5 mM, in which silica removal was more than 90% with little effect for presence NaCl on silica removal efficiency.

To study the effect of pH on silica removal as silica solubility is highly pH-dependent (Hamrouni & Dhahbi, 2001a), silica removal at a range of pH values of 10.5 - 13.01 was investigated. It was observed that when pH values are above 13, silica removal dropped significantly to less than 30% at pH 13.01, compared to 94% at pH of 11.8, with a similar trend observed in the presence of 150mM NaCl. This could be explained by the fact that above pH 12.45, lime would precipitate and no lime will be available in the medium to react with silica as a result, Most of the lime added into the reaction would precipitate immediately at higher pH values without being available for silica removal. In addition, silica solubility was found to be higher at high pH reaching about 890, and 1500 mg/l at pH values of 10 and 11, respectively compared to only 116 mg/l at pH 7 (Hamrouni & Dhahbi, 2001a; Koo et al., 2001).

The effect of temperature on silica removal was also investigated at temperatures of 30, 40 and 50 °C, where high silica removal of more than 95% was obtained over the range of temperature from ambient up to 50 °C, with little effect for the presence of sodium chloride. This can be attributed to the fact that solubility of calcium and magnesium silicates, which are the basic forms of silicate precipitates, have little dependence on temperature (Qing et al., 2007).

In conclusion, the proposed chemical treatment of ultra-high lime with alumina UHLA process was found to be highly efficient for removal of silica at different experimental conditions, with expect to high pH medium above 13. The addition of sodium aluminate was found to highly improve the removal of silica above that obtained by lime addition indicating the formation of more complex solids than that of calcium and magnesium silicate, potentially formed of the calcium-aluminum-silicate system such as calcium aluminosilicate (Ahmed Abdel-Wahab & Batchelor, 2006; Latour, Miranda, & Blanco, 2013).

4.3.3 Kinetics and Equilibrium of Combined Sulfate and Silica Removals:

A set of experiment was performed to study the kinetics of sulfate and silica removals from model brine solution in a fashion similar to that for sulfate, and silica removal explained previously. The model brine solution had the concentrations of different constituents as outlined in table 3.3, and according to experimental protocol explained in 3.3.6.

Figure 4.21 shows that high removals of sulfate and silica were obtained within the first 2hrs, in behavior very close to that obtained in previous kinetic experiments on individual sulfate and silica removals in 4.3.1 and 4.3.2. The pH of the solution was found to have the same trend suggesting the strong dependence of the removal of sulfate and silica on pH which is mainly due to lime addition.

A set of equilibrium experiments was conducted at room temperature for 2 hours, as concluded to be the equilibrium time from the kinetic experiments (by which more than 75% removal of sulfate was achieved), to evaluate the effects of lime doses which varied from 0–80 mM, and sodium aluminate doses of 0–40 mM.

Figure 4.22 shows the effect of lime and sodium aluminate doses on sulfate removals from the model brine solution. It is clearly seen that increase of both lime and sodium aluminate doses increase the removal of sulfate significantly, increase of sodium aluminate dose from 0 to 40 mM improved the sulfate removal at 10 mM lime dose from about 8% to 50%, and similar trend was noticed at 80 mM lime dose increasing the removal from 28% to 92%.

Figure 4.23 shows the effect of lime and sodium aluminate doses on silica removals from the model brine solution. It is clearly seen that addition of lime alone results in the very high removal of silica up to 75% at a lime dose of 10 mM. The increase of both lime and sodium aluminate doses was found to increase the removal of silica, with greater impact for lime dose increase over that of sodium aluminate.

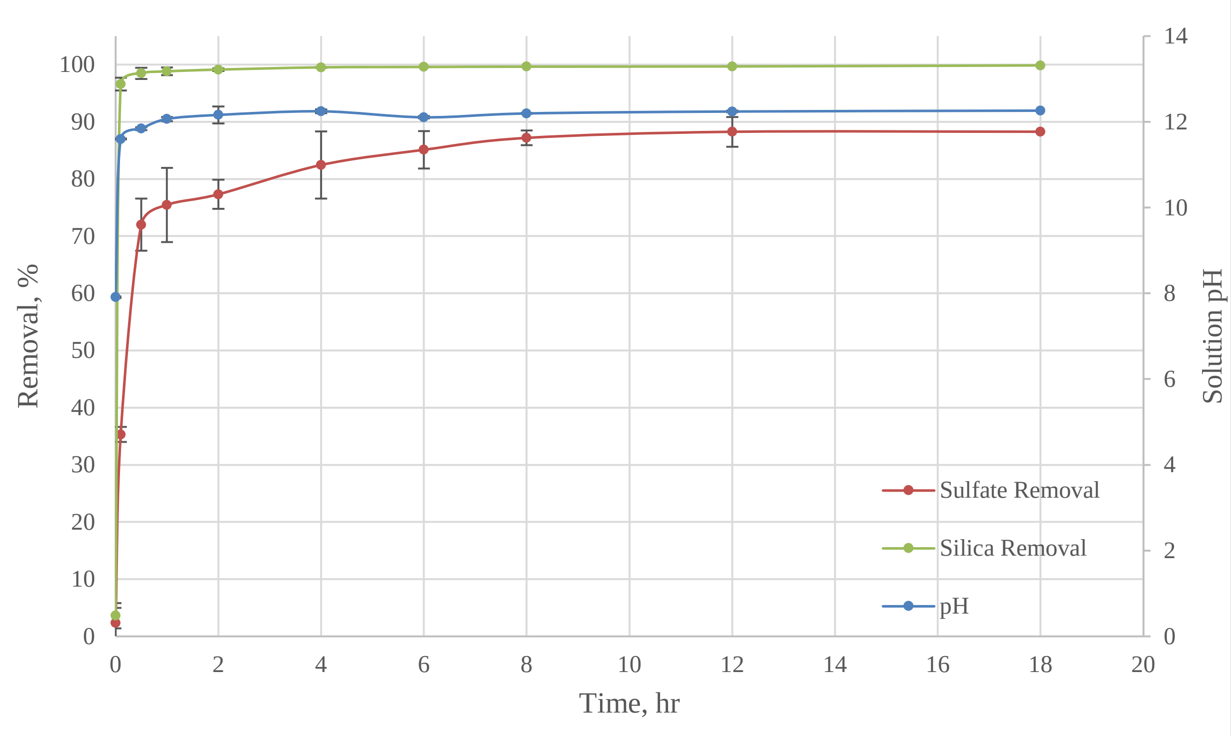


Figure 4.21 Kinetics of sulfate and silica removals from model brine in advanced softening treatment.

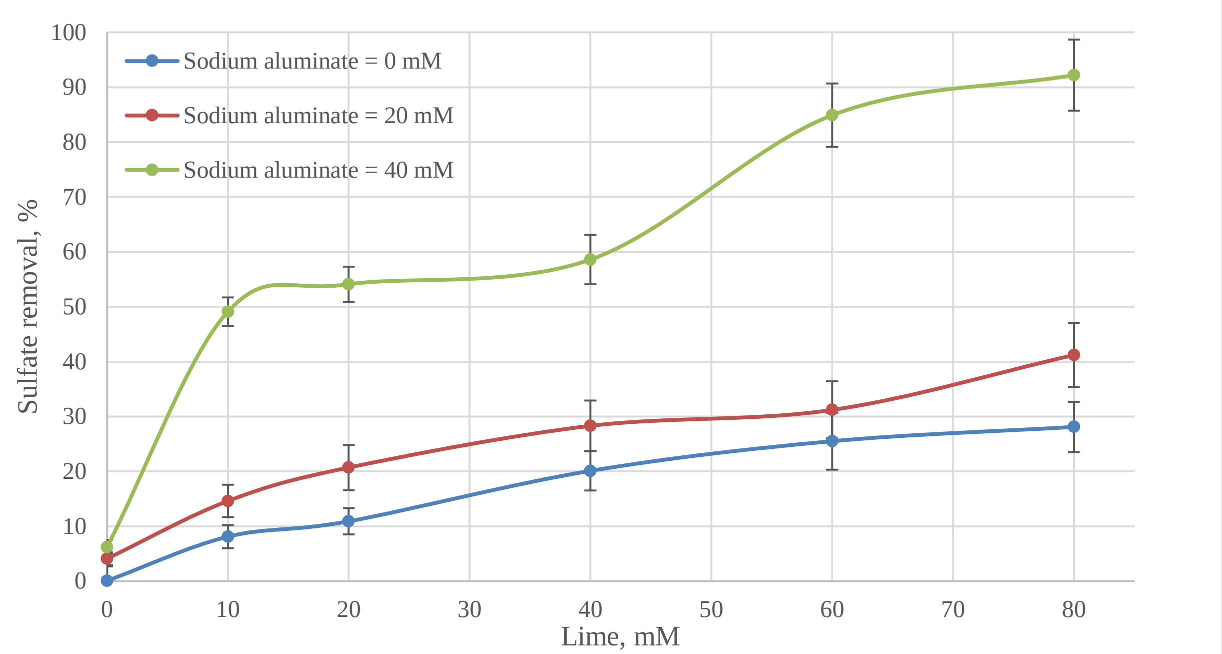


Figure 4.22 Effect of lime and sodium aluminate doses on the removal of sulfate from model brine in advanced softening treatment.

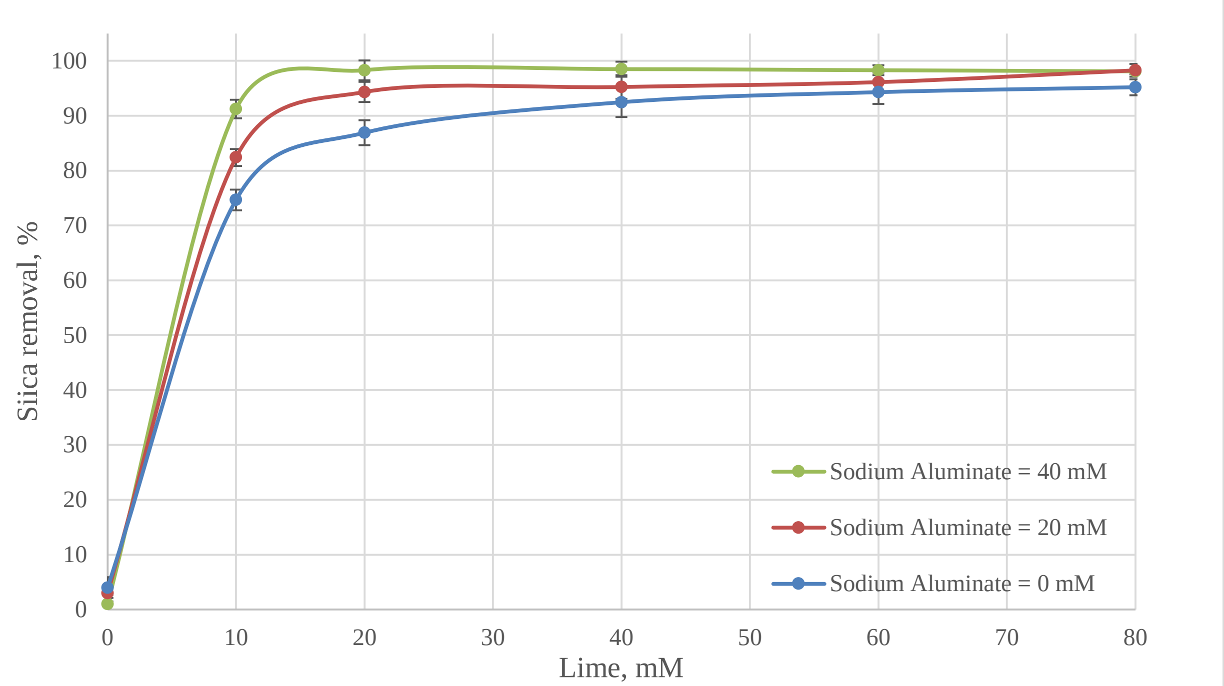


Figure 4.23 Effect of lime and sodium aluminate doses on the removal of silica from model brine in advanced lime softening.

Figure 4.24 below shows the effect of lime and sodium aluminate doses on final concentrations of calcium in the treated model brine. It is clear that there is a significant drop in calcium concentration upon addition of lime, even at low doses of 10 mM. This is mainly due to the rapid increase in pH value, as indicated in figure 4.25. The increase of medium pH enhances the precipitation of calcium carbonate, as well as calcium sulfate, hence decreasing the calcium concentration to a minimum at a lime dose of about 20 - 40 mM. Upon further addition of lime, the pH further increases, leading to more precipitation of calcium carbonate, however, the total calcium present in the solution increases as well, so higher final calcium concentration was present. The lime dose of about 60 mM would be recommended at these conditions which result in both high removal efficiencies of sulfate and silica, along with lower final calcium concentration at reasonable sodium aluminate dose of about 40 mM.

Figure 4.25 shows the effect of lime and sodium aluminate on the final pH of the treated brine; it is clearly shown that as lime dose increases, the pH of the treated brine increases as well. The same trend was noticed for sodium aluminate as sodium aluminate dissolution in water results in a pH increase. The increase in solution pH was associated with high removal of sulfate and silica, as it is favored at high pH values.

In conclusion, the kinetics and equilibrium of sulfate and silica removals from model brine solution of brackish groundwater desalination was found to be similar to the individual removals of sulfate and silica. Equilibrium experiments have confirmed that the removals efficiencies increases with the increase of lime and sodium aluminate, indicating the formation of wide range of precipitates ranging from simple calcium carbonate, calcium sulfate, and calcium and magnesium silicate to more complex salts upon presence of aluminum ion through addition of sodium aluminate such as calcium aluminosilicate and calcium aluminosilicate (Ahmed Abdel-Wahab & Batchelor, 2006; Batchelor, B.; McDevitt, M.; Chan, 1985; Christoe, 1976).

Application of lime softening processes as an intermediate chemical treatment of primary RO brine aimed mainly at removals of calcium and silica, achieving high removal of these constituents up to 90% respectively, however such treatment processes aimed at removal of sulfate as gypsum, hence leaving the solution saturated with respect to gypsum with sulfate concentration of about 3,200 mg/l (C. J. Gabelich et al., 2011, 2007; Rahardianto et al., 2010; Subramani et al., 2012).

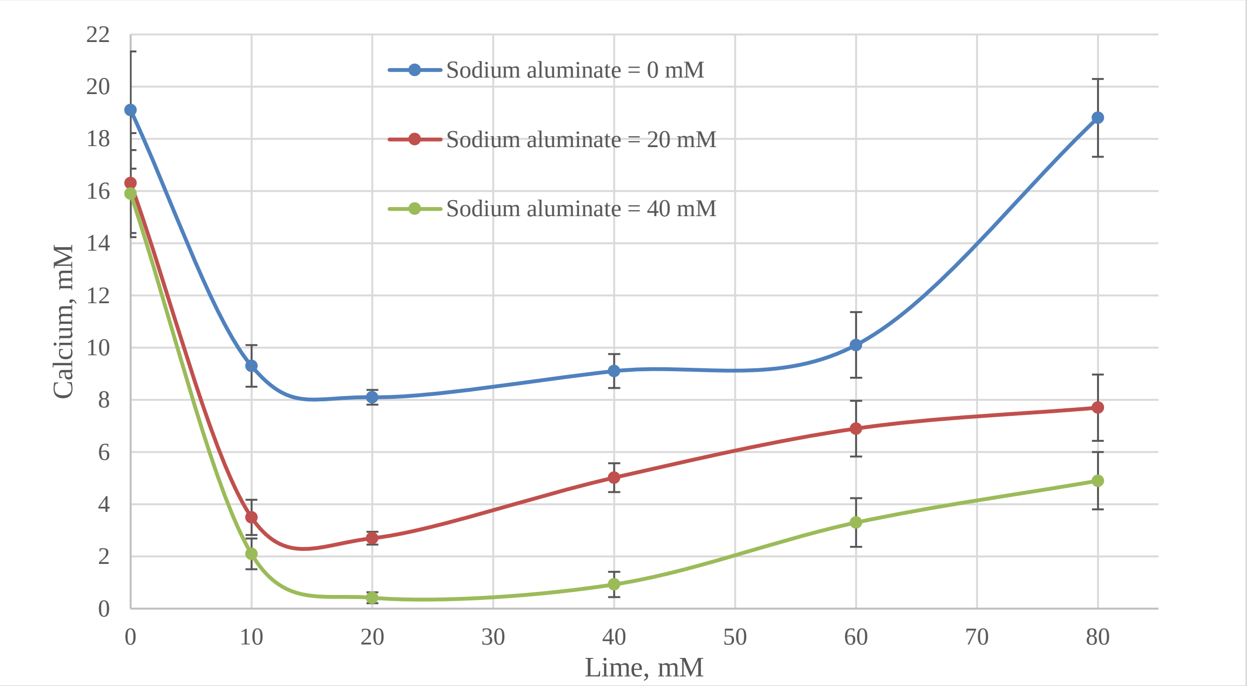


Figure 4.24 Effect of lime and sodium aluminate doses on final calcium concentration of treated model brine in advanced lime softening.

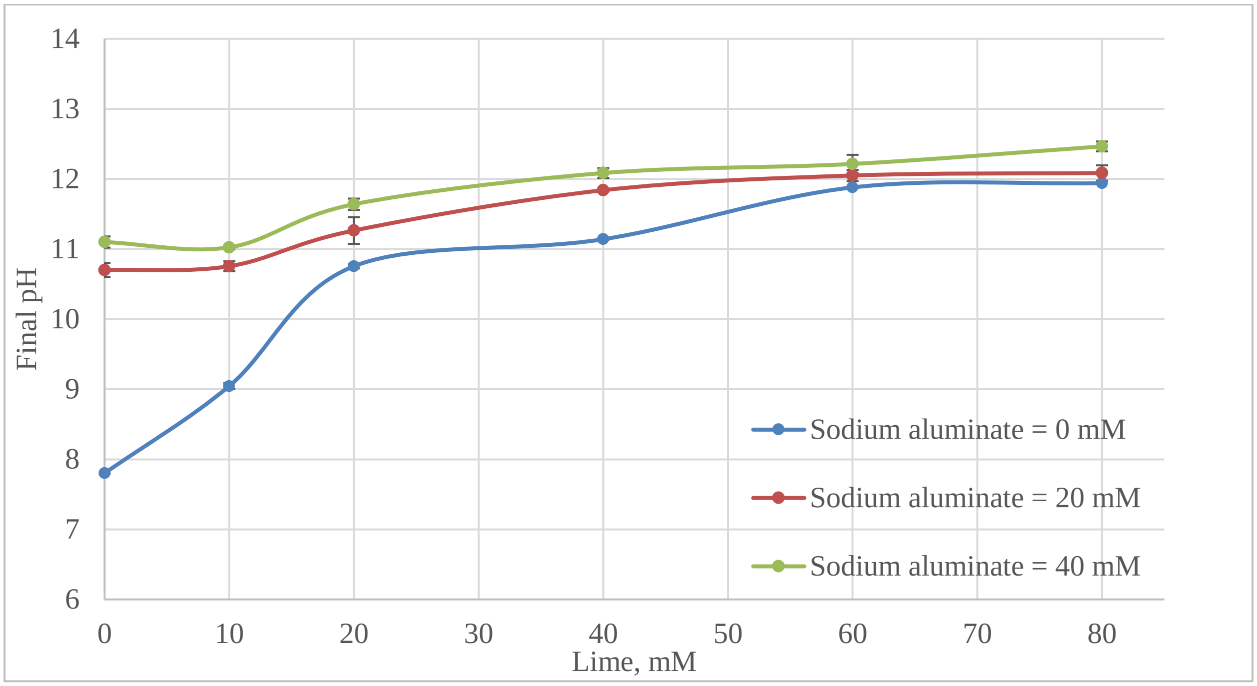


Figure 4.25 Effect of lime and sodium aluminate doses on final pH of the model brine in advanced softening treatment.

