

Calcium Scaling in Direct Contact Membrane Distillation (DCMD) at High Salinities

by

Zhewei Zhang

Bachelor of Environmental Engineering, Jilin University, 2017

Bachelor of International Economics & Trades, Jilin University, 2017

Master of Environmental Engineering, University of Pittsburgh, 2021

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SWANSON SCHOOL OF ENGINEERING

This dissertation was presented

By

Zhewei Zhang

It was defended on

July 13, 2022

and approved by

Radisav D. Vidic, Professor, Ph.D., Department of Civil and Environmental Engineering

Vikas Khanna, Associate Professor, Ph.D., Department of Civil and Environmental Engineering

Carla Ng, Associate Professor, Ph.D., Department of Civil and Environmental Engineering

Lei Li, Associate Professor, Ph.D., Department of Chemical and Petroleum Engineering

Dissertation Director: Radisav D. Vidic, Professor, Ph.D., Department of Civil and
Environmental Engineering

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Zhewei Zhang, Ph.D.

University of Pittsburgh, 2022

Direct contact membrane distillation (DCMD) is a thermally driven membrane desalination process with the capability of treating hypersaline solutions. However, calcium scaling is commonly encountered in DCMD with a profound impact on permeate flux and energy efficiency. The goal of this study was to investigate the crystallization of calcium in hypersaline solutions during the desalination process, analyze the severity of calcium scaling in DCMD in comparison with other membrane separation process and provide potential pretreatment strategy to alleviate this problem.

Among the calcium salts most often associated with scaling issues in water treatment systems, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is one of the major foulants that adversely impact performance (i.e., fouling, wetting). The solubility indices (SI) of gypsum in hypersaline solutions (0.5M~5M) were first predicted with multiple models and then compared with the results obtained using in-situ electrochemical impedance spectroscopy (EIS) to monitor the crystallization process. EIS results showed reasonable agreement with both equilibrium and kinetic predictions.

Calcium scaling (i.e., gypsum and calcite) was also studied in thermal (DCMD) and pressure driven (nanofiltration, NF) membrane processes operated at identical feed temperature (i.e., 40 °C) and shear conditions (i.e., $\text{Re} = 771 \pm 28$) at feed salinities from 3,000 to 30,000 mg/L. This study demonstrated that the impact of calcium scaling is affected by both feed salinity and separation driving force, and is much less severe in thermally than pressure driven membrane processes.

Calcium scaling is a significant challenge when treating inland brackish water reverse osmosis (BWRO) reject that contains high concentration of both calcium and sulfate and a proper mitigation strategy is needed. Barite precipitation was utilized to remove about 4,000 mg/L of sulfate from actual BWRO concentrate to prevent scaling. The pre-treated BWRO concentrate was used as feed in DCMD system and 85% water recovery was achieved without any indication of membrane scaling.

Based on the comprehensive understanding of calcium crystallization under hypersaline conditions, this study offers fundamental insights into the impact of this adverse phenomena in both thermal and pressure driven membrane processes and options for calcium scaling control in membrane desalination processes.

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Preface

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*To see a World in a Grain of Sand
And a Heaven in a Wild Flower
Hold Infinity in the palm of your hand
And Eternity in an hour*

Nomenclature

α	<i>Water activity</i>
β	<i>Scale proportion</i>
γ	<i>Water activity coefficient</i>
δ	<i>Membrane thickness</i>
ϵ	<i>Permittivity of dielectric</i>
ζ	<i>Concentration polarization coefficient</i>
η_H	<i>Heat transfer efficiency</i>
η_M	<i>Mass transfer efficiency</i>
κ_M	<i>Effective thermal conductivity</i>
μ	<i>Viscosity</i>
μ_s	<i>Water viscosity</i>
ρ	<i>Density</i>
ϕ	<i>Phase shift</i>
χ	<i>Molar fraction of salt</i>
ω	<i>Angular velocity</i>