4.4. Equilibrium Modelling of the Chemical Treatment Process:

The key element for success in the proposed ZLD process is the brine treatment, which aims at removing most of the scale-forming constituents typically calcium Ca^{2+}, alkalinity as bicarbonate HCO_3^-, sulfate SO_4^{2-}, and silica SiO_2. The proposed chemical treatment process here is based on treating the brine stream by advanced lime softening, namely ultra-high lime with alumina UHLA process.

The ultimate objective of the chemical treatment process here is to convert the soluble ions into insoluble salts by modifying the medium pH, and/or introducing the counterpart ion of insoluble salt form. Due to the presence of so many ions in the reaction medium i.e. brine, there is a wide range of reactions that take place due to the interactions among different ions present.

A basic model of the chemical reactions and processes taking place during the chemical treatment of the brine is developed in order to predict the concentrations of different constituents such as sulfate, silica, calcium,…etc. in the effluent stream i.e. treated brine utilizing the information on the chemical reagent doses and concentrations in the brine stream. Reactions considered in this model are those of dissolution and precipitation as explained in 3.41 and 3.4.2. Precipitation is to be assumed as the mechanism to controls the solubility of different species present in the system. The experimental conditions and results representing various kinetic and equilibrium conditions have been used to validate the equilibrium model.

OLI stream analyzer (OLI Systems, 2016) has been used in this study to model the equilibrium modeling of the chemical treatment of the model brine. Results obtained from OLI have been compared with those obtained experimentally for removal of sulfate and silica, as well as for final concentration of calcium and pH values.

Figure 4.26 below shows that OLI model results can predict the sulfate removals to good agreement with the experimental results more specifically at lime doses up to 80 mM at sodium aluminate doses of 0 and 20 mM, and models predictions tend to under-predict the sulfate removal at high lime doses of 60 and 80 mM at sodium aluminate dose of 40 mM. The relative error for sulfate removal was found to reach a maximum error of -12% at the highest lime and sodium aluminate doses of 80 and 40 mM respectively.

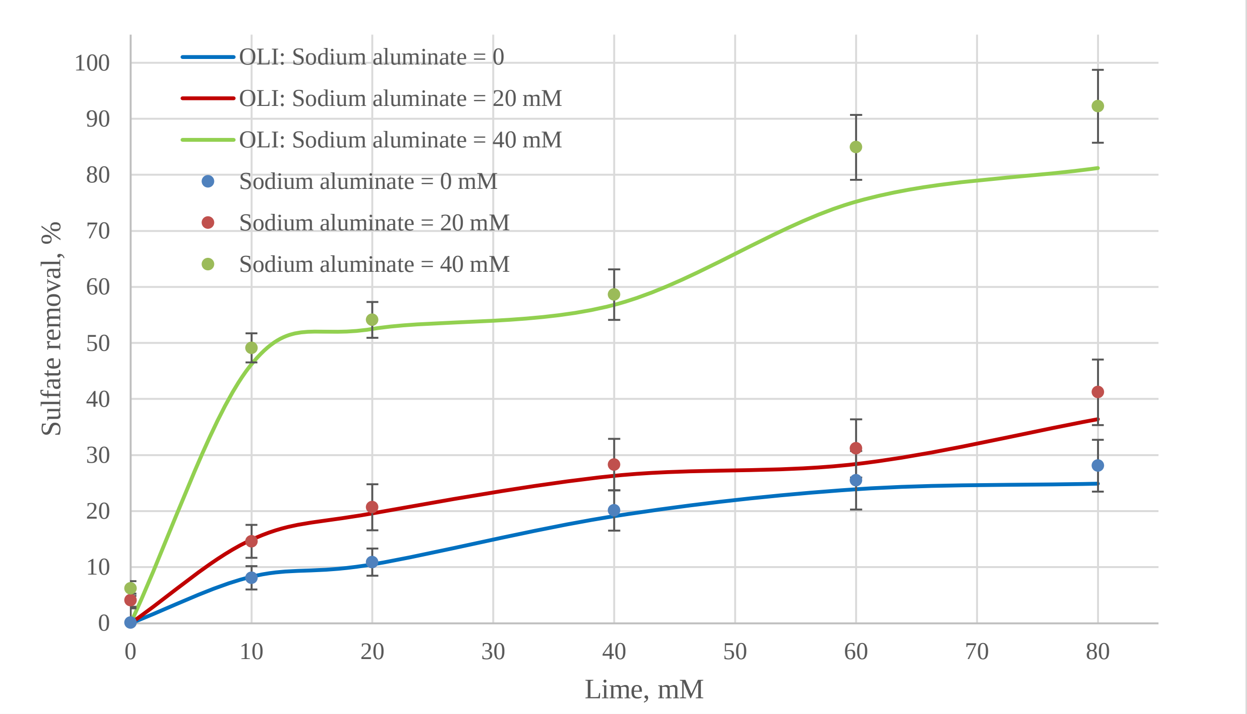


Figure 4.26 Result of OLI equilibrium modeling for sulfate removal from model brine in advanced softening treatment.

Figure 4.27, and 4.28 show that OLI model results can predict the silica removal and calcium concentration, respectively, at good agreement with the experimental results over the range of lime and sodium aluminate doses tested in the equilibrium experiments, with a relative error within ±1.2 and ±6% for silica removal and calcium concentration, respectively.

Figure 4.29 shows that OLI model results can predict the pH value during the chemical treatment to a good extent, and this good agreement depends on the lime and sodium aluminate doses. Results have shown that up to a lime dose of 40 mM, the relative error is within ±8%. The error seems to decrease at higher lime doses down to be within ±4%. The error values were found to decrease as well as the sodium aluminate dose increases.

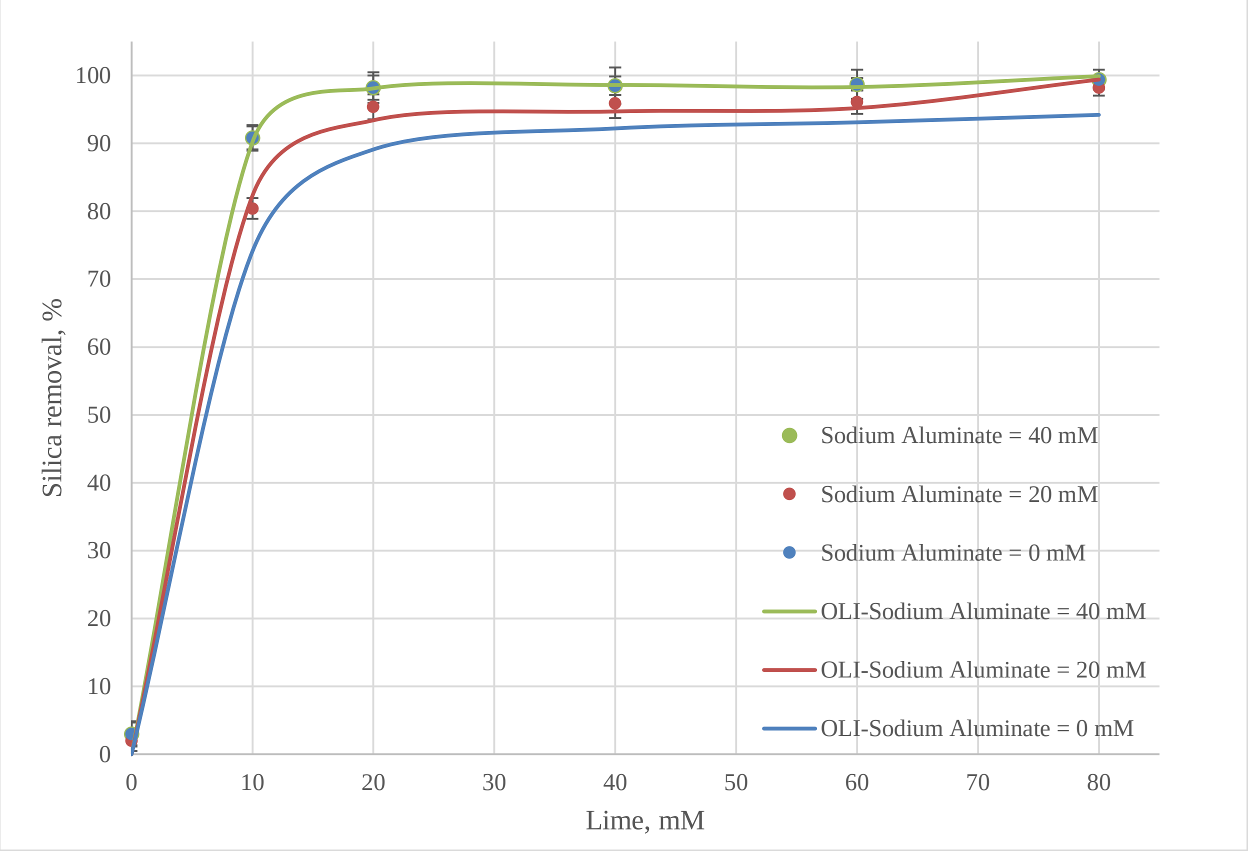


Figure 4.27 Result of OLI equilibrium modeling for silica removal from model brine in advanced softening treatment.

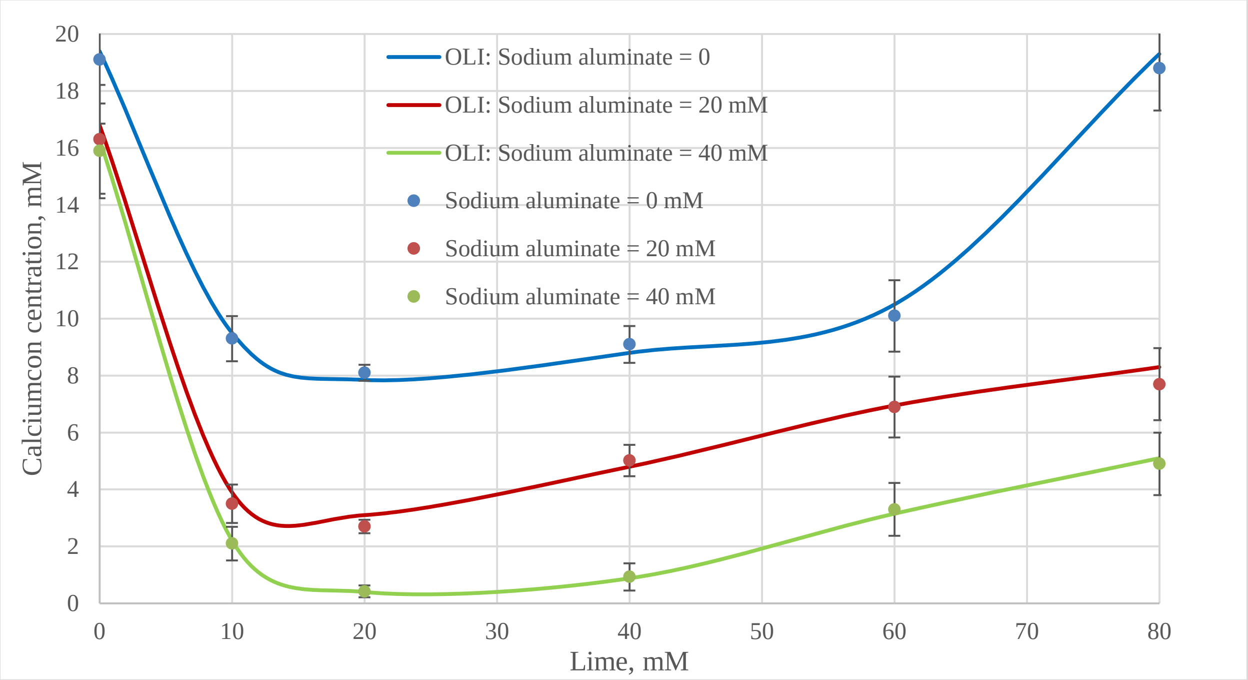


Figure 4.28 Result of OLI equilibrium modeling for final calcium concentration of treated model brine in advanced softening treatment.

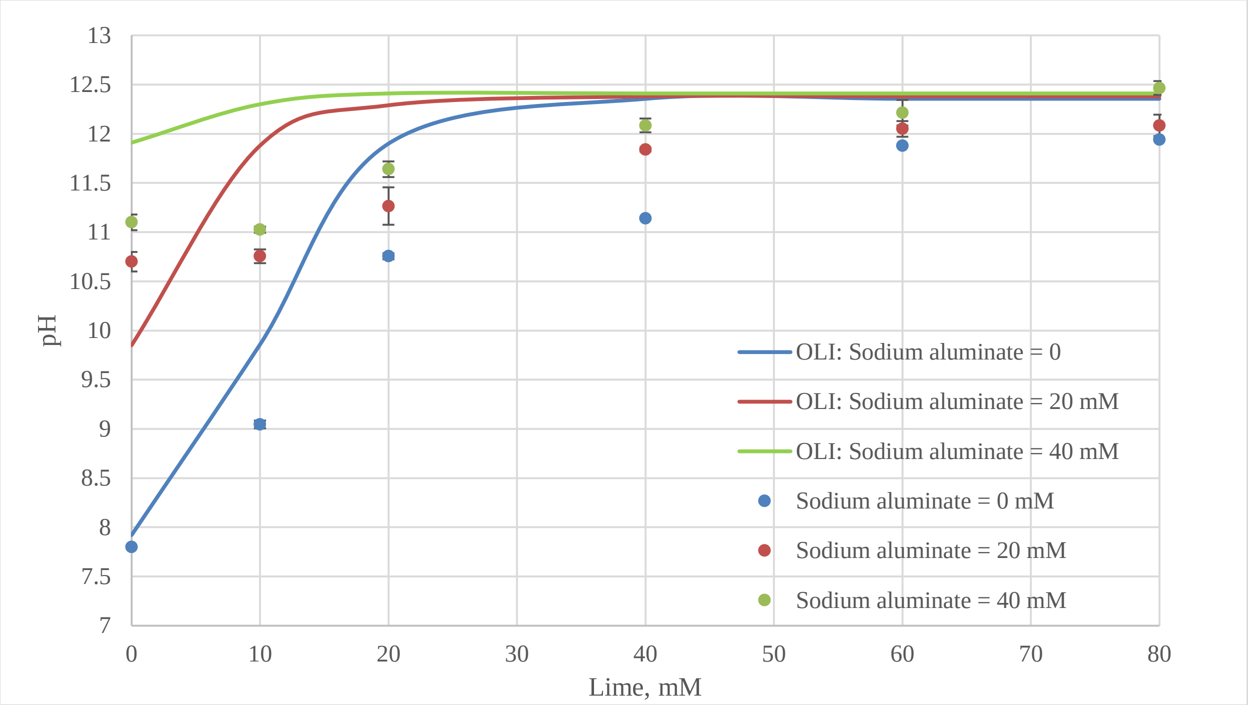


Figure 4.29 Result of OLI equilibrium modeling for pH during the treatment of model brine in advanced softening treatment.

The overall conclusion from this section is that OLI stream analyzer can be effectively used to well predict the equilibrium of chemical treatment of brine in the advanced lime softening process under different treatment conditions. Although the model has under-predicted the sulfate removal at high lime doses of 60 and 80 mM along with high sodium aluminate dose of 40 mM, the model was able to well predict the equilibrium concentration of different constituents present in the brine as well as pH of the treated brine, to very good agreement with the experimental results.

OLI tends to underestimate the value of sulfate removal; it can be utilized as a conservative measure for the overall process modeling of the groundwater desalination for the modeling of the chemical treatment during brine treatment. The equilibrium model utilizing OLI will have failed if it tends to overestimate the removals, as this might lead to subsequent problems in secondary RO unit utilizing the treated brine as feed, due to the calculated higher scaling tendency.

4.5 Identification and Characterization of Precipitated Solids.

In order to develop a complete environmentally benign technology for inland desalination with zero liquid discharge, all process wastes should be handled environmentally, and as a result, it was paramount to look at the solid products from the proposed chemical treatment process. The solids formed during the chemical treatment of model brine in the advanced softening process is being characterized to identify the different solids present, and to explore the applications at which these solids can fit.

Two different approaches have been followed to identify the solids formed during the chemical treatment. The first approach is to utilize the developed equilibrium model which is to indicate the different solids that are to precipitate in the system at equilibrium conditions as indicated by the saturation indices. The second approach is to identify and characterize the collected solids analytically using X-ray techniques.

4.5.1 Identification of Precipitated Solids Using the Equilibrium Model.

The first approach followed to identify these solids was based on utilizing the information result from the mineral equilibrium modeling of the chemical treatment. As discussed before the equilibrium modeling carries out thermodynamic equilibrium calculations of solid and aqueous species to be present at equilibrium in the solution. The results of the equilibrium model contain information on saturation indices of different solid phases that can be present in the solution at equilibrium conditions.

Saturation indices for the expected solids have been investigated to explore if the treated model brine is supersaturated with such solids or not. Tables 4.5 and 4.6 present the saturation indices data for the expected solids for different lime doses of 10, 20, and 40 mM without sodium aluminate, as in table 4.5, and with sodium aluminate dose of 20 mM as presented in table 4.6.

It is clearly shown that all the expected solids have a positive saturation index, indicating that solution is supersaturated with respect to such solids. Furthermore, as shown in table 4.6, more solid phases are to be formed with the addition of sodium aluminate, and more specifically Calcium Sulfoaluminate, i.e. Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}$ which helps in enhancing the removal of sulfate further than that for saturation with respect to gypsum, with saturation index ranges 3.12 – 7.59, relative to that of gypsum which is in the range of 0.09 – 0.20 only. The same result was noticed for silicate as more calcium/magnesium-aluminum-silicate solids are formed at much higher saturation index, which helps increase the extent of silica removal.

Table 4.5 Results from equilibrium modeling for saturation indices of supersaturated solids in the chemically treated model brine at sodium aluminate dose of 0 mM.

Solid	**SI at Lime doses, mM**		
	10	20	40
Calcium Carbonate, $CaCO_3$	2.55	2.59	2.6
Calcium Magnesium Silicate, $CaMg(SiO_3)_2$	9.93	10.52	10.65
Calcium Sulfate, Gypsum, $CaSO_4.2H_2O$	0.08	0.17	0.2
Calcium Magnesium Carbonate, Dolomite, $CaMg(CO_3)_2$	5.75	5.26	5.13
Magnesium Hydroxide, $Mg(OH)_2$	4.08	4.61	4.72

Table 4.6 Results from equilibrium modeling for saturation indices of supersaturated solids in the treated model brine at sodium aluminate dose of 20 mM.

Solid	**SI at Lime doses, mM**		
	10	20	40
Calcium Carbonate, $CaCO_3$	2.55	2.59	2.6
Calcium Magnesium Carbonate, $CaMg(CO_3)_2$	5.75	5.26	5.13
Magnesium Hydroxide, Brucite $Mg(OH)_2$	4.08	4.61	4.72
Calcium Silicate, $CaSiO_3$	2.09	2.43	2.58
Magnesium Silicate, $MgSiO_3$	3.71	3.72	3.17
Calcium Magnesium Silicate, $CaMg(SiO_3)_2$	9.93	10.52	10.65
Calcium Aluminosilicate, $Ca_2AlSi(OH)_{14}$	10.13	10.25	10.28
Calcium Sulfate, Gypsum, $CaSO_4.2H_2O$	0.08	0.17	0.2
Calcium Sulfoaluminate, Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}$	3.12	6.70	7.59

4.5.2 Analytical Identification of Precipitated Solids Using X-Ray Techniques.

The second approach followed to identify the solids precipitated was to analyze the solids produced from the chemical treatment of model brine in advanced softening at specific conditions of lime and sodium aluminate doses as outlined in table 3.5 using x-ray solid analysis techniques, basically XRF and XRD. XRF is to provide general information on the elemental analysis i.e. % of different elements such as calcium, silicon…etc. The results can be obtained as well in oxide form i.e. % calcium oxide, silicon oxide…etc. However, XRF will not provide information on the type of solids formed for example is the calcium present as calcium carbonate or calcium sulfate. XRD analysis, on the other hand, provides detailed information on the different solids present. Furthermore, it can efficiently identify the different phases of the same solid i.e. is calcium carbonate present as calcite or aragonite and to what extent it is present.

Table 4.7 below shows the elemental analysis using XRF techniques for the solid precipitates result from model brine treatment in advanced softening processes at the indicated lime and sodium aluminate doses. As shown in the table, calcium accounts for most of the solid with a percentage ranging from 43–49%. The analysis also indicates the presence of sulfate in the precipitate with a percentage of 16 – 21% (as Sulfur). The analysis indicates the presence of silica as silicon, magnesium, and aluminum. More interestingly, the analysis indicates the presence of sodium and chloride, which were believed not be present in the precipitated solids due to their very high solubility.

Table 4.7 XRF results of % elemental analysis for selected solid precipitates.

Element, %	**SB-40-20** **Lime = 40 mM** **Sodium Aluminate = 20 mM**	**SB-80-20** **Lime = 80 mM** **Sodium Aluminate = 20 mM**	**SB-80-40** **Lime = 80 mM** **Sodium Aluminate = 40 mM**
Na	9.51	11.7	12.7
Mg	3.12	2.94	1.1
Al	9.78	10.9	13.7
Si	1.41	1.29	1.21
S	18.9	21.1	16.3
Cl	8.06	5.01	5.15
Ca	43.4	46.7	48.9

As XRF provides net elemental analysis without information on the type of solids present, XRD analysis is performed to identify the different solids present. Solid precipitate produced in experiment SB-80-40 (refer to table 3.5) was chosen for further analysis using XRD technique. Figure 4.30 and 4.31 below show the raw and processes XRD data, respectively, obtained by scanning the dried solids precipitate at 2θ/min and scanning range from 2θ = 5 – 80.

The figure shows clearly the peaks related to the main phases detected of calcium sulfate i.e. gypsum $CaSO_4.2H_2O$, calcium carbonate i.e. calcite, $CaCO_3$, Calcium-Magnesium Carbonate, $CaMg(CO_3)_2$, Calcium Sulfoaluminate i.e. Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}$, Aluminum hydroxide i.e. gibbsite $Al(OH)_3$ and unreacted lime i.e. portlandite $Ca(OH)_2$, and calcium aluminum oxide. However, XRD has identified the presence of Fridel's salt, which is calcium chloroaluminate salt $Ca_2Al(OH)_6Cl.(H_2O)$, similar to the calcium aluminosulfate, which can be the source for chloride indicated in the XRF analysis. Fridel's salt was found to form in systems of similar chemistries at high pH and calcium concentration in presence of aluminum and chloride (Birnin-Yauri & Glasser, 1998).

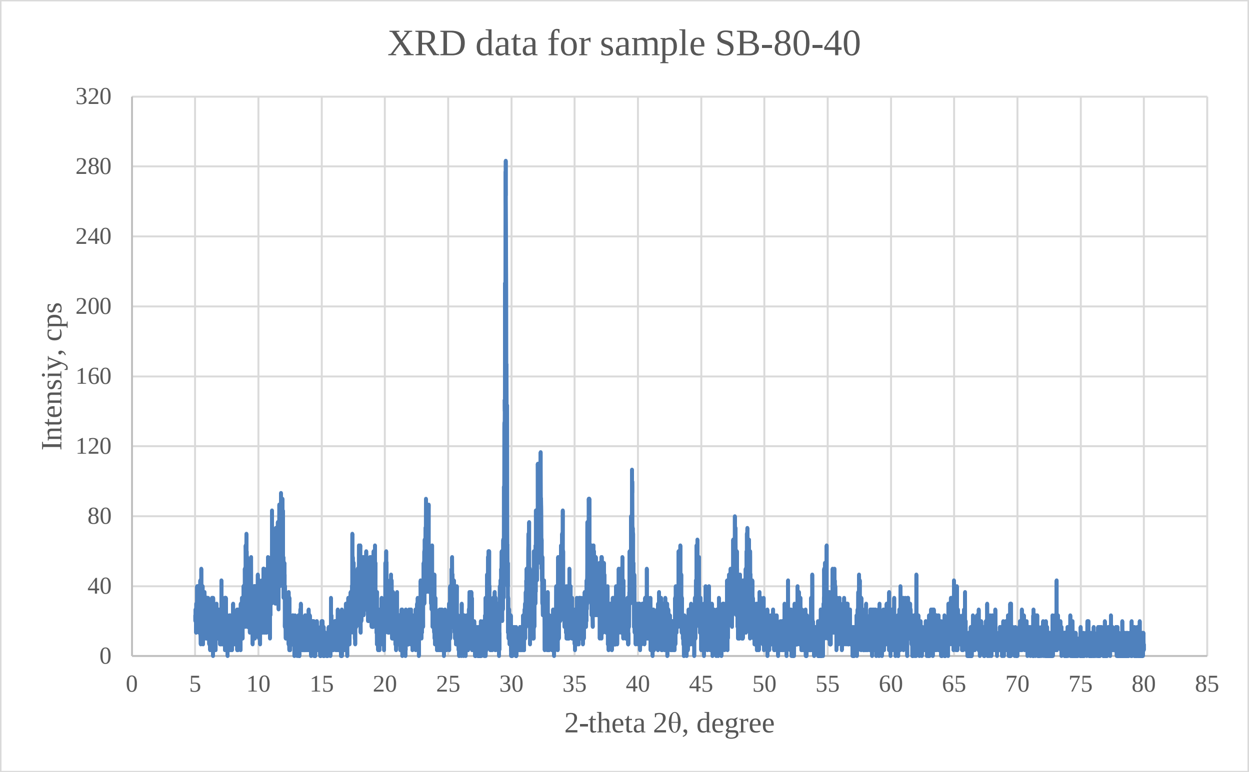


Figure 4.30 Raw XRD data for solid precipitate SB-80-40.

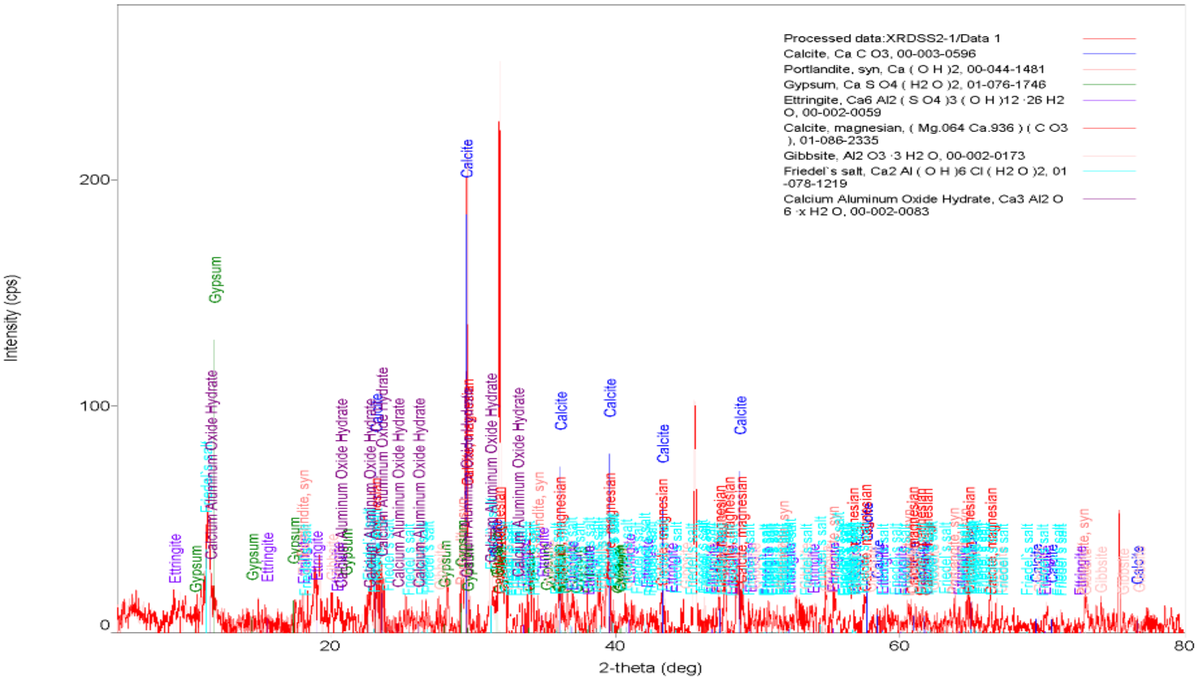


Figure 4.31 Identified solids for XRD data of solid precipitate SB-80-40.

4.5.3 Potential Applications of the Precipitated Solids.

The main solids produced during the chemical treatment of brine can be mainly categorized into two classes:

1- Traditional lime softening precipitates such as:
   a. Ca- compounds: mainly calcium carbonate $CaCO_3$, however, calcium silicate CaH_2SiO_4 and calcium sulfate, as gypsum $CaSO_4.2H_2O$ are additionally present here.
   b. Mg compounds: mainly magnesium hydroxide $Mg(OH)_2$, and magnesium silicate MgH_2SiO_4.
2- Special solids relevant to advanced softening such as:
   a. Ca-SO_4-Al compounds: calcium sulfoaluminate $Ca_6Al_2(SO_4)_3(OH)_{12}$, and calcium mono sulfoaluminate $CaAl(SO_4)(OH)_{12}.6H_2O$.
   b. Ca/Mg-SiO_2-Al compounds: calcium aluminosilicate $Ca_2Al_2Si(OH)_{14}$,
   c. Ca-Cl-Al compounds: Fridel's salt, which is calcium chloroaluminate salt $Ca_2l(OH)_6Cl.(H_2O)$.

Solids of calcium sulfoaluminate, calcium mono sulfoaluminate, calcium aluminosilicate, and calcium chloroaluminate belong to a family of compounds called Layered Double Hydroxides LDH or anionic clays (J. He et al., 2006). This type of compounds have many beneficial physical and chemical properties, making it very useful in many applications (F. Li & Duan, 2006).

As a result, we can categorize the applications for the produced solids into two main categories:

1- High-value applications: where the solids have to be characterized to determine the main structure and composition, ion exchange capacity, surface area…etc. The high-value applications of LDHs are very wide in this case and the main and well established applications are in the following fields (Das, Patra, Baliarsingh, & Parida, 2006; Duan et al., 2006; F. Li & Duan, 2006; Meyn, Beneke, & Lagaly, 1990; Richardson, 2007):
   a. Catalyst and Catalyst Support,
   b. Ion-Exchange,
   c. Adsorption,
   d. Pharmaceutics,

2- Low-value applications: where the solids can be used directly without carrying out any characterization tests. In this case, it can act as a rich source of many elements at the same time such as calcium, silica, sulfate, aluminum, and magnesium, and such combination can be used in:
    a. Cement industry: to be added to the feed with limestone and clay.
    b. Road pavements: as sub-grade.

4.6 Development of Complete Process Model.

It is very crucial to develop a complete process model for the proposed ZLD technology; the model should include the different units involved in the process such as membrane separation units i.e. primary and secondary RO units, along with chemical treatment unit. The main objective of the complete process model is to predict the performance and effectiveness of the whole process for a given input condition of feedwater quality and flowrate, chemical reagents doses, and to maximize the water productivity i.e. recovery.

In section 4.4, OLI has been found to model the chemical treatment to a very good extent. One more advantage of OLI that it can be easily integrated with one of the major chemical process simulator Aspen Plus, and is a ready Adds-Ins with dedicated OLI engine to work with Aspen. Due to this reason, and many others as explained in 3.6.2, Aspen Custom Modeler ACM, is used to model the membrane separation process. The model equations developed in section 3.6.2 have been implemented into ACM to solve and simulate the membrane separation model. The developed ACM code for the developed model is provided in appendix B.

ACM is a very powerful modeling tool that has been developed by Aspen Plus to model user-defined processes, which are not present in the ready Aspen Plus model library of different chemical processes and equipment, which is similar to our case of RO membrane model. The ACM environment enables as well efficient parameter estimation of the model parameters given a set of experimental data, and ACM uses the error minimization or least square of errors method to estimate the model parameters.

Most of the models present in literature consider two permeability coefficients only for water and salt (Oh et al., 2009; Sundaramoorthy et al., 2011). However, in this study, a more rigorous and comprehensive approach has been considered, by assuming different permeabilities for monovalent and di-valent ions present in water. This was considered mainly due to the fact that membrane separation, in general, has different rejection or passage to different ions depending on their valency and ionic size. This is in addition to handling these different species in the ionic form rather than neutral salt form, which is considered a novel approach in membrane separation modeling, which is to account for the fact that high speciation salts have in the water, and present mainly in ionic form rather than neutral salt form.

4.6.1 Model Validation and Parameters Estimation.

The developed RO membrane separation model has a set of distinct parameters that needs to be estimated in order to utilize the model for design and simulation of the complete process model. Experimental data generated utilizing standard commercial small-scale RO unit, with standard single membrane element of 2.5” diameter and 40” length, was utilized for this purpose. The main membrane characteristic parameters are:

i- Water/solvent permeability coefficient through membrane A,
ii- Solute permeability coefficient through membrane B (B_{imv}, B_{dmv}, B_s, B_g),
iii- Parameter of mass transfer coefficient, mt
iv- Flow friction coefficient in brine and permeate channels K_b, and K_P respectively.

The parameters have been estimated using ACM fed with different experimental data provided by running the lab scale RO unit at different recovery levels and recording all the process parameters such as flowrates, pressures, and temperatures. In addition, samples of the permeate and concentrate are collected and analyzed for quantification of the individual concentration of ions present in water.

The experimental data were then fed into the ACM model to estimate the different model parameters in addition to solving the membrane model. Results obtained from the ACM model have been compared to original experimental results to show to what extent the model fits well with experimental data. Table 4.8 and 4.9 below show the different experimental results obtained on the lab-scale unit at 25 ^oC and 35 ^oC respectively, which have been used to validate the model. The results from parameters estimation carried out by ACM are presented in table 4.10 for the given experimental data.

Figures 4.32 – 4.36 shows the comparison between values obtained experimentally and those predicted by the model for required feed pressure, pressure drop, net driving pressure, specific energy consumption, and permeate salinity or TDS as major unit performance parameters. In general, the model predictions and the experimental results match to a large extent. However, the model seems to overestimate the membrane pressure drop by about 8% at 25 °C, which increases to about 13% for 35 °C. A similar trend was noticed for the specific energy consumption within 6% for 25 °C and 9% for 35 °C.

Table 4.8 Experimental results of lab scale RO operation at 25 °C.

Feed Flowrate	m^3/hr	1.36			
Recovery	%	2	4	6	8
Product flow	m^3/hr	0.027	0.055	0.082	0.109
Feed pressure	bar	5.91	9.17	12.67	16.51
Concentrate pressure		4.8	8.15	11.58	15.43
Pressure drop		0.77	0.76	0.75	0.76
Power	kW	0.28	0.43	0.6	0.78
Specific Energy	kW/m^3	10.27	7.96	7.34	7.17
Feed TDS	mg/l	4,250			
Product TDS		60	32	23	18
Concentrate TDS		4339	4428	4523	4621

Table 4.9 Experimental results of lab scale RO operation at 35 ^{o}C.

Feed Flowrate	m^3/hr	1.36			
Recovery	%	2	4	6	8
Product flow	m^3/hr	0.027	0.055	0.082	0.109
Feed pressure	bar	4.94	7.14	9.43	11.86
Concentrate pressure		3.92	6.13	8.44	10.87
Pressure drop		0.68	0.66	0.65	0.65
Power	kW	0.23	0.34	0.45	0.56
Specific Energy	kW/m^3	8.58	6.2	5.46	5.15
Feed TDS	mg/l	4,250			
Product TDS		108	58	41	33
Concentrate TDS		4,340	4,430	4,520	4,620

Table 4.10 Results of parameters estimation for the RO membrane model by ACM.

Parameter	**Value**
Water/solvent permeability coefficient through membrane, A (m^3/m^2/bar/hr)	1.37284E-3 ± 2.7457E-5
Solute permeability coefficient through membrane for monovalent ions, B_{imv} (kmol/m^2/bar/hr)	1.35952E-4 ± 1.4955E-6
Solute permeability coefficient through membrane for divalent ions, B_{dmv} (kmol/m^2/bar/hr)	1.40215E-4 ± 4.2065E-6
Parameter of mass transfer coefficient, mt (dimensionless)	400 ± 5.4
Flow friction coefficient in brine channels, K_b (bar/cp)	2.38165E-4 ± 9.5266E-6
Flow friction coefficient in permeate channels, K_p (bar/cp)	2.052225E-4 ± 7.7985E-6

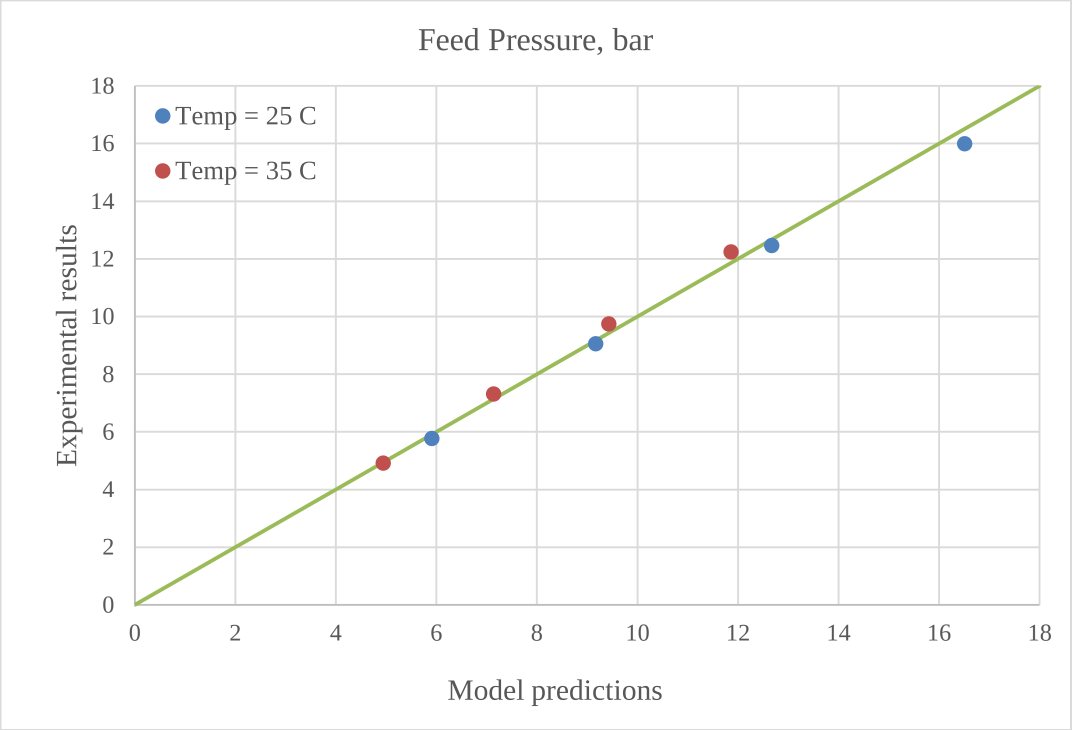


Figure 4.32 Comparison of model prediction to experimental results for feed pressure.