A	<i>Area</i>
A_f	<i>Functional membrane area</i>

A_{in}	<i>Inactive membrane area</i>
A_{total}	<i>Total membrane area</i>
C_p	<i>Specific heat</i>
C_m	<i>Electrical capacitance</i>
CPC	<i>Concentration polarization coefficient</i>
$DCMD$	<i>Direct Contact Membrane Distillation</i>
d	<i>Hydraulic diameter</i>
E_t	<i>Excitation signal</i>
EEC	<i>Electrical equivalent circuit</i>
EIS	<i>Electrochemical Impedance Spectroscopy</i>
H	<i>Heat transfer coefficient</i>
H_f	<i>Heat transfer coefficient on feed side</i>
H_m	<i>Heat transfer coefficient in membrane</i>
H_p	<i>Heat transfer coefficient on permeate side</i>
H_v	<i>Vapor enthalpy</i>
J	<i>Flux</i>
I_t	<i>Response signal</i>
IAP	<i>Ionic activity product</i>
K_{sp}	<i>Solubility Product</i>
K	<i>Thermal conductivity</i>
k	<i>Reaction rate coefficient</i>
L	<i>Length</i>

M	<i>Mass</i>
Nu	<i>Nusselt number</i>
NF	<i>Nanofiltration</i>
P	<i>Vapor pressure</i>
PP	<i>Polypropylene</i>
$PTFE$	<i>Polytetrafluoroethylene</i>
$P_{b,f}$	<i>Feed side bulk vapor pressure</i>
$P_{b,p}$	<i>Permeate side bulk vapor pressure</i>
$P_{m,f}$	<i>Feed side vapor pressure near membrane</i>
$P_{m,p}$	<i>Permeate side vapor pressure near membrane</i>
P_v	<i>Vacuum side vapor pressure</i>
Pr	<i>Prandtl number</i>
Q	<i>Heat transfer flux</i>
Q^0	<i>Numerical value of the admittance</i>
Q_f	<i>Feed side heat transfer flux</i>
Q_m	<i>Membrane heat transfer flux</i>
Q_p	<i>Permeate side heat transfer flux</i>
R_m	<i>Resistors connected in parallel</i>
R_s	<i>Resistors connected in series</i>
Re	<i>Reynolds number</i>
RO	<i>Reverse osmosis</i>
SEM	<i>Scanning electron microscopy</i>

Sh	<i>Sherwood number</i>
SI	<i>Saturation Index</i>
T	<i>Temperature</i>
T_b	<i>Bulk temperature</i>
$T_{b,f}$	<i>Feed bulk temperature</i>
T_m	<i>Average membrane temperature</i>
$T_{m,f}$	<i>Feed side membrane surface temperature</i>
$T_{m,p}$	<i>Permeate side membrane surface temperature</i>
TPC	<i>Temperature polarization coefficient</i>
t	<i>Time</i>
u	<i>Water flow velocity</i>
Z	<i>Impedance</i>

1.0 Introduction

As the global water crisis became more severe in recent decades due to population growth, the increasing demand for fresh water has forced a search for alternative water sources (Charcosset, 2009). It is expected that the demand for deeper layer brackish groundwater will dramatically increase for arid and semi-arid inland areas because of the difficulty in acquiring fresh groundwater and insufficient precipitation (Jennifer S Stanton & Dennehy, 2017). Desalination has been developed as one of the key approaches to acquire fresh water from brackish water resources for public and industrial use. Among several desalination processes, membrane-based technologies have been shown to be both efficient and economical in a variety of applications, including seawater desalination, inland brackish water desalination and shale gas wastewater desalination (Mehdizadeh, 2006; Shaffer, Yip, Gilron, & Elimelech, 2012). However, the presence of dissolved components in the target water affects the process performance as the water recovery increases. Chemical precipitation is particularly detrimental as the inorganic scales can dramatically reduce permeate flux and require frequent membrane cleaning (Alkhudhiri, Darwish, & Hilal, 2012). These precipitants (or foulants) are typically inorganic compounds, including calcium sulfate, calcium carbonate, magnesium carbonate, silica and other salts with limited solubility (Jarusutthirak, Mattaraj, & Jiraratananon, 2007; Liu, Xu, & Das, 2019). Calcium scaling is one of the most common problem encountered in all membrane desalination processes (Antony et al., 2011; Gryta, 2009; Le Gouvellec & Elimelech, 2002; C. Tzotzi, T. Pahiadaki, S. G. Yiantisios, A. J. Karabelas, & N. Andritsos, 2007b). Understanding the impact of calcium scaling on permeate flux, membrane permeability and energy efficiency is