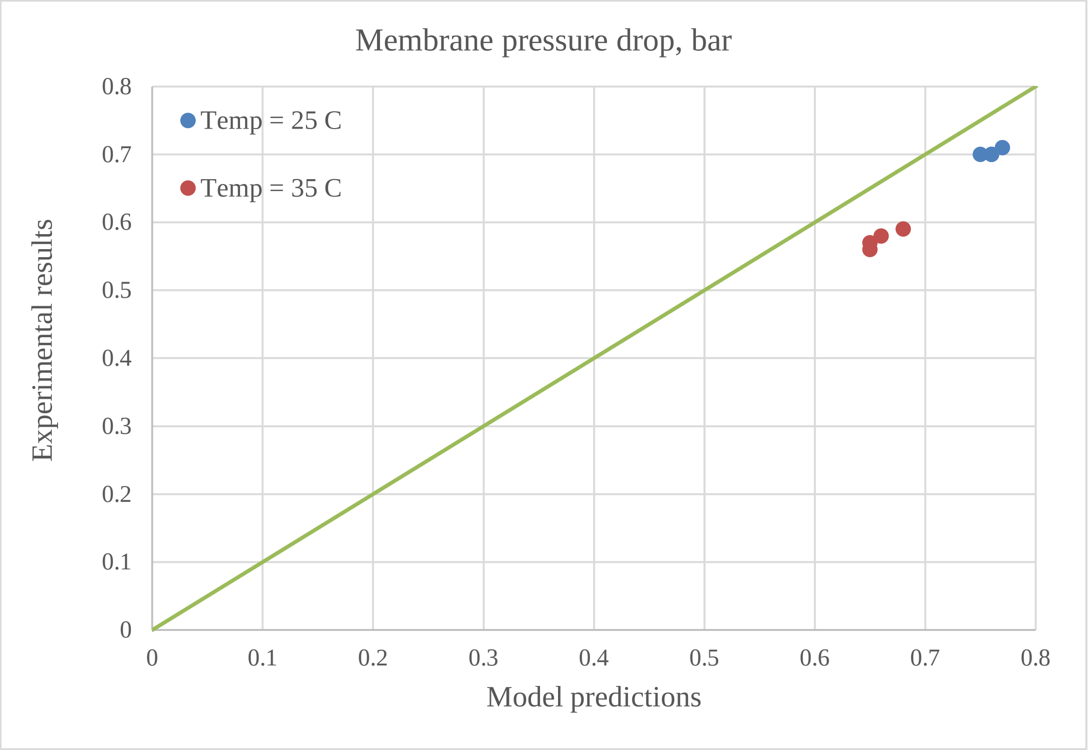


Figure 4.33 Comparison of model prediction to experimental results for pressure drop.

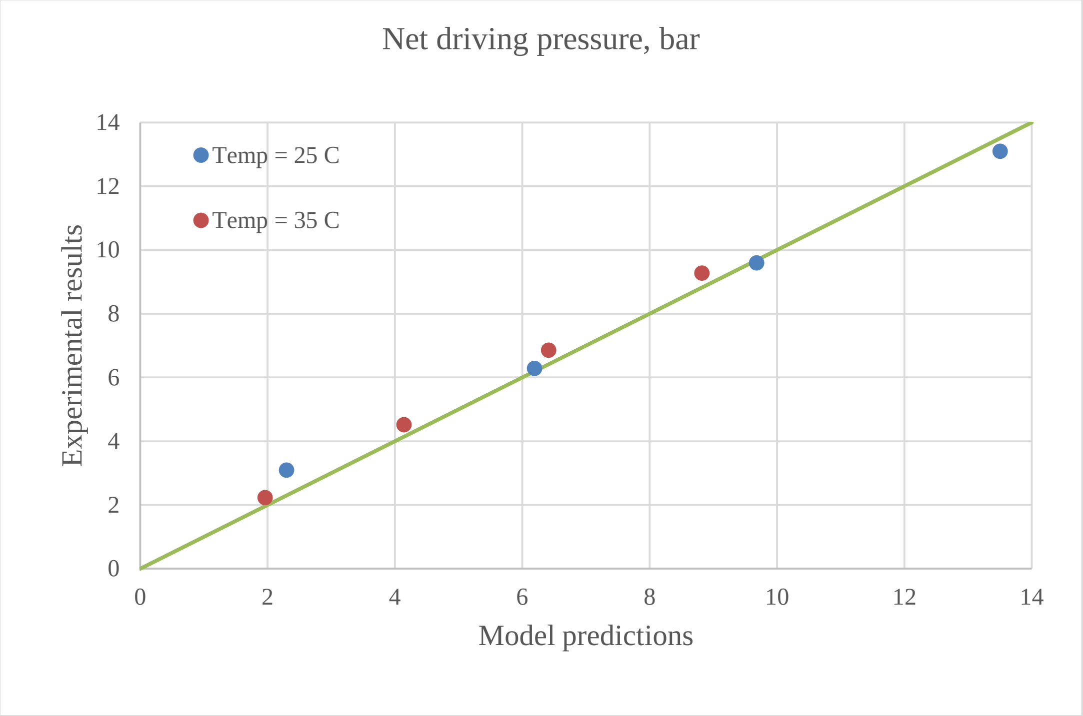


Figure 4.34 Comparison of model prediction to experimental results for net driving pressure.

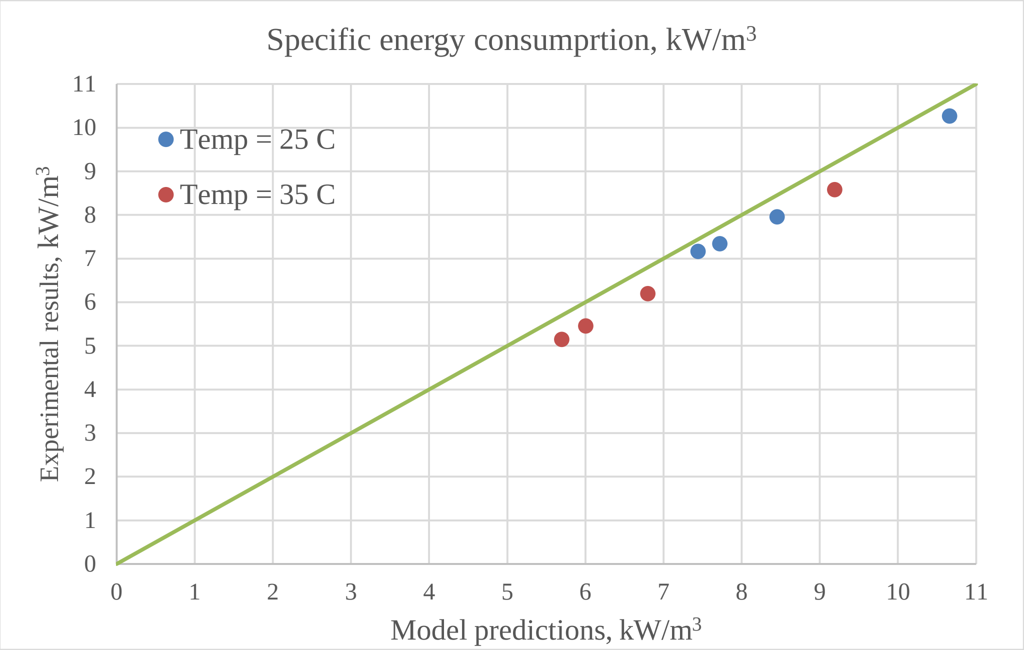


Figure 4.35 Comparison of model prediction to experimental results for specific energy consumption.

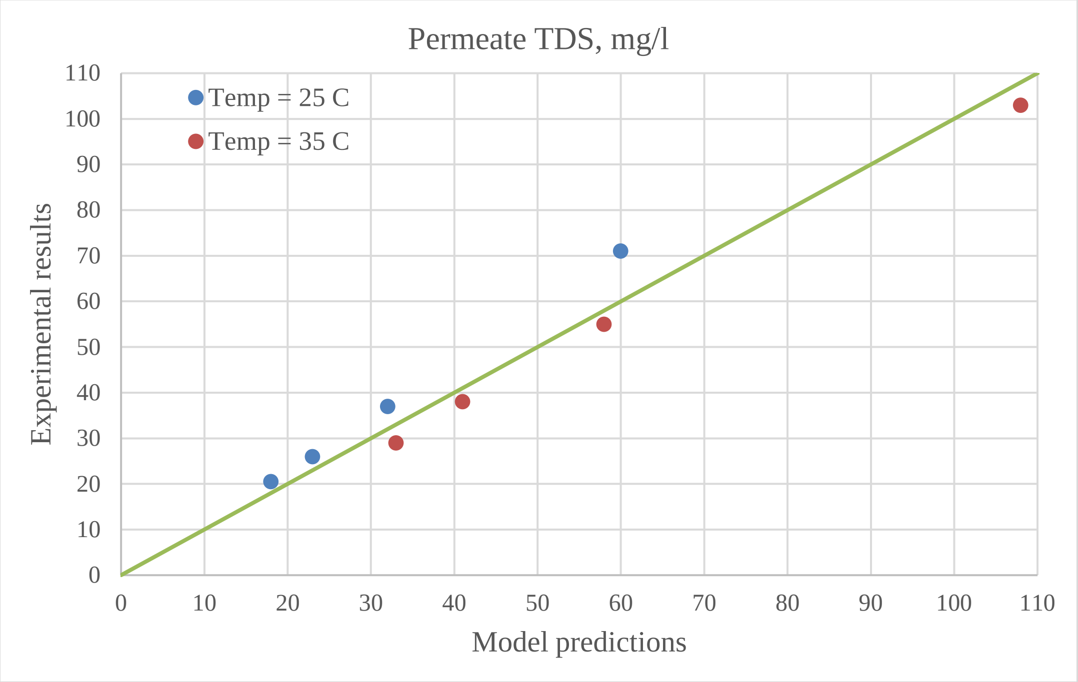


Figure 4.36 Comparison of model prediction to experimental results for permeate salinity.

One of the assumptions that have been considered during the modeling is that membrane has a fixed rejection toward ions, and this differs only from monovalent to divalent. In model input, monovalent ions and silica have been assumed to have a rejection of 99%, while divalent ions were assumed to have a rejection of 99.5%. RO membrane rejections to different ions are usually not constant, and vary from ion to another, depending on the pressure, membrane age, temperature..., etc. However, it is very hard to have the rejection as an explicit equation in the model and for simplifications have been assumed to be constant.

Figure 4.37 and 4.38 shows the calculated rejections of different ions at 25 ^{o}C and 35 ^{o}C respectively, for the RO membrane used in the lab unit as calculated from experimental results obtained. The figures show clearly that the rejections do not have a fixed value and it largely depends on the recovery i.e. feed pressure, and temperature. This can explain to a large extent some of the deviations observed when comparing the experimental results to model predictions at the same recovery conditions.

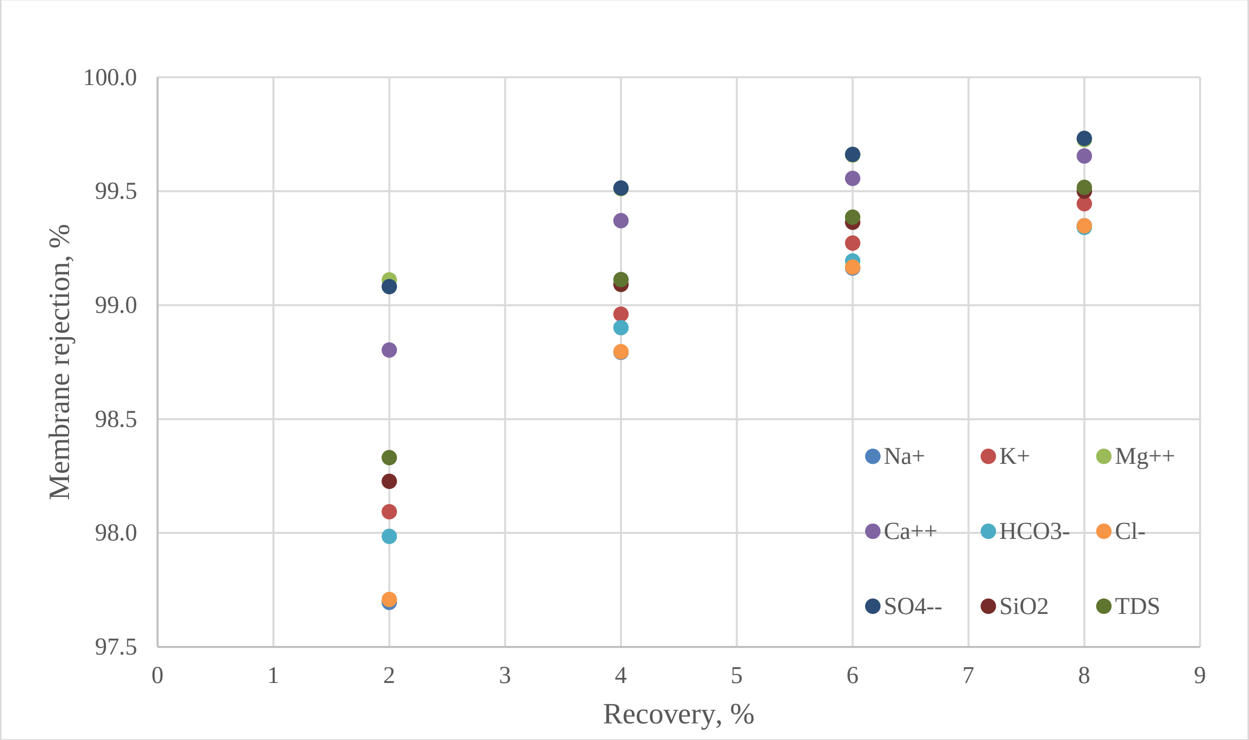


Figure 4.37 RO membrane rejection to different ions at 25 ^oC.

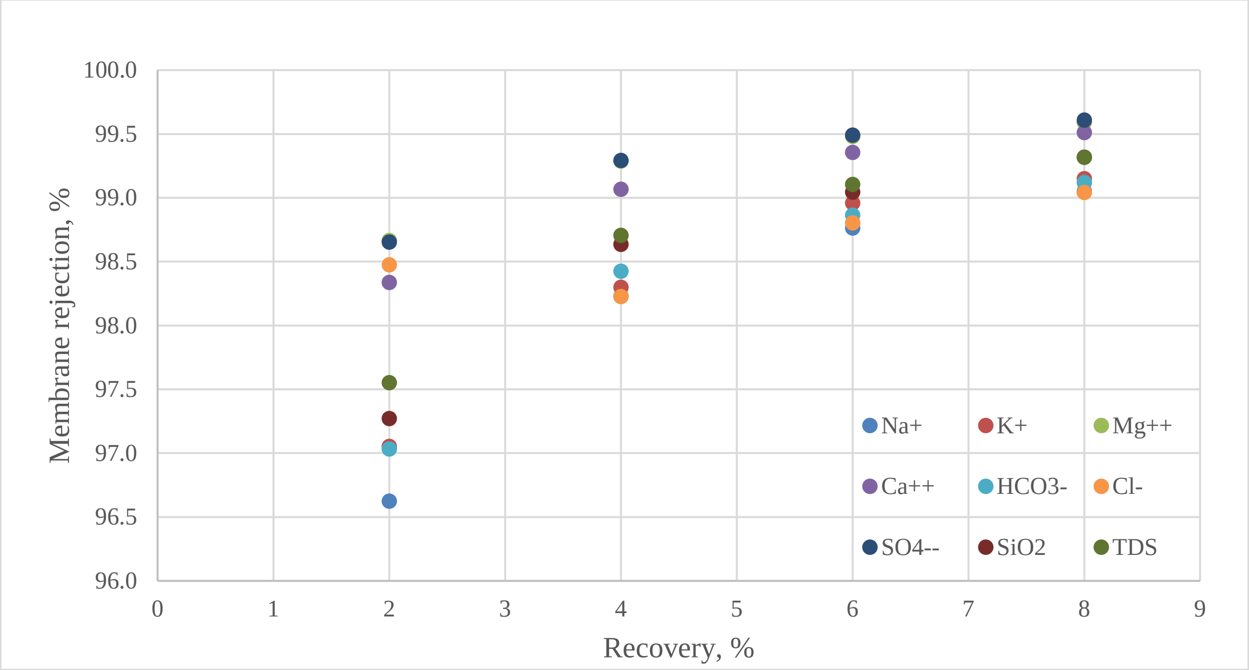


Figure 4.38 RO membrane rejection to different ions at 35 ^oC.

4.6.2 Sensitivity Analysis for the Membrane Separation Model.

The developed RO membranes model has a set of crucial model parameters that have been estimated by ACM, utilizing the experimental data obtained at lab scale. The model has high sensitivity to such parameters, as it is very critical to test the validity of the model predictions considering these model parameters as well as the important model inputs or conditions.

Sensitivity analysis SA is a well-established technique to study how the uncertainty of model outputs due to uncertainty or variation of crucial model inputs and parameters. Sensitivity analysis can be obtained through different techniques and methodologies. The method implemented in this work belongs to variance-based methods. The sensitivity analysis performed in this study by running multiple simulation runs, while varying model inputs around a nominal value, which is a type of local SA as it investigates the results of key model outputs, based on changes in model inputs close to the nominal values, which is very suitable for input factors with low-to-medium uncertainty (Marino et al., 2009).

Table 4.11 Range for model inputs and parameters utilized for sensitivity analysis.

Parameter	**Value**
Water/solvent permeability coefficient through membrane, A ($m^3/m^2/bar/hr$)	1.37284E-3 ± 2.7457E-5
Solute permeability coefficient through membrane for monovalent ions, B_{imv} ($kmol/m^2/bar/hr$)	1.35952E-4 ± 1.4955E-6
Solute permeability coefficient through membrane for divalent ions, B_{dmv} ($kmol/m^2/bar/hr$)	1.40215E-4 ± 4.2065E-6
Parameter of mass transfer coefficient, mt (dimensionless)	400 ± 5.4
Feed Flow, kmol/hr	903 ± 20
Feed pressure, bar	17.5 ± 7.5
Feed temperature, ºC	25.00 ± 15.00

Table 4.11 above shows the critical model parameters and input conditions considered for performing the SA along with their variation range. Multiple simulations have been performed with results for recovery, and rejections of monovalent and divalent ions as the main model outputs. Figure 4.39 below shows the response surface of recovery at different model input conditions of pressure and temperature over the set range, which shows a smooth response surface

over these condition range. The response surface shows the expected behavior of the system over temperature and pressure ranges, with higher recovery obtained at increased pressures and temperatures.

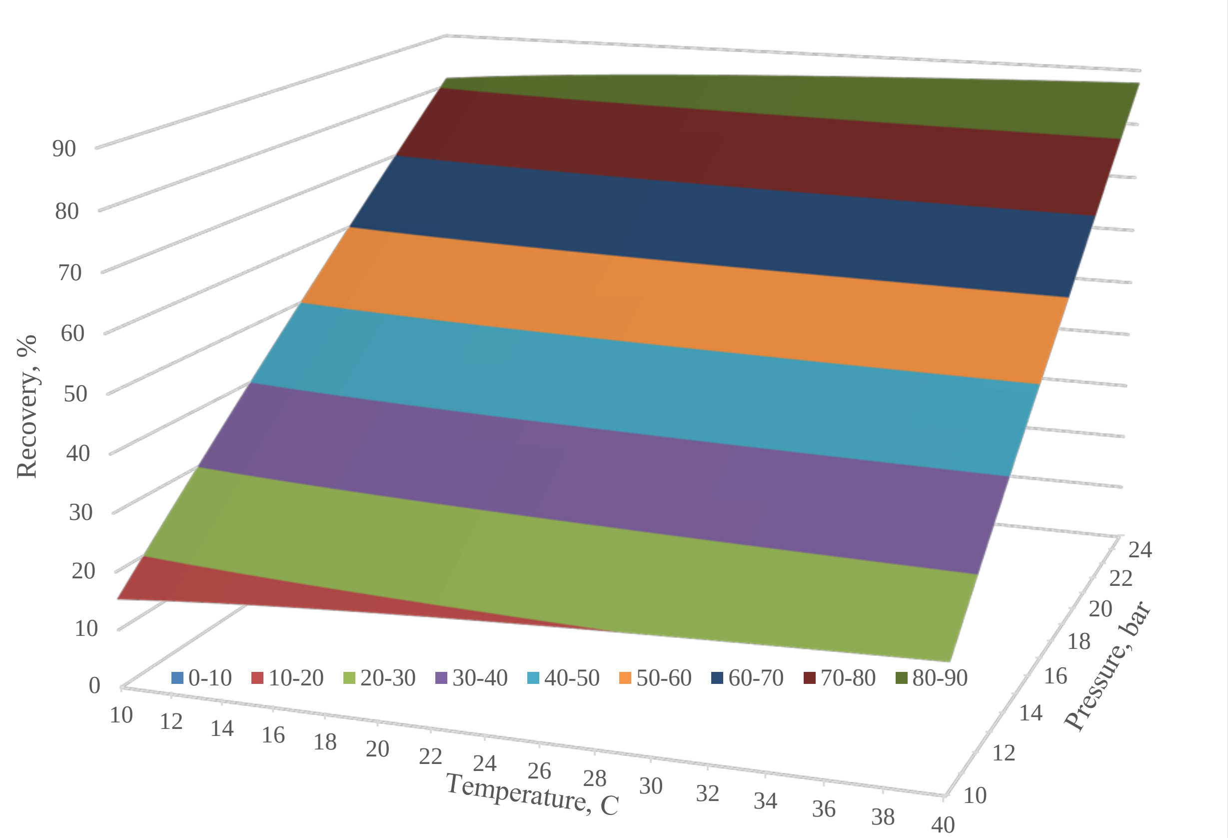


Figure 4.39 Sensitivity Analysis of model inputs of pressure and temperature on system recovery.

4.6.3 Complete Process Modelling.

The developed RO membranes model, along with equilibrium model used to model the chemical treatment has been all integrated into Aspen Plus V8.8 process simulation environment. The developed membrane model in aspen custom modeler has been imported to Aspen Plus as a user-defined model. The chemical treatment has been integrated in the simulation as two separate unit; the first is stream mixer at which the brine along with the added chemical reagents will be homogenously mixed enabling dissolution of lime and sodium aluminate, the second unit is precipitator at which solid separation takes place to separate solids as precipitate from the treated brine stream. The RO model has then applied again to the secondary RO unit. Figure 4.40 shows the schematic diagram for the complete process units as developed in Aspen Plus environment.

OLI has been chosen as the property model package for the whole simulation so it can be utilized in the RO model for calculation of osmotic coefficient and pressures, ions interaction, and scaling potential. Furthermore, as concluded in section 4.4, OLI is used as well to model the chemical equilibrium during the chemical treatment in both the mixer and solid precipitation unit.

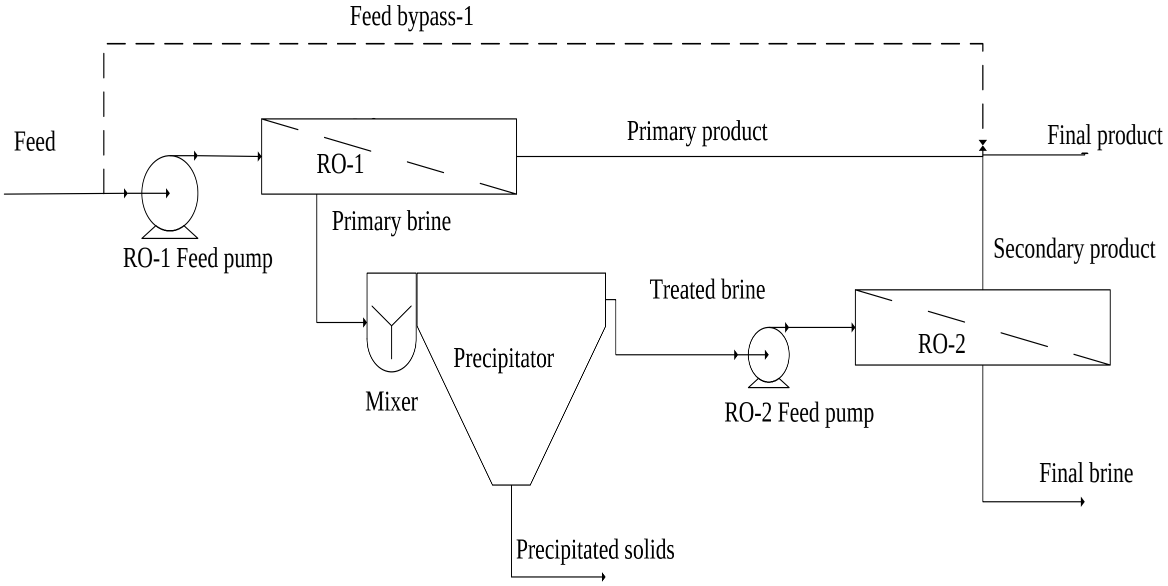


Figure 4.40 Schematic diagram of the complete proposed ZLD setup.

The complete process model is then used to simulate and maximize the recovery of brackish groundwater desalination, using analysis and information for actual groundwater at brackish groundwater desalination site. The brackish groundwater has the analysis as indicated in table 4.11; the table indicates as well the saturation indices of different considerable scale-forming constituents such as carbonate, sulfate…etc. as calculated by OLI.

It is well noticed that the groundwater is undersaturated with respect to all scale-forming constituents except for calcium carbonate and barium sulfate, but given the low barium concentration, this is considered as a secondary concern; however, the groundwater is close to saturation by calcium sulfate or gypsum. The LSI/SDSI for the groundwater can be lowered to an acceptable level by acid addition in the pretreatment. OLI calculations have shown that with pre-acidification to pH 7, LSI and SDSI will drop to 0.64 and 0.39 respectively.

A brackish groundwater desalination plant has been setup in Aspen Plus V8.8 to simulate and optimize the operation of the proposed Zero Liquid Discharge scheme. The plant is to process a brackish groundwater feed of 100 m^3/d (≈ 4 m^3/h) which is the well-pumping capacity.

Table 4.12 Typical groundwater analysis.

Parameter	**Value**
Total dissolved solids TDS, mg/l	4,250
Electrical conductivity, µS/cm	6,567
pH	7.41
Calcium Ca^{2+}, mg/l (mM/l)	451
Magnesium Mg^{2+}, mg/l (mM/l)	135
Sodium Na^{+}, mg/l (mM/l)	729
Potassium K^{+}, mg/l (mM/l)	57.7
Strontium Sr^{2++}, mg/l (mM/l)	5.7
Barium Ba^{2++}, mg/l (mM/l)	0.025
Bicarbonate HCO_3^-, mg/l (mM/l)	273
Chloride Cl^-, mg/l (mM/l)	1213
Sulfate SO_4^{2-}, mg/l (mM/l)	1360
Fluoride F^-, mg/l (mM/l)	0.9
Silica SiO_2, mg/l (mM/l)	22.1
LSI	1.058
SDSI	0.809
$CaSO_4$ SI (K_{sp})	-0.26 (0.55 K_{sp})
$BaSO_4$ SI (K_{sp})	0.44 (2.75 K_{sp})
$SrSO_4$ SI (K_{sp})	-0.51 (0.30 K_{sp})
SiO_2 SI (K_{sp})	-0.82 (0.15 K_{sp})

Quality and flowrate of brackish groundwater feed have been put into the model in Aspen Plus in addition membrane characteristics as given in table 3.6 for brackish groundwater membranes. The output from running the model would be the primary RO performance at different recoveries, as well as the maximum achievable recovery. Then the chemical doses required achieving the highest removal level of sulfate present in the brine stream in order to de-supersaturate the brine making it suitable for further processing in the secondary RO. The model is to provide results as well for the performance of the secondary RO unit, and the maximum achievable recovery, and finally the overall system recovery.

4.6.3.1 Base Case Brackish of Groundwater Desalination Plant.

The base case investigates the design and operation of conventional desalination plant of one RO unit, investigating the maximum achievable recovery. At the given feed quality in table 4.11, and membrane characteristics given in table 3.6, the basic RO model developed in Aspen Custom modeler has run individually to investigate the optimum operating conditions of single RO unit, as shown in the schematic diagram of figure 4.41.

Figures 4.42 shows the dependence of feed pressure and specific energy requirement at recovery range of 50–80%. It is clearly shown that both increase as recovery increase with strong, close to exponential, dependence of specific energy requirement on recovery as higher pressure, and hence a higher energy consumption to drive higher recovery as pressure difference is the main driving force for water transport through the RO membrane. This is in coherence with eq. 3-17 as water transport i.e. water recovery is directly proportional to the net driving pressure applied on the membrane, which is directly proportional to the feed pressure as well as per eq. 3-16.

Figure 4.43 shows the dependence of permeate TDS and permeate flux on the recovery, in which permeate flux has a linear relation with recovery, however, permeate TDS have a strong dependence, close to exponential on recovery. The higher the recovery of the RO system, the higher the feed pressure required. This, in turn, leads to higher transport of water according to eq. 3-17, which results in higher concentration of salt on feed/brine side of the membrane, which leads to higher salt transport according to eq. 3-18, hence increasing the salinity of the permeate.

Figure 4.44 shows dependence of saturation indices for calcium sulfate, calcium carbonate (as SDSI), and silica on recovery, indicating linear dependence, the figure shows as well that recovery should be limited to 75-78% to avoid exceeding the saturation limit of gypsum, which was found to have an exponential type of dependence on system recovery. Upon increasing the recovery, more water is extracted from the feed/brine membrane side, which results in increase of concentration of different ions present in feed as with a concentration factor up to 4 or 5 at recoveries of 75 and 80%, respectively in accordance to equation 2-1, which in turn increases the ionic activity product to levels close to that of solubility product as explained in 2.6, and hence leading to scale formation. Addition of antiscalant helps inhibit the crystal growth and scale formation above saturation levels as shown in figure 4.44

The results obtained for the base case indicating that the maximum operating recovery is limited to 75%, so for a feedwater of 100 m^3/d (4 m^3/h). The summary of results obtained is outlined in table 4.13 with and without feed-product blending. The model results indicated that a total of 12 membrane elements are required, arranged in 3 parallel pressure vessels, 4 membrane elements each. The permeate product will have a salinity of 67 mg/l and specific energy consumption of 1.26 kW/m^3. Exploring feed by-pass as one of the mixing options with final product salinity of 500 mg/l as an objective, the system was found to have an overall recovery of 77% with specific energy consumption of 1.13 kW/m^3.

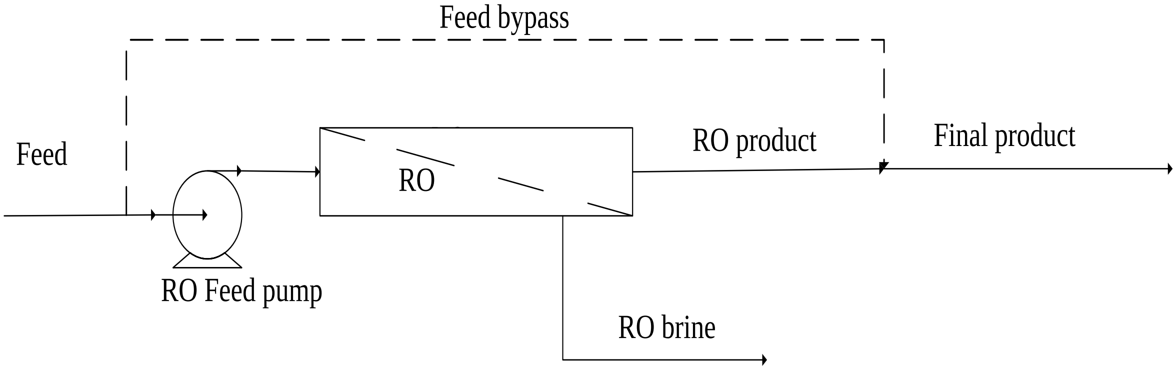


Figure 4.41 Schematic diagram for the base case.

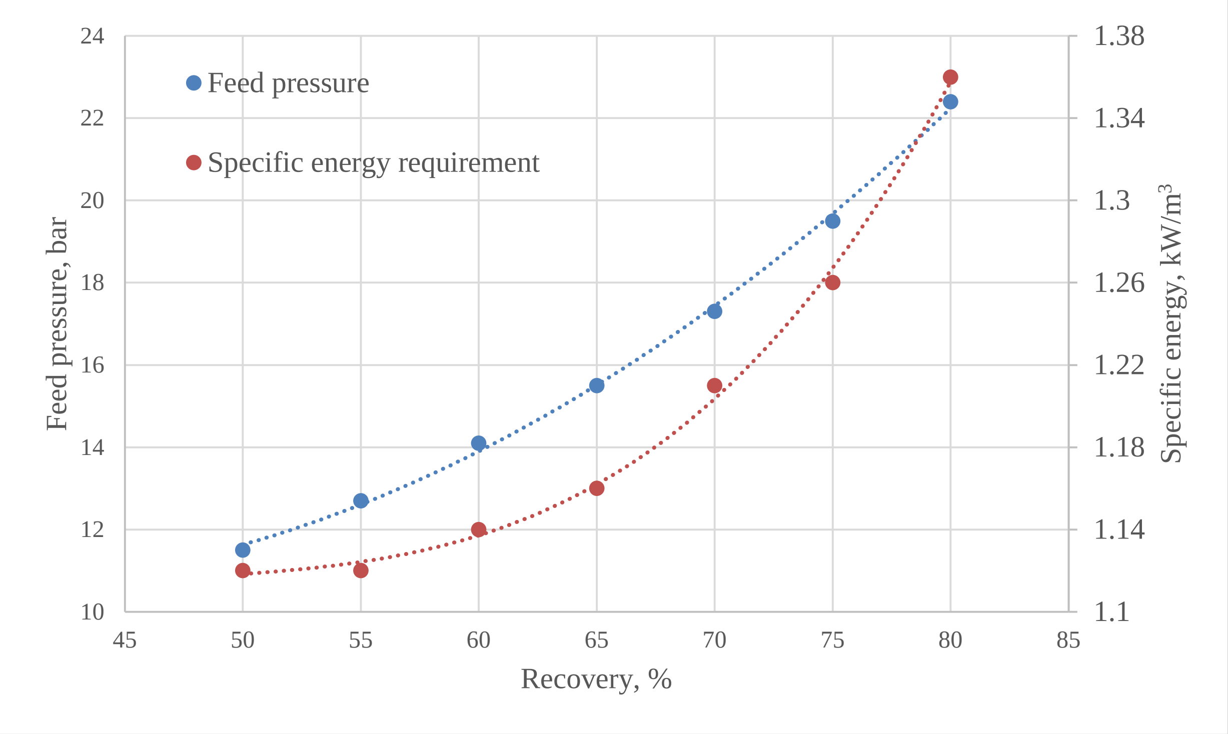


Figure 4.42 Feed pressure and specific energy requirement for single RO at different recoveries.

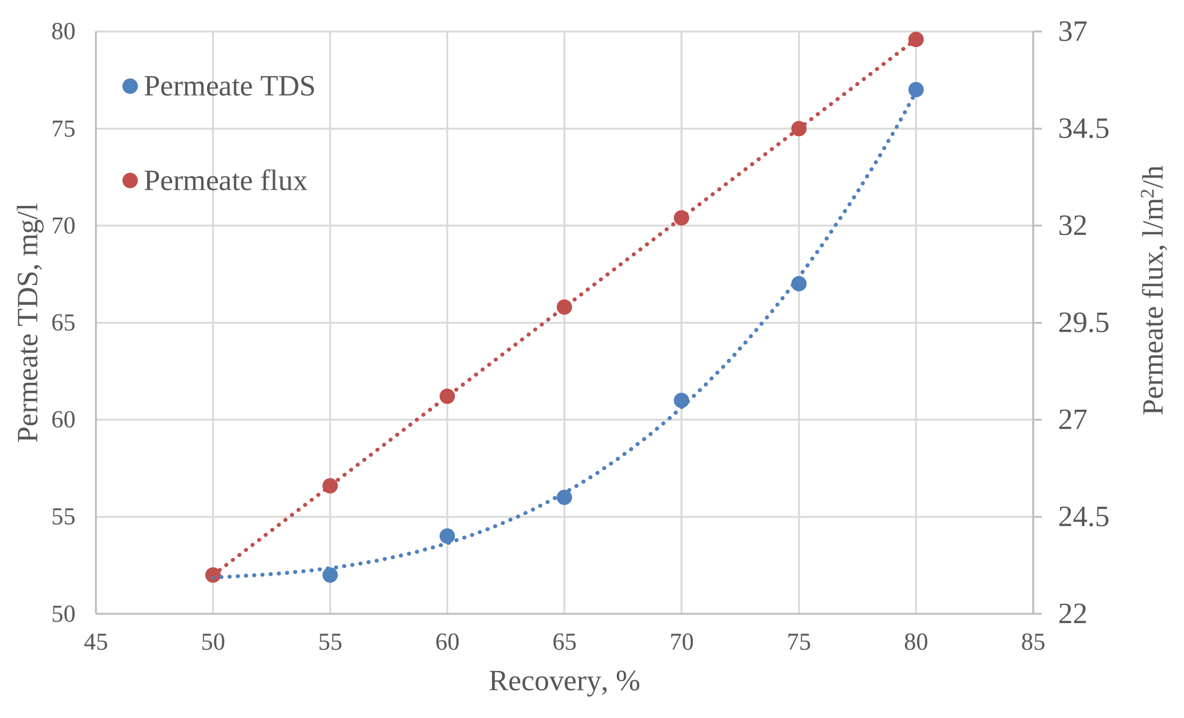


Figure 4.43 Permeate TDS and flux for single RO at different recoveries.

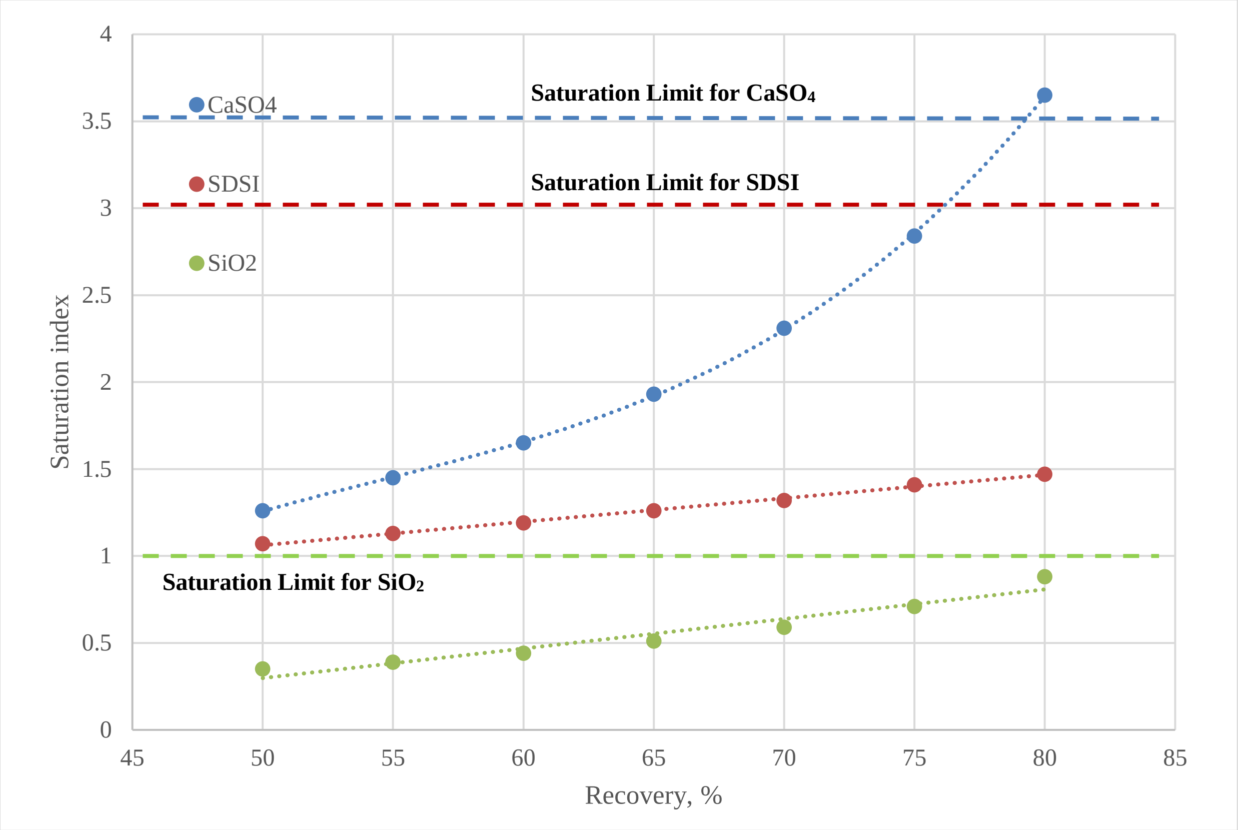


Figure 4.44 Saturation indices for different scales in single RO at different recoveries.