crucial to the development, optimization and application of membrane desalination (Gryta, 2008a, 2009; Tzotzi et al., 2007b).

1.1 Calcium Scaling on Membranes

Scaling has become one of the major problems in industrial processes since the invention of the steam engine. In recent years, due to the increasingly severe world fresh water shortage, water reuse processes especially membrane desalination processes have gradually become a popular topic (Mehdizadeh, 2006), and scale formation has risen up again as a main issue to be solved. Some scales, such as calcium sulfate and barium sulfate, are difficult to be removed once being formed (Kamal, Hussein, Mahmoud, Sultan, & Saad, 2018). Accordingly, understanding the mechanism of scale formation and the scaling mitigation methods is beneficial to making progress on the research of scale inhibition.

The scaling process is influenced by the solution conditions (i.e. temperature, pH, ionic strength, etc.) and the characteristic of scalant, thus the scale formation process may vary among different solids and solutions (S. Lee, Kim, & Lee, 1999), but generally all scale formation processes involve three steps, which are supersaturation, nucleation and crystallization (Antony et al., 2011). Supersaturation always occurs with the decrease of solvent in solution due to the mass loss or transfer in industrial processes or water recovery processes, which causes the dissolved solids or ions concentration going above the saturation point. After supersaturation, nuclei are required for dissolved solids or ions to separate out from solution, thus nucleation will happen at a critical point where the required Gibbs free energy change for nucleation is

decreased (Erdemir, Lee, & Myerson, 2009). The formation of solid on the nuclei, which is known as crystallization, is presented in two pathways in respect of the nucleation and crystallization position as reported by Gilron et al.(Gilron & Hasson, 1987). The schematic illustration of scale formation is shown in Figure 1.1 by Antony et al.(Antony et al., 2011).

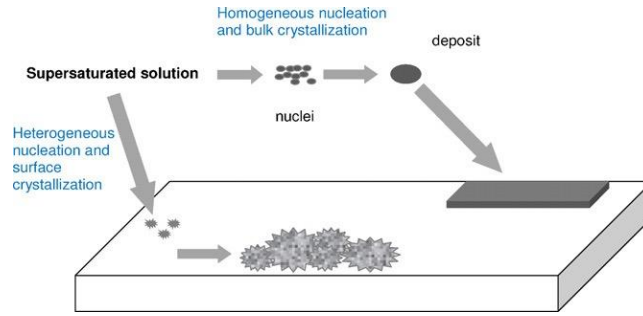


Figure 1.1 Schematic illustration of scale formation (Antony et al., 2011)

When the solvent in a solution keeps diminishing, the concentration of ions will increase and eventually exceed its saturation limit in the solution, and the solution will be supersaturated, this process is called supersaturation. The level of supersaturation can be measured with saturation index:

$$SI = \frac{IAP}{K_{sp}} \quad (1-1)$$

Where IAP is ionic activity product and K_{sp} is solubility product. When $IAP > K_{sp}$, $SI > 1$, which means the solution is supersaturated. At this stage, even though the supersaturated solute has the tendency to solidify, crystallization cannot happen without nuclei.