4.6.3.2 Zero Liquid Discharge Case of Brackish Groundwater Desalination Plant.

The second case to be considered for the proposed zero liquid discharge, in which two RO units are involved with the intermediate chemical treatment of the brine with ultra-high lime with alumina UHLA as an advanced lime softening process. As in the base case, the brackish groundwater quality and flowrate were input to the complete process model developed and utilized in Aspen Plus V8.8, utilizing the RO model developed in the Aspen Custom Modeler ACM.

In order to better understand the simulation results, it is very important to investigate the results of each unit individually. In order to be able to compare the performance of the ZLD scheme with the single unit scheme, the feed flowrate to the primary RO unit has been fixed at the same value of 4 m^3/h, and let the model calculate the system feed required. The results obtained by the complete process model for the primary RO was basically the same as those obtained as single RO unit, which is well expected.

The main difference in performance should result from the effect of performing the chemical treatment of the brine stream, and the further desalination in the secondary RO unit. The results obtained for the performance of the chemical treatment unit is shown in figure 4.45 as a function of lime dose for sodium aluminate dose of 10 mM. The figure shows that there is a strong dependence of sulfate removals to the medium pH, reaching steady state removal at a lime dose of about 40 mM, at which sulfate removal reach about 70%.

It is also worth mentioning that alkalinity as bicarbonate has been completely removed at all lime doses, which is due to the increased pH value, with precipitation as calcium carbonate and/or calcium/magnesium carbonate i.e. dolomite. Strontium and barium have been completely removed as well over the lime dose range in a fashion similar to that of alkalinity, mainly as sulfates of strontium and barium. Calcium removal seems to decrease as the lime dose increase, which is mainly due to the increased total calcium present in the brine as lime dose increases.

It has been noticed as well that there is a drop of the overall stream salinity. This is mainly due to the very high removal of some constituents such as magnesium, alkalinity, and silica, as well as to the partial removal of sulfate and calcium, in spite of the increase in sodium concentration due to the addition of sodium aluminate. The removals of sulfate, silica, and alkalinity obtained during the chemical treatment made the treated brine undersaturated with respect to calcium sulfate, calcium carbonate, and silica enabling further desalination of the brine stream.

The performance of the secondary RO unit has shown a very similar trend to that obtained for the primary RO unit as shown in figures 4.46 – 4.48. The main differences are the feed pressure ranges, which is to be higher ranging from 20 to 35 bars compared to 11.5 – 22.5 bars for the primary RO. This is mainly due to the higher osmotic pressure of the secondary RO feed of 7.15 bar relative to 2.25 bar for the primary RO feed. In addition, specific energy follows the same trend as pressure, with values in the ranges of 3.15 to 3.8 kW/m^3 relative to 1.1 to 1.35 kW/m^3 for the primary RO unit.

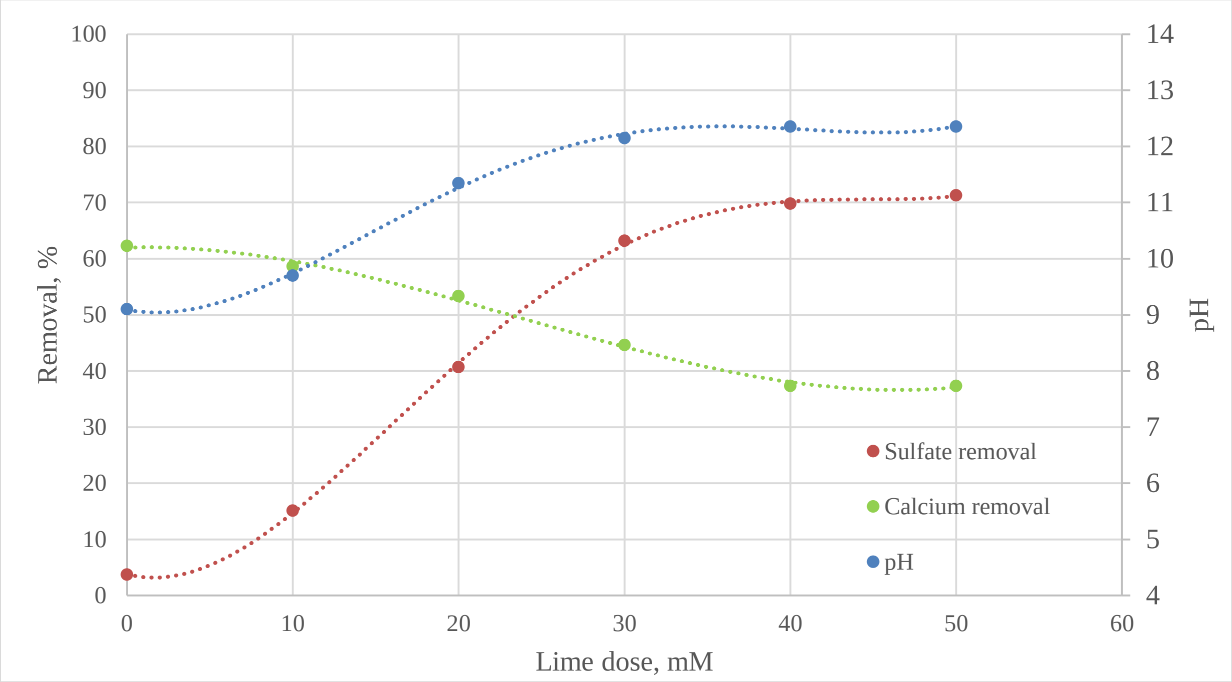


Figure 4.45 pH value and removals during the chemical treatment of brine at different lime doses and 10 mM of sodium aluminate.

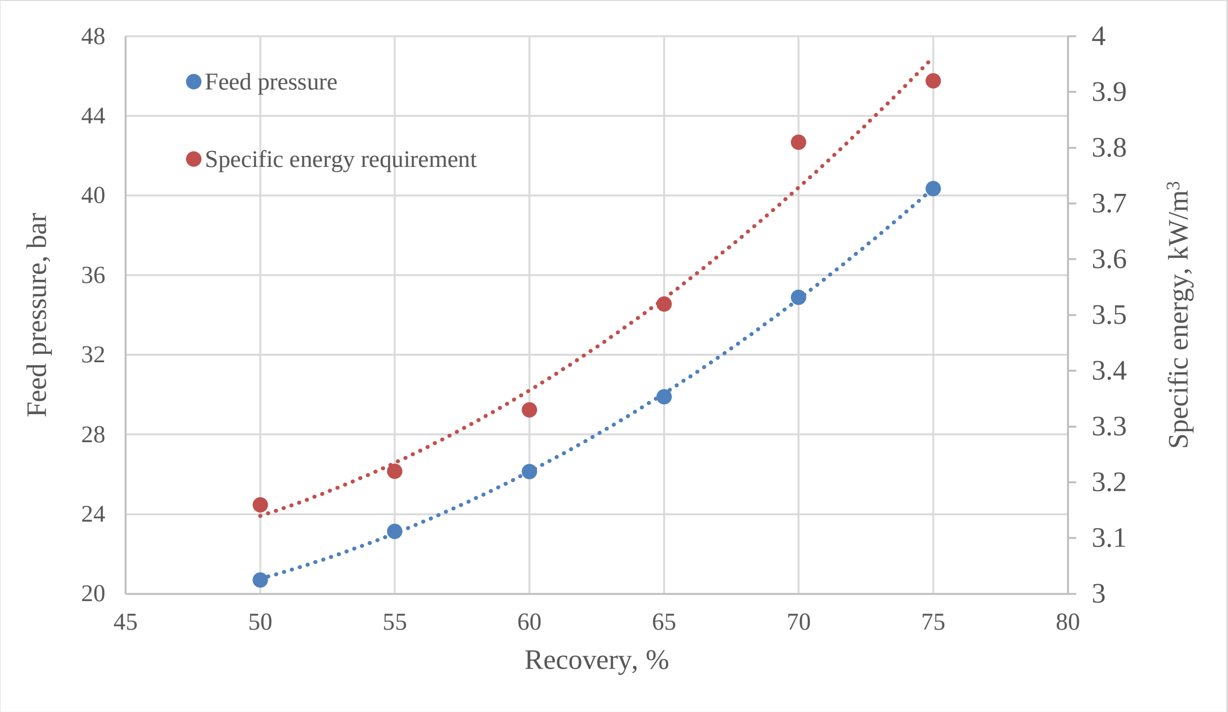


Figure 4.46 Feed pressure and specific energy requirement for secondary RO at different recoveries.

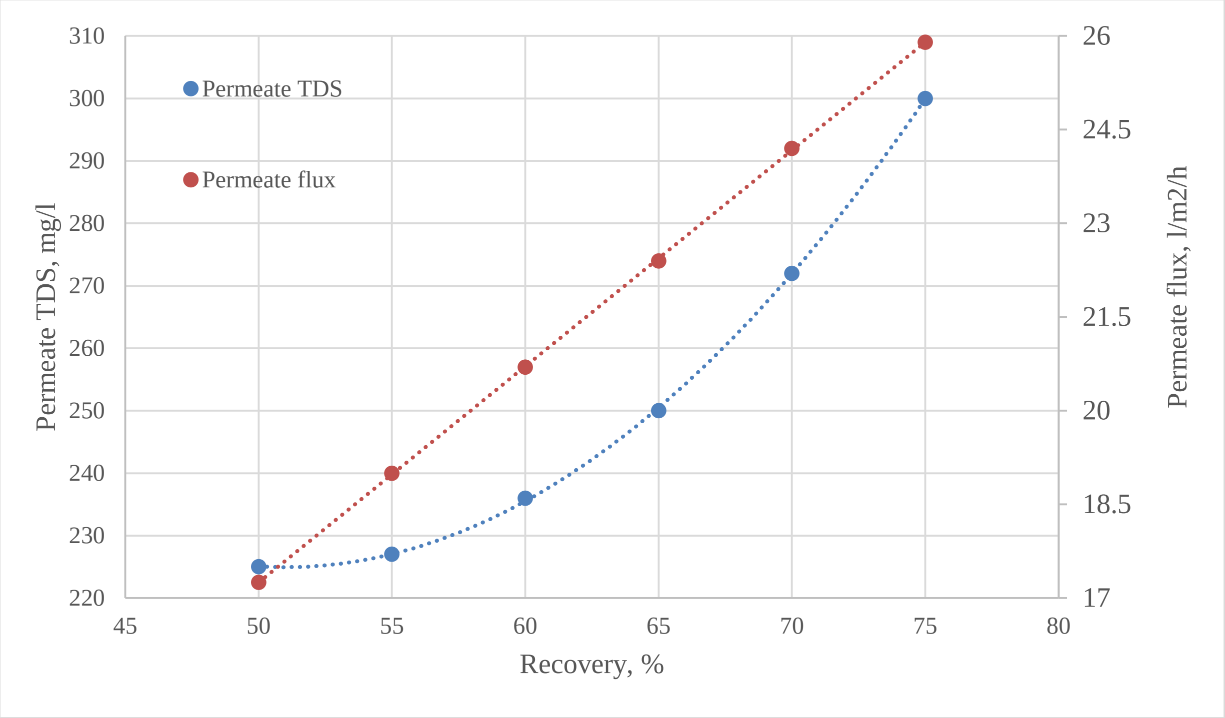


Figure 4.47 Permeate TDS and flux for secondary RO at different recoveries.

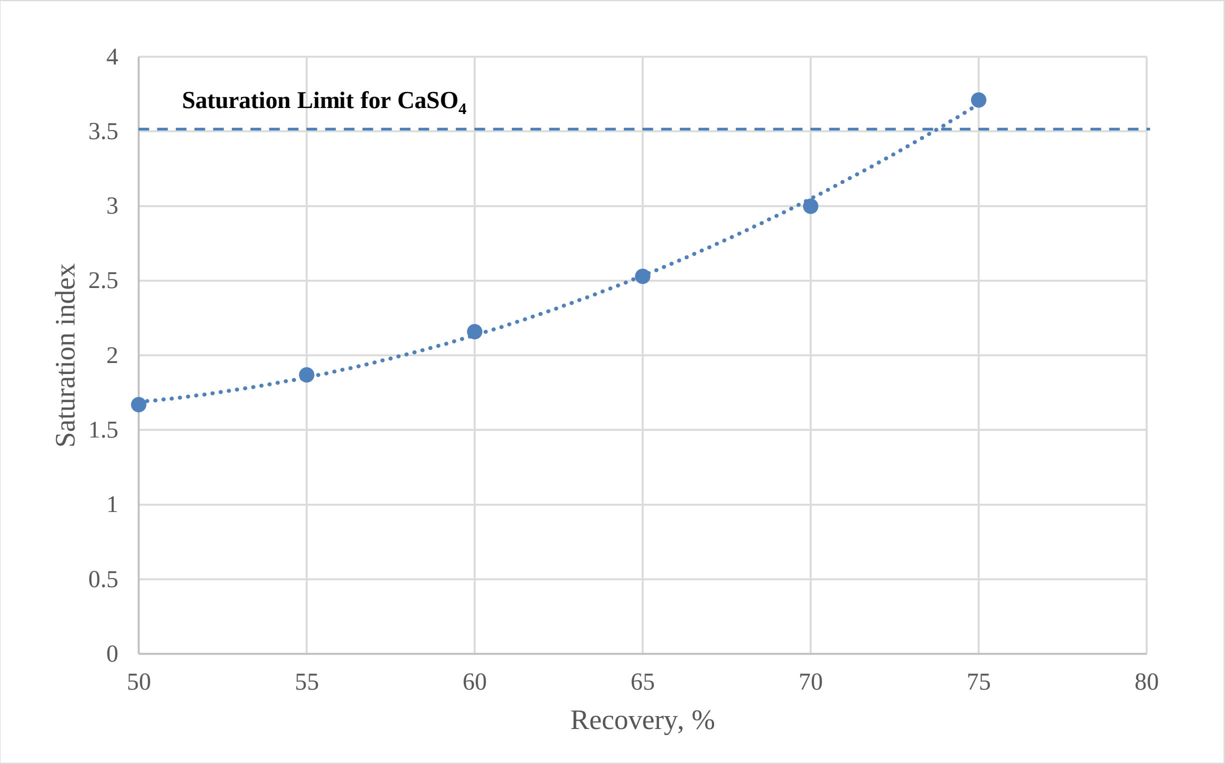


Figure 4.48 Saturation index of calcium sulfate in secondary RO at different recoveries.

Permeate flux was lower compared to those obtained for the primary RO, in addition to higher permeate salinity due to the higher salinity of the feed, and higher operating pressures. The almost complete removal of silica, and calcium carbonate during the intermediate chemical treatment results in the absence of any scaling prosperity due to these two constituents. However, saturation of brine with respect to calcium sulfate limit the recovery to only 70% in the secondary RO unit, despite the high sulfate removal of about 65% during the chemical treatment.

The results obtained for the zero liquid discharge ZLD case indicate that the maximum operating recovery is limited to 75% and 70% for the primary and secondary RO units, respectively, with the intermediate chemical treatment of brine for removal of most scale-forming constituents. The summary of results obtained for the base case and the ZLD case are outlined in table 4.13 for the two options of no feed-product blending, and feed-product blending.

Table 4.13 shows that the proposed ZLD scheme can increase the system recovery from 75% up to 92.5% without feed blending to get a product water quality of about 108, which is far acceptable for drinking and irrigation purposes. The recovery increases to 93.4 with feed blending to get a product quality of 500 mg/l that meets the guidelines for drinking water quality, and far better for irrigation purposes.

The specific energy consumption for single unit conventional groundwater desalination was found to be 1.26 kW/m^3 without feed blending, dropping to 1.13 kW/m^3 with feed blending, however for the proposed ZLD the energy consumption was higher at 1.75 kW/m^3 without feed blending, and it drops to 1.51 kW/m^3 with feed blending. The increase in energy consumption was about 39% for the case of no-feed blending, dropping to 33% with feed blending, which pays off for recovery increase of 17.5% and 16.4% respectively. Given the legal and environmental limitation on brine disposal, it is very crucial to increase the recovery at affordable energy consumption.

The increased recovery upon feed blending indicates the importance of optimizing the proposed ZLD process given the different stream options of flowrates and quality within the same general stream matrix of water. Further investigations of stream mixing options of bypass and recycling should be screened and tested as it might result in further increase of overall system recovery, and reduction of chemicals to be used. The cost associated with the proposed ZLD should be considered as well as process system engineering and optimization. However, the focus of this work was to investigate the feasibility of developing ZLD with the main objective of increasing the overall system recovery.

Table 4.13 Results summary for brackish groundwater desalination.

Parameter	**Single RO**		**Proposed ZLD**	
	No feed bypass	Feed bypass	No feed bypass	Feed bypass
System feed flowrate, m^3/h	4	4.346	4	4.6
Primary RO feed flowrate, m^3/h	4			
Feed salinity TDS, mg/l	4,250			
Primary RO brine flowrate, m^3/h	1			
Primary RO brine salinity TDS, mg/l	16,800			
Primary RO product flowrate, m^3/h	3			
Primary RO product salinity TDS, mg/l	67			
Primary RO recovery, %	75			
Secondary RO feed TDS, mg/l	-		11,260	
Secondary RO brine flowrate, m^3/h			0.3	
Secondary RO brine salinity TDS, mg/l	-		36,950	
Secondary RO product flowrate, m^3/h	-		0.7	
Secondary RO product salinity TDS, mg/l	-		270	
Secondary RO recovery, %	-		70	
Feed bypass flowrate, m^3/h	0	0.346	0	0.6
System product flowrate, m^3/h	3	3.346	3.7	4.3
System product salinity TDS, mg/l	67	500	108	500
Overall system recovery, %	75	77	92.5	93.4
Overall Specific energy consumption, kW/ m^3	1.26	1.13	1.75	1.51

Rahardianto et al. (Rahardianto et al., 2007) has reported high recovery of desalination system of about 95–98% for brackish water from Colorado river, which has a salinity of about 1,000 mg/l, achieving about 90% recovery in the primary RO alone, mainly due to the low feed salinity and low scaling propensity as calcium sulfate, and silica saturation hit as low as 0.07, and 0.1 respectively, a combined with low calcium, sulfate, silica, and alkalinity as low as 95, 322, 11.6, and 174 mg/l.

Precipitative softening accompanied by air stripping was proposed and tested by Hasson et al. (Hasson, Segev, Lisitsin, Liberman, & Semiat, 2011; Segev, Hasson, & Semiat, 2011) to increase the overall recovery from 78% to 90% for brackish water, with brine salinity of about 9,500 mg/l, however this brine was lean in sulfate with sulfate concentration of about 614 mg/l, and hence low scaling propensity of gypsum, and the main process objective was to desupersaturate the brine with respect to calcium carbonate.

The literature contains some work aimed at developing high recovery desalination systems of brackish groundwater, aiming at recovery above 90%. McCool et al. (McCool et al., 2013) have achieved overall recovery of about 83% and 93% for straight-through and by-pass/recycle schemes, respectively, of brackish groundwater from agriculture drainage at San Joaquin Valley of central California, utilizing Chemically-Enhanced Seeded Precipitation CESP. CESP works to desupersaturate the brine with respect to calcium carbonate and calcium sulfate. Primary RO brine has a saturation index of about 1.71, relative to 3.5 in the current study, in which CESP was able to reduce it to 1.15.

Work conducted by Sanciolo et al. (P. Sanciolo, Milne, Taylor, Mullet, & Gray, 2014; Peter Sanciolo et al., 2012) on silica removal from brine rich with silica up to 160 mg/l from RO desalination of groundwater from an Australian mining and processing operation has reached an overall recovery of about 90-95%, however the brine with lean in alkalinity, calcium, and sulfate at concentrations of about 510, 280, and 810 mg/l, with saturation indices for LSI, calcium sulfate, and silica of 1.8, 0.16, and 0.81 respectively. Removal of silica by adsorption to activated alumina AA was found to be very effective. However, it was associated with high capital and operating costs up to \$5.6/m^3.

Closed Circuit Desalination CCD of brackish groundwater is another technology looking to deliver high recovery systems (Efraty, 2012; Septon & Efraty, 2016) achieving about 88 - 90% overall recovery brackish groundwater at salinity of about 6000 mg/l, however the process encountered some difficulties for applications at large scale, and was very sensitive to feedwater quality.

In conclusion, the proposed process for zero liquid discharge for brackish groundwater desalination in this study has been found to be very effective and promising, while achieving a benchmark overall recovery of about 93.4% at reasonable treatment levels and process mixing. The overall recovery of 93.4 achieved in this work is distinctly higher than most of the reported literature for similar systems, which achieved only up to 90% for lower salinity brackish groundwater. The process has more potential of maximizing the recovery at higher treatment levels to be applied during the intermediate chemical treatment, which in turn increases the achievable recovery in the secondary RO. Furthermore, investigation of more stream mixing, specifically, treated brine recycle in addition to feed-bypass has huge potential to increase the overall system recovery beyond 95%.

V. SUMMARY AND CONCLUSIONS

Groundwater is generally considered as one of the main water sources for public water supplies, specifically for rural communities. In general, groundwater is considered to have high and quite uniform quality. However, a disadvantage of groundwater supplies is that it have moderate-to-high dissolved solids, which in turn led to the use of desalination to produce good quality water.

Desalination is a reliable process which is used to reduce the content of dissolved solids in water, with high technical and economic feasibility. Membrane desalination processes in general, and reverse osmosis RO membrane processes, in particular, have a high share of desalination market, due to their favorable low power requirements, moderate, and flexible capacity to different necessities. Nevertheless, the major problem of desalination is the generation of concentrate or brine stream that has to be properly managed to avoid many environmental issues.

In brackish groundwater desalination, fouling by sparingly soluble salts i.e. scaling is a phenomenon that results in a decline of water production at certain energy input in desalination process, so it is essential to operate at recovery levels that fouling is not likely to happen. Moreover, working at low recovery to mitigate fouling will increase the volume of brine generated, which representing the main trade-off.

Management of brine from brackish groundwater desalination plants, which usually located far from the coast or natural water channels i.e. inland is a significant problem. Options for brine disposal are limited, more specifically for inland desalination plants. Options are evaporation ponds, deep-well injection, disposal into surface water bodies or municipal sewers, and finally irrigation of plants tolerant to high salinities.

Factors influencing the selection of a disposal method are the quantity or volume of brine, the quality and chemical composition of brine, physical and geographical characteristics of plant location, and finally capital and operational costs. Improper disposal can result in many environmental problems such as leakage to groundwater resources, decline in production from agricultural lands, the formation of eyesores, and unsuitability of treated municipal sewage effluent for irrigation. In most cases of inland desalination, brine management is very critical, and hence the demand for efficient inland desalination has become essential worldwide.

Where concentrate management is a problem, the alternative is Zero Liquid Discharge ZLD, in which concentrate or brine is treated for further water production, leaving semi-dry salts. Most ZLD processes in application today treat industrial wastewater using thermal and/or membrane processes. However, thermal processes are known for high energy consumption with high operational and capital, in addition, application of membrane processes alone was not found to be successful to provide complete ZLD solution.

Given the need for ZLD for inland desalination and the different drawbacks of existing methods, it is imperative to develop an affordable ZLD treatment process for concentrate management. The approach proposed in this study for ZLD for the case of inland desalination is to treat the brine generated chemically in such way to have it suitable for further processing, the treatment aims to reduce or eliminate the scale-forming material, that limits the recovery in membrane systems, and to further process it, enabling more recovery of water, and further reduction in the volume of final brine that can be processed final solid-liquid separation process.

Therefore, the goal of this work is to develop an efficient and environmentally benign process for brackish groundwater inland desalination of that approaches Zero liquid discharge ZLD. The technical approach for the proposed ZLD process is to combine two-stage RO units with highly efficient intermediate brine treatment process to remove the scale-forming constituents, making the brine suitable for further and more efficient processing in secondary RO unit. The application of intermediate treatment will lead to maximizing recovery and minimizing the volume of final brine stream that to be managed at an affordable cost.

The goal of this work was achieved by accomplishing the following objectives:

1) Preliminary process analysis of groundwater: performing a quantitative and qualitative assessment of groundwater resources at specific study area as case-study.
2) Preliminary process analysis of brackish groundwater desalination: for the previously studied groundwater resources, with respect to recovery limitation i.e. scale-forming constituents.
3) Study the kinetics and equilibrium of the removal of scale-forming material in the proposed advanced lime-softening based chemical treatment processes at bench scale.
4) Develop equilibrium model to simulate the chemical treatment process, to predict the effluent water quality and solid precipitates formed under different treatment conditions.

5) Identify beneficial uses of solids produced during the intermediate chemical treatment as added value product.
6) Develop a complete processes model for the proposed ZLD scheme investigating the overall system recovery for a given brackish groundwater quality and flowrate.

Six-task program was conducted to accomplish the six research objectives. The first task was to perform a preliminary analysis of groundwater resources in arid areas, with a specific case study in the State of Qatar. The assessment focuses on studying groundwater resources both quantitatively, in terms of groundwater balance, and qualitatively, in terms of groundwater salinity in general, and other constituents related to different purposes of drinking and irrigation. The quantitative assessment has shown that the groundwater balance is always negative due to the low rainfall, which when combined with the high evaporation rates, result in minimal aquifer recharge, along with an increase in abstractions for rural communities and agriculture activities.

The qualitative assessment of groundwater resources has shown that most of the groundwater wells have water quality unsuitable for drinking purposes, and only about 10% of the wells have a groundwater suitable for irrigation purposes, and about 16% having a high salinity of more than 5,000 mg/l. Other components such as the individual ion concentrations and sodium adsorption ratio SAR for irrigation water has been studied as well, and most cases it exceeds the set limits for irrigation water quality. The overall conclusion from the assessment was the necessity of applying desalination processes to be able to utilize such groundwater resources for obtaining water suitable for drinking and irrigation purposes.

The second task focused on preliminary process analysis of brackish groundwater desalination in membrane processes, with a focus on the maximum achievable recovery, as well as the quality and characteristics of the resultant concentrate stream. Focus was given to scaling tendency by different sparingly soluble salts in specific as found to be the recovery limiting factor for the desalination, thus helping determine the target components to be removed from concentrate stream during the chemical treatment process in order to increase the overall system recovery.

It was found that most of the groundwater in the case-study area, i.e. the State of Qatar, is saturated with respect to calcium carbonate as indicated by the positive values for the LSI and SDSI. On the other hand, saturation with respect to calcium sulfate was found to present only 15%

of the wells, while with respect to silica saturation, all groundwater was found to be undersaturated with maximum silica concentration of 24 mg/l. Although most of the groundwater was found to be undersaturated with respect to calcium sulfate, supersaturation with respect to calcium sulfate was found to be the main recovery limitation, with recovery ranging between 60 to 85%, with groundwater having a low recovery in the range of 60-70% in about 20% of groundwater.

The third task aimed at studying the kinetics and equilibrium of sulfate and silica removals during the proposed chemical treatment of ultra-high lime with alumina UHLA process. The effect of different parameters such as feedwater quality i.e. salinity, initial concentrations of such scale-forming constituents, doses of chemical reagents for the softening processes. The experimental work mainly focused on the removal efficiency of different scale-forming constituents from model saline solutions of brackish groundwater concentrate with respect to sulfate and silica.

The kinetics experiments revealed that high removals of sulfate of more than 85% could be achieved within 6 hrs, and reasonable removal of 70-80% can be achieved within 2 hrs from water containing only sulfate. Silica removal, on the other hand, was found to be very fast with more than 95% removal within 0.5 hr. Similar results for the removal of sulfate and silica were obtained for model brine solution that mimics the actual groundwater brine with interaction from other ions in water at high ionic strength.

The increase of lime and sodium aluminate doses were found to improve the removal efficiency of both sulfate and silica. However for sulfate removal it was found that the highest removal was obtained at lime: sodium aluminate: sulfate molar ratio of approximately 3:1:1, meanwhile lime alone was found to be very effective for removal of silica, which was further improved with the addition of sodium aluminate.

Other factors such as initial sulfate or silica concentration, temperature, mixing speed, ionic strength, and the presence of chloride as interacting ion were found to have little effect on the removal efficiency, however, pH was found to have a high effect on silica removal, with silica removal dramatically decreases at pH values above 13. This might be due to the formation of soluble solid phases at this pH, or less lime available for reaction as lime solubility is minimal above pH of 12.5. This trend was also observed during the study of the equilibrium removal of sulfate and silica from the model brine solution.

The intermediate chemical treatment process based on advanced lime softening of ultra-high lime with alumina UHLA process proposed and examined in this study was found to very effective for brine treatment. In addition to the high removal of silica and alkalinity, as in most intermediate chemical treatment processes available in the literature, this process was found to be highly effective for removal of sulfate far below 1,200 mg/l, which is achieved in other treatment processes. This very high removal was attributed to the aluminum ion introduced in this treatment as sodium aluminate, which results in forming of more complex solids of calcium aluminosilicate and calcium sulfoaluminate as confirmed by XRF and XRD analysis, the main characteristic of such salts is the very low solubility.

The fourth task was dedicated to developing an equilibrium model for the chemical treatment process that is able to predict the effluent water quality as well as the formed solid precipitates at specific influent water quality, chemical reagents, and reagent doses. OLI stream analyzer was used to model the chemical treatment as a powerful modeling tool for mineral equilibrium in water systems. The OLI results have been compared and validated versus the different experimental results obtained in the third task.

OLI was found to well predict the removals and concentrations of different constituents at different conditions of lime and sodium aluminate reagent doses. The relative error was different from one output to another, from about 2.5% at low lime doses, to about -13% at high lime doses, increasing as sodium aluminate dose increases. This indicates that OLI can be used to predict sulfate removals at low lime doses very well, while for silica removal the relative error was ±1.2% indicating that silica removals can be well predicted using OLI at all lime and sodium aluminate doses range. OLI was found to predict calcium concentration and pH in water very well with a relative error within ± 4 - 8%.

The equilibrium modeling of the chemical treatment process is very helpful, as it can be efficiently utilized for the overall ZLD process modeling, as OLI equilibrium modeling package can be easily integrated into a wide number of process simulators. This is a novel approach for modeling of ZLD systems, which helps to reduce time and cost associated with bench and pilot testing of different chemical processes for different brine qualities.

The fifth task was to identify and characterize the solids formed during the chemical treatment of brine and to investigate the beneficial uses of such solids. The solids precipitated are expected to be mainly calcium and magnesium salts of carbonate, sulfate, silicate, and aluminate depending on the chemical reagents used and treatment levels. Utilization of such solids offers the potential to lower overall process costs and potential environmental problems associated with solid waste disposal, being considered as added value products. The solids produced during the chemical treatment of the brine has been predicted by the developed equilibrium modeling and characterized by analysis of solids using X-Ray Diffraction XRD and X-Ray Florescence XRF techniques.

Results from equilibrium model indicated that the treated brine is supersaturated with calcium carbonate i.e. limestone, calcium sulfate i.e. gypsum, calcium/magnesium carbonate i.e. dolomite, magnesium hydroxide, calcium/magnesium silicate, calcium aluminosilicate i.e. ettringite, and calcium aluminosilicate, in addition to any unreacted lime or sodium aluminate.

XRF elemental analysis has shown that elemental composition has varied mainly depending on the lime and sodium aluminate. Calcium was found to be present by about 43–49%, followed by S (as an indication for sulfate) by about 16-19%, and aluminum at the range of 9.8–13.7%, and magnesium at 1–3%. XRD analysis has confirmed the presence of the solids expected from the equilibrium model and furthermore identified the chloride-containing solid phase as indicated the presence of Friedel's salt, which is calcium chloroaluminate salt $Ca_2Al(OH)_6Cl.(H_2O)$.

The applications identified for the solids produced mainly depend on their chemical composition, however, due to low quantity produced, in addition to being a mixture of different solids, general use, in which the solids are used directly, is highly recommended. Applications require solids containing calcium, magnesium, aluminum, sulfate and silica can be the best fit for utilizing such solids. These applications can be cement industry, fillers, or road pavement. Other high-value applications of solids such as calcium aluminsulfate, calcium aluminosilicate, and calcium chloroaluminate, which is known to belong to layered double hydroxides that have a wide range of applications as catalyst and catalyst support, adsorbents, and ion exchange resins are possible but will require sophisticated separation and purification processes.

The sixth task was dedicated to developing a complete process model enabling the study of the effect of different process variable on the process performance, and more specifically the overall system recovery. A complete process model with primary RO, chemical treatment, and secondary RO has been built in Aspen Plus simulation environment with membrane separation model to model the RO unit built in Aspen Custom Modeler ACM, to ease the parameter estimation and process performance optimization.

Membrane separation model has been built in ACM and validated versus experimentally obtained data from small lab scale RO unit. Experimental data were utilized to estimate the different model parameters of permeability coefficients of water and different ions through the membrane, as well as the friction coefficient for feed and permeate flow through the feed and permeate channels respectively.

The membrane separation model developed in this study has distinguished advantage over membrane separation models available in the literature by the distinct treatment of mono-valent and di-valent ions, estimating different permeability coefficient for each. This is different from most of the models which consider only water and salt permeability coefficients. This was found to better model and simulate the performance of the membrane system as it accounts for the different nature of ions present in water according to their ionic valency, as well as to the fact that salt is highly dissociated in water under different conditions.

The complete process model of the primary and secondary RO units, utilizing the user defined membrane model built in ACM, along with Aspen ready models for mixing and precipitation to simulate the chemical treatment unit. The complete model has utilized the OLI as the property model, so it can model the mineral equilibrium attained during the chemical treatment of brine stream from the primary RO unit, as well as accurately calculate the osmotic pressures and activity coefficients. The complete process model was then tested for a given feedwater quality and flowrate in order to simulate the proposed ZLD to calculate the overall system recovery and quality of product water, at maximized recovery conditions.

The results obtained show that the overall system recovery has increased from 75% for conventional brackish groundwater desalination (as base case) with product salinity of 67 mg/l to about 92.5% with product salinity of 108 mg/l for the proposed ZLD that are far below the guideline for drinking water salinity, with intermediate chemical treatment removing about 65% of sulfate present in the brine stream. This was associated with an increase in the specific energy required from about 1.26 kW/m^3 to 1.75 kW/m^3 by 39% of energy consumption relative to 17.5% increase in water recovery. Nevertheless, due to legal and environmental consideration, this 17.5% increase in recovery is highly valuated.

The model results show that overall recovery can be increased by considering feed-bypass or to product water to obtain final product quality of 500 mg/l, which is the drinking water salinity guideline. In this case the recovery increased from 75% for the conventional RO to 77%, and from 92.5% to 93.4% for the proposed ZLD, along with lowering the specific energy required from 1.26 kW/m^3 to 1.13 kW/m^3 for the conventional RO and from 1.75 kW/m^3 to 1.51 kW/m^3 for the proposed ZLD.

The increased recovery upon feed blending indicates the importance of optimizing the proposed ZLD process given the different stream options of flowrates and quality within the same general stream matrix of water. Further investigations of stream mixing options of bypass and recycling should be screened and tested as it might result in further increase of overall system recovery, and reduction of chemicals to be used. The cost associated with the proposed ZLD should be considered as well along with process system engineering and optimization. However, the focus of this work was to investigate the feasibility of developing ZLD with the main objective of increasing the overall system recovery.

The complete process model developed is an efficient tool to simulate the behavior of the proposed ZLD system under different operating conditions and feedwater qualities. The model will effectively enable process optimization and cost estimation to maximize overall recovery at a reasonable cost. The complete processes model applied a novel approach to developing custom model for the RO unit in a well-established and highly effective simulation environment of Aspen Plus utilizing Aspen Custom Modeler, as well as building the complete simulation of the process in the Aspen Plus, in addition to utilizing OLI, which has effectively used for the equilibrium modelling of chemical treatment, through OLI engine Add-Ins in Aspen Plus.

In conclusion, a process for high recovery brackish groundwater desalination for the inland plant has been developed in this work. The results obtained 93.5% overall recovery approaching zero liquid discharge, compared to about 90% for another high recovery brackish water desalination processes. The approach adopted to chemically treat the brine from traditional RO making it suitable for further processing in secondary RO, was found to be very efficient. The complete process model developed in this study was found to simulate the performance of the proposed ZLD scheme very well enabling process design of such systems at different feedwater qualities and flowrates. Recovery can be further increased with in-depth process system engineering and optimization. Utilization of final solid-liquid separation such as solar evaporation can provide an alternative to achieve complete ZLD utilizing renewable energy sources in the chemical-free process, as the water volume needs to be evaporated been far reduced, relative to initial volume from traditional RO groundwater desalination.

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APPENDIX A

GROUNDWATER DATA

A1. North Basin Groundwater Data

Well No.	TDS mg/l	EC µS/cm	pH	HCO_3^-	Cl^-	SO_4^{2-}	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sr^{2+}	Ba^{2+}	SiO_2
				mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/ l	mg/l	mg/l
A6	5720	9,533	7.59	212	2088	1536	1.0	369	142	1415	97.9	10.5	0.030	26
A9	3940	6,567	7.41	273	1213	1360	0.9	451	135	729	57.7	5.8	0.025	22
A10	2670	4,450	7.79	445	716	850	1.0	274	97	513	43.3	6.1	0.018	20
A11	3530	5,883	7.98	300	1202	897	0.9	254	90	823	56.2	12.0	0.018	20
A13	4050	6,750	7.67	264	1331	1153	1.9	351	121	842	63.2	6.7	0.019	19
A14	2230	3,717	7.08	217	680	597	2.0	229	50	428	36.3	8.2	0.020	16
A14a	1234	2,057	7.82	421	269	232	1.0	105	59	193	26.5	8.6	0.017	20
A17	7620	12,700	7.55	274	3341	1195	2.2	465	186	1904	76.4	14.3	0.030	16
A20a	1254	2,090	7.68	333	308	166	1.9	110	40	186	26.1	6.0	0.020	20
A24	2260	3,767	7.63	320	611	666	2.5	217	87	393	41.7	17.0	0.017	21
A26	3890	6,483	7.22	410	1439	592	1.0	332	123	692	103	6.2	0.018	20
A27	3200	5,333	7.67	300	961	882	2.0	213	79	741	35.1	12.0	0.019	22
B5	3600	6,000	7.09	244	906	1887	4.0	514	183	612	50.3	11.8	0.014	14
B6	2670	4,450	7.55	251	571	1467	2.8	285	150	508	73.7	7.0	0.016	17
B9	3210	5,350	7.01	338	622	1925	1.5	525	145	543	43.3	5.2	0.040	20
B16	3160	5,267	7.04	297	616	1868	1.5	527	129	524	48.0	5.3	0.040	21
B17	3150	5,250	7.07	300	611	1870	3.0	535	127	520	46.8	10.0	0.014	17
B24	3430	5,717	7.04	285	854	1838	2.5	515	202	538	41.0	15.0	0.012	24
B25	2890	4,817	7.41	282	501	1950	2.8	592	162	340	57.7	14.9	0.013	25
B26	2260	3,767	8.06	346	377	1390	3.3	407	148	262	45.6	17.0	0.020	25
B28	2700	4,500	7.82	303	413	1665	4.0	496	153	283	57.3	10.0	0.017	21
B30	2310	3,850	7.38	312	408	1435	3.0	396	164	269	51.9	8.0	0.010	19
B31a	1968	3,280	7.55	287	377	1044	2.0	237	109	338	54.2	6.0	0.017	23
B34a	5910	9,850	6.91	310	1935	2481	2.6	751	252	1175	63.2	17.5	0.010	33
B35	891	1,485	7.09	497	166	45	2.0	104	44	104	16.4	8.0	0.072	20
B39	2030	3,383	7.18	338	519	881	2.9	267	143	288	28.9	15.0	0.018	22
P1	1494	2,490	7.85	240	318	504	1.4	195	72	154	35.5	4.7	0.031	20
P22	3210	5,350	7.10	310	629	2070	2.1	474	202	554	50.7	5.4	0.022	21
P22a	3180	5,300	7.00	325	623	1874	2.1	488	156	534	49.5	5.5	0.023	22
UEA1	2510	4,183	7.42	202	436	1483	2.5	449	134	271	40.6	13.0	0.010	23
UEA2	3430	5,717	7.89	328	893	1492	2.6	481	141	568	46.0	14.0	0.010	24

A2. South Basin Groundwater Data

Well No.	TDS mg/l	EC µS/cm	pH	HCO_3^-	Cl^-	SO_4^{2-}	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sr^{2+}	Ba^{2+}	SiO_2
				mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/ l	mg/l	mg/l
B1	7260	12,100	7.62	77	3402	1592	3.8	543	207	1927	78.4	12.2	0.017	18
B10	3630	6,050	7.25	389	1014	1403	1.5	387	128	750	60.8	20.0	0.013	25
B19	3590	5,983	7.49	271	784	2120	2.8	680	166	499	42.1	12.2	0.015	26
B29	3580	5,967	7.49	270	796	2101	2.8	672	172	497	42.1	13.3	0.010	27
B43	6530	10,883	7.63	221	2255	2694	5.0	665	278	1484	87.4	15.0	0.016	23
C2	7490	12,483	8.12	219	2904	2939	4.0	764	361	1753	81.5	14.7	0.008	33
C2a	3540	5,900	8.05	161	1063	1577	3.5	464	114	729	40.2	14.3	0.012	30
C4	2730	4,550	8.10	176	1040	2005	2.3	627	195	587	33.2	13.0	0.008	30
P5	3850	6,417	8.11	163	1113	2028	1.9	674	178	616	35.9	20.0	0.020	31
P7	3430	5,717	8.17	182	951	1731	4.0	524	137	623	43.3	14.6	0.006	30
P16	771	1,285	8.38	226	197	119	2.9	119	38	64	12.1	13.0	0.010	31
P17	1407	2,345	8.50	479	349	391	1.3	262	69	152	14.8	21.0	0.021	31
P18	896	1,493	8.22	202	223	307	2.4	120	54	120	12.1	13.0	0.017	26

A3. Abu Samra Basin Groundwater Data

Well No.	TDS mg/l	EC µS/cm	pH	HCO_3^-	Cl^-	SO_4^{2-}	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sr^{2+}	Ba^{2+}	SiO_2
				mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/ l	mg/l	mg/l
M7	3480	5,800	8.10	184	1327	1033	5.0	323	135	773	35.9	12.0	0.014	14
M9	5630	9,383	8.11	199	2266	1712	6.0	511	196	1362	64.7	14.0	0.015	18
M14	3080	5,133	8.14	190	1140	974	7.0	331	124	642	30.0	12.0	0.014	16
M18	5110	8,517	8.06	104	1975	1623	9.0	518	84	1327	57.7	13.0	0.018	15
M21	3790	6,317	8.01	167	1163	1785		571	161	690	26.9			

APPENDIX B

Aspen Custom Modeler Code for Membrane Model

```
Model SPW

Ions as ComponentListName("OnlyIons");          // IONS component
WpIons as ComponentListName("WaterPlusIons");  // WaterIons
Ions_1 as ComponentListName("OneValentIons");
Ions_2 as ComponentListName("TwoValentIons");

// Parameters
Rgas                as RealParameter  (description:"Universal gas constant J/kmol/K/", value:8.315);
Ncel                as integerparameter(description: "Number of discetization segments", value:10);
MaximumRecovery     as RealParameter (description: "Maximum recovery",value:0.9);
MinRejection        as RealParameter (description: "Minimum rejection",value:0.9);
Multi               as RealParameter (description: "Multiplicator",value:1e5);
Valence(Ions)       as IntegerParameter(description: "Valence of ions");

// Domain

x as LengthDomain (HighestOrderDerivative:1, Length: 1, SpacingPreference: 1/Ncel,
DiscretizationMethod: "BFD1");

/*Model variables

  */
//------------------------------PORTS ---------------------------------------------------
  // Ports

Feed  as Input MainFeed  (Description:"Feed membrane port");
Brine as Output MainBrain (Description:"Brine outlet  port");
Perm  as Output MainPerm (Description:"Permeate outlet  port");

//--------------------------------Variables-----------------------------------------------
//-------------------------------------------------------------------------------------------
// Feed Connection variables

F_feed                  as flow_mol     (Description:"Molar flow rate, kmol/s");
```

```
// Membrane characteristics - permeabilities

L               as length       (description: "membrane length in meters",spec:Fixed);
W                as length       (description: "membrane width in meters", spec:Fixed);
Height_Brine      as length       (description:"feed channel height in meters",spec:Fixed);
Akoeff           as RealVariable (description: "coefficent for layer formation", spec:Fixed);
A                as RealVariable (description: "water permeability trough membrane",spec:Fixed);
B(IONS)          as RealVariable (description: "ions permeability trough membrane");
Beta1            as RealVariable (description: "ions permeability with valence of one  trough
membrane",spec:Fixed);
Beta2            as RealVariable (description: "ions permeability with valence of two  trough
membrane",lower:0);
Nleaves          as RealVariable (description: "Number of membrane leaves", spec:Fixed);
Hmt_dP             as RealVariable (spec:Fixed,value:1);
Hmt_Op             as RealVariable (spec:Fixed,value:1);
Kf               as RealVariable(description:"friction factor,units m2",spec:fixed);

// System variables
Recovery as RealVariable(description: "water recovery, % of water passed trough membrane");

// Model variables

Temp    as temperature (description:"System temperature, K");
Press_Brine as pressure (description:"Pressure on the brine side, Pa");
Press_Perm as pressure (description:"Pressure on the brine side, Pa",spec:fixed,value:1.01325);
F_Brine (Ions)    as Distribution1D (XDomain is x,  highestorderXderivative:1,description:"ions
brine molar flowrte") of flow_mol;
F_Perm  (Ions)    as Distribution1D (XDomain is x,  highestorderXderivative:1,description:"ions
permeate molar flowrte",initial,value.lower:0) of flow_mol ;
F_Solid (ComponentList)   as flow_mol (description:"solid component molar flowrate");
TotalFlowSolid     as flow_mol (description:"total solid component molar flowrate");
F_Brine_Water     as Distribution1D (XDomain is x,
highestorderXderivative:1,description:"permeate molar flowrte") of flow_mol ;
F_Perm_Water     as Distribution1D (XDomain is x,
highestorderXderivative:1,description:"permeate molar flowrte") of flow_mol ;
Press_Brine_Seg  as Distribution1D (XDomain is x,
highestorderXderivative:1,description:"Pressure on the brine side",initial,value.upper:Feed.P) of
pressure;
Press_Brine_Side ([0:X.EndNode] )as pressure;
Z_comp_brin(WpIons,[0:X.EndNode] ) as molefraction (description:"mole fraction of
component in brine",value:1);
Z_comp_perm(WpIons,[0:X.EndNode] ) as molefraction (description:"mole fraction of
component in permete",value:1);
Z_comp_surf(WpIons,[0:X.EndNode] ) as molefraction (description:"mole fraction of
component at membrane surface",value:1);
```

```
dens_water  as dens_mol_liq (description: "density of water at given T and pressure kmol/m3");
dens_Brine([0:X.EndNode])  as dens_mol_liq (description: "density of brine at given T and
pressure",value:1/Feed.V);
dens_Perm([0:X.EndNode])  as dens_mol_liq (description: "density of permeate at given T and
pressure",value:1/Feed.V);
dens_Surf([0:X.EndNode])  as dens_mol_liq (description: "density at memb surface at given T
and pressure",value:1/Feed.V);
viscosity_brine([0:X.EndNode]) as viscosity (description: "viscosity of brine,units cP");
gamma_surf (WpIons,[0:X.EndNode]) as  act_coeff_liq(value:1);//
J_salt(Ions,[0:X.EndNode]) as flux_mol (description:"Molar flux of
components",units:"kmol/hr/m2");
J_water ([0:X.EndNode]) as flux_vol (description:"Volumetric flux of water",units:"m3/hr/m2");
PI_osmtic_surf ([0:X.EndNode]) as pressure (description:"Osmotic pressure at membrane
surface Pa");
PI_osmtic_surf_ideal ([0:X.EndNode]) as pressure (description:"Ideal osmotic pressure at
membrane surface Pa");
koeff ([0:X.EndNode]) as RealVariable (description:"coeffiecent of polarization zone, m/s");
vel_B ([0:X.EndNode]) as velocity (description:"velocity from brine side");
Osm_coeff([0:X.EndNode]) as RealVariable (description:"osmotic
coefficient",lower:0.6,upper:1.6);
Rejection (Ions) as RealVariable (description:"Rejection of Components");
One_ions_comp as realvariable;
Two_ions_comp as realvariable;

AratioBrine as realvariable;

AratioPerm as realvariable;

Feed.F = F_feed*(Nleaves  - 1)*2;

For component in ComponentList Do

If component in WpIons then

 F_Solid (component)=0;

Else

  F_Solid (component)=F_feed*Feed.z(component);

endif
endfor

TotalFlowSolid = SIGMA(FOREACH(k in ComponentList)  F_Solid (k));
```

```
One_ions_comp=SIGMA(FOREACH(k in Ions_1) Feed.z(k)*Valence(k));

Two_ions_comp=SIGMA(FOREACH(k in Ions_2) Feed.z(k)*Valence(k));
Beta2*Multi =-One_ions_comp/Two_ions_comp*Beta1*Multi;

dens_water = -13.851+ 0.64038*(Feed.T+273.15) - 1.9124e-3 *(Feed.T+273.15)^2 + 1.8211e-
6*(Feed.T+273.15)^3;

Feed.P=Press_Brine;

FOR component in Ions Do

  IF component in Ions_1 THEN

  B(component) = Beta1;
ELSE
  B(component) = Beta2;

ENDIF
ENDFOR

Press_Brine_Seg(0) = Feed.P;
F_Perm_Water(0) = 0;

FOR component in WpIons Do

  IF component in Ions Then
  F_Brine(component).value(0) = Feed.z(component)*F_feed;

   F_Perm(component).value(0) = 0;
 ELSE
   F_Brine_Water(0) = Feed.z(component)*F_feed;
ENDIF
ENDFOR

Press_Brine_Seg.value.upper : Feed.P;
J_water.upper : A*Feed.P;
J_water:A*(Feed.P - Press_Perm);

vel_B.upper : F_Feed/(dens_water*W*Height_Brine/2*3600);
vel_B:vel_B.upper ;

koeff.lower: Akoeff*(vel_B.upper*(1-MaximumRecovery))^0.5*1e-6*3600;
koeff.upper:  Akoeff*(vel_B.upper)^0.5*1e-6*3600;
koeff: (koeff.lower + koeff.upper)/2;
```

```
FOR component in WpIons Do
 IF component in Ions Then

   Z_comp_brin(component).upper : Feed.z(component)/(1-MaximumRecovery );

   Z_comp_perm(component).upper :(1-MinRejection )*Z_comp_brin(component).upper ;

   J_salt(component).upper : B(component)*dens_water* Z_comp_brin(component).upper
*exp(J_water.upper/koeff.lower);

   J_salt(component):B(component)*dens_water* Z_comp_brin(component).upper
*exp(J_water.upper/koeff);

   Z_comp_surf (component).upper :
Z_comp_brin(component).upper*exp(J_water.upper/koeff.lower);

   ELSE

   PI_osmtic_surf_ideal : 1e-2*Rgas*(Feed.T+273.15)*dens_water*(1-Feed.z(component));

   PI_osmtic_surf: 1e-2*Rgas*(Feed.T+273.15)*dens_water*(1-Feed.z(component));

   Z_comp_surf(component).lower:Feed.z(component)*MinRejection;

ENDIF
ENDFOR

FOR x in X.interior + X.EndNode DO

   Press_Brine_Seg(x) : Feed.P;
   Press_Brine_Side(x):Feed.P;
   PI_osmtic_surf(x):1.10325;

FOR component in WpIons Do
 IF component in Ions Then
    Z_comp_brin(component,x) : Feed.z(component);

    Z_comp_surf (component): Feed.z(component);

    Z_comp_perm(component,x) : Feed.z(component)*(1-MinRejection) ;

    F_Brine(component,x) : Feed.z(component)*F_feed;
```

```
   F_Perm(component,x):    (1-MinRejection)*Feed.z(component)*F_feed;
 ELSE
Z_comp_brin(component,x) : Feed.z(component);

Z_comp_surf (component): Feed.z(component);

Z_comp_perm(component,x) : 1;

F_Brine_Water(x) : Feed.z(component)*F_feed;

F_Perm_Water(x):   Feed.z(component)*F_feed;
 ENDIF
 ENDFOR
 ENDFOR

FOR x in X.interior + X.EndNode DO

1/L*Press_Brine_Seg(x).ddx=-viscosity_brine(x)*vel_B(x)/Kf*1e-9;

koeff (x)= Akoeff*vel_B(x)^0.5*1e-6*3600;

FOR component in WpIons Do
  IF component in Ions Then
   Multi  *1/L*F_Brine(component,x).ddx = - J_salt (component)(x)*W*Multi  ;
   Multi  *1/L*F_Perm(component,x).ddx = J_salt (component)(x)*W*Multi  ;

  Multi  * Z_comp_brin (component)(x)*(SIGMA(FOREACH(icomp in Ions)
F_Brine(icomp)(x))+ F_Brine_Water(x)+TotalFlowSolid) = Multi  *F_Brine(component)(x);

   Multi  *Z_comp_perm (component)(x)*(SIGMA(FOREACH(jcomp in Ions) F_Perm
(jcomp)(x))+ F_Perm_Water(x)) =  Multi  *F_Perm (component)(x);

   Multi  *dens_Surf(x)* Z_comp_surf (component)(x) =
   Multi  *(dens_Perm(x)* Z_comp_perm (component)(x) +(dens_Brine(x)* Z_comp_brin
(component)(x) -dens_Perm(x)* Z_comp_perm (component)(x))*exp(J_water(x)/koeff (x)));

   J_salt (component)(x) = B(component)*( dens_Brine(x)*  Z_comp_brin (component)(x)-
dens_Perm(x)*Z_comp_perm (component)(x))*exp(J_water(x)/koeff (x));

  ELSE
   Multi  *1/L* F_Brine_Water(x).ddx =-J_water(x)*dens_water*W*Multi  ;

   Multi  *1/L* F_Perm_Water(x).ddx =  J_water(x)*dens_water*W*Multi  ;
```

```
   Multi  *Z_comp_brin (component)(x)*(SIGMA(FOREACH(icomp in Ions)
F_Brine(icomp)(x))+ F_Brine_Water(x)+TotalFlowSolid) = Multi  *F_Brine_Water(x);

   Multi  *Z_comp_perm (component)(x)*(SIGMA(FOREACH(jcomp in Ions) F_Perm
(jcomp)(x))+ F_Perm_Water(x)) = Multi  *F_Perm_Water(x);

   (Z_comp_surf (component)(x)+ SIGMA(FOREACH(lcomp in Ions)Z_comp_surf
(lcomp)(x)))*Multi  =1*Multi  ;

   Multi  *Z_comp_surf (component)(x)*gamma_surf(component,x)=Multi  *exp(-
Osm_coeff(x)*(1-Z_comp_surf (component)(x)));

   PI_osmtic_surf_ideal(x) = 1e-2*Rgas*(Feed.T+273.15)*dens_water*(1-Z_comp_surf
(component)(x));

   PI_osmtic_surf(x)=Hmt_Op*PI_osmtic_surf_ideal(x)*Osm_coeff(x);

   Press_Brine_Side(x)=(1-Hmt_dP)*Press_Brine + Hmt_dP*Press_Brine_Seg(x);
  ENDIF
ENDFOR

J_water(x)=A*( Press_Brine_Side(x) - Press_Perm -   PI_osmtic_surf(x));

Call(dens_Brine(x)) = pDens_Mol_Liq(Feed.T, Press_Brine, Z_comp_brin (WpIons,x))WpIons;
Call(dens_Perm(x))  = pDens_Mol_Liq(Feed.T, Press_Perm, Z_comp_perm
(WpIons,x))WpIons;
Call(dens_Surf(x))  = pDens_Mol_Liq(Feed.T, Press_Brine, Z_comp_surf (WpIons,x))WpIons;
CALL(gamma_surf(WpIons,x))= pAct_Coeff_Liq(Feed.T, Press_Brine, Z_comp_brin
(WpIons,x))WpIons;

Call (viscosity_brine(x)) = pVisc_Liq(Feed.T, Press_Brine, Z_comp_brin (WpIons,x))WpIons;

  SIGMA(FOREACH(icomp in Ions) F_Brine(icomp)(x))+ F_Brine_Water(x) + TotalFlowSolid
= vel_B (x)*dens_Brine(x)*W*Height_Brine/2*3600;

ENDFOR

FOR component in Ions Do

Rejection(component)*F_Brine(component,0)=F_Brine(component,Ncel)*100;

ENDFOR

SIGMA(FOREACH(icomp in Ions) Valence(icomp)*F_Brine(icomp,Ncel))=AratioBrine;
SIGMA(FOREACH(icomp in Ions) Valence(icomp)*F_perm(icomp,Ncel))=AratioPerm;
```

```
//Aratio=0;

Recovery*F_Brine_Water(0)=F_Perm_Water(Ncel)*100;

//Diff_Brine = Feed.F - (SIGMA(FOREACH(icomp in Ions) F_Brine(icomp)(Ncel))+
F_Brine_Water(Ncel))*(Nleaves  - 1)*2
 //          - (SIGMA(FOREACH(jcomp in Ions) F_Perm (jcomp)(Ncel))+
F_Perm_Water(Ncel))*(Nleaves  - 1)*2;

Brine.F = (SIGMA(FOREACH(icomp in Ions) F_Brine(icomp)(Ncel))+
F_Brine_Water(Ncel)+TotalFlowSolid)*(Nleaves  - 1)*2;
Brine.T = Feed.T;
Brine.h = Feed.h;
Brine.P = Press_Brine_Side(Ncel);
Brine.V*dens_Brine(Ncel)=1;
Perm.F =  (SIGMA(FOREACH(jcomp in Ions) F_Perm (jcomp)(Ncel))+
F_Perm_Water(Ncel))*(Nleaves  - 1)*2;
Perm.T = Feed.T;
Perm.h = Feed.h;
Perm.V*dens_Perm(Ncel)=1;
Perm.P =Press_Perm;

FOR component in ComponentList Do
  IF component in WpIons THEN
    IF component in Ions Then
Brine.z(component)*(SIGMA(FOREACH(icomp in Ions) F_Brine(icomp)(Ncel))+
F_Brine_Water(Ncel)+TotalFlowSolid) = F_Brine(component,Ncel);
  ELSE
 Brine.z(component)*(SIGMA(FOREACH(icomp in Ions) F_Brine(icomp)(Ncel))+
F_Brine_Water(Ncel)+TotalFlowSolid) = F_Brine_Water(Ncel);
 ENDIF
Perm.z(component) = Z_comp_perm (component,Ncel);
ELSE
Brine.z(component)*(SIGMA(FOREACH(icomp in Ions) F_Brine(icomp)(Ncel))+
F_Brine_Water(Ncel)+TotalFlowSolid) =F_Solid (component);
Perm.z(component) = 0;
ENDIF
ENDFOR

End
```