There are now two mainstream theories about the nucleation of solid in solution: the classical nucleation theory and two-step nucleation theory. In the classical nucleation theory, the solute molecules will form clusters before nucleation and the formation of nuclei has to get over the required free energy change (Yau & Vekilov, 2001). According to Erdemir et al. (Erdemir et al., 2009), the free energy change for nuclei formation (ΔG) can be expressed as:

$$\Delta G = \Delta G_v + \Delta G_s \quad (1-2)$$

Where ΔG_v is the required free energy change for phase transformation and ΔG_s is the required free energy change for the formation of a surface. Because solid is a rather stable form comparing to liquid, ΔG_v is a negative value. When molecule cluster is small, ΔG_s is dominant and rises up with the increasing radius of cluster, hence ΔG will also elevate with cluster radius. As the size of molecule cluster keeps enlarging, ΔG_v will become dominant and more negative and ΔG will thus decrease, making the nucleation process more favorable. There will be a critical radius where a highest Gibbs free energy change (ΔG_{crit}) can be achieved (Figure 1.2). While the classic nucleation theory can explain most of the nucleation process, it failed when being applied to water-rich aqueous alcohol or acetone solutions (Strey & Viisanen, 1993). Therefore, two-step nucleation theory was brought forward to make a better explanation.

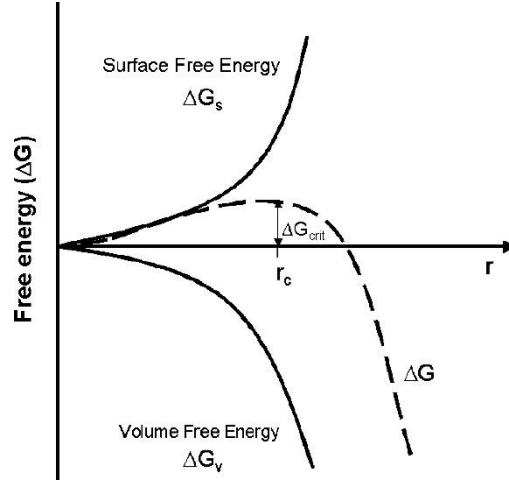


Figure 1.2 Free energy for nucleation (Erdemir et al., 2008)

Two-step nucleation theory suggests that instead of the molecule clusters directly form nuclei, there is an intermediate step where a liquid-like particle will come into being first. This theory has a better match to experimental data than the classic theory, but more complicated when being used to predict the formation of solid in solution (Knezic, Zaccaro, & Myerson, 2004). Generally, the classic theory is regarded as a simplification of two-step theory and is sufficient to predict nucleation in most situations (Oxtoby, 2003).

After nucleation process, crystallization will begin on the surface of nuclei under the driving force of the change of Gibbs free energy (ΔG_{cryst}). The crystallization equilibrium constant can be expressed as (Vekilov, 2010):

$$K_{cryst} \equiv \exp\left(-\frac{\Delta G_{cryst}}{RT}\right), K_{cryst} = C_e^{-1} \quad (1-3)$$

Where C_e is the solubility of scale, R is the gas constant and T is the temperature of solution. Crystallization happens in supersaturated solution, in which the concentration of scale (C) is always higher than C_e . The driving force of crystallization can be expressed as (Vekilov, 2010):

$$\Delta\mu = RT\ln\left(\frac{C}{C_e}\right) \quad (1-4)$$

Therefore, as long as the scale concentration in the solution is higher than the solubility of scale, crystallization can keep going on, until the scale concentration decreases to the solubility under the current solution condition.

According to the United States Geological Survey (USGS) official report of brackish groundwater in the United States (Jennifer S. Stanton et al., 2017), the brackish groundwater all over U.S. is divided into four groups with respect to its dominant component, the data for the four groups of brackish water can be concluded in table 1.1.

Table 1.1 Four dominant brackish groundwater group in U.S. (USGS, 2017)

Group	Dominant salt	Mean TDS (ppm)	Well Amount	Percentage
1	Sodium Bicarbonate	1810	3597	24%
2	Calcium Sulfate	2460	5257	35%
3	Sodium Chloride	8440	3484	23%
4	Mixed salts with high Silica	1360	2641	18%

The distribution of shallow brackish water (≤ 3000 ft below the surface) is presented in Fig. 3 by USGS (Jennifer S. Stanton et al., 2017).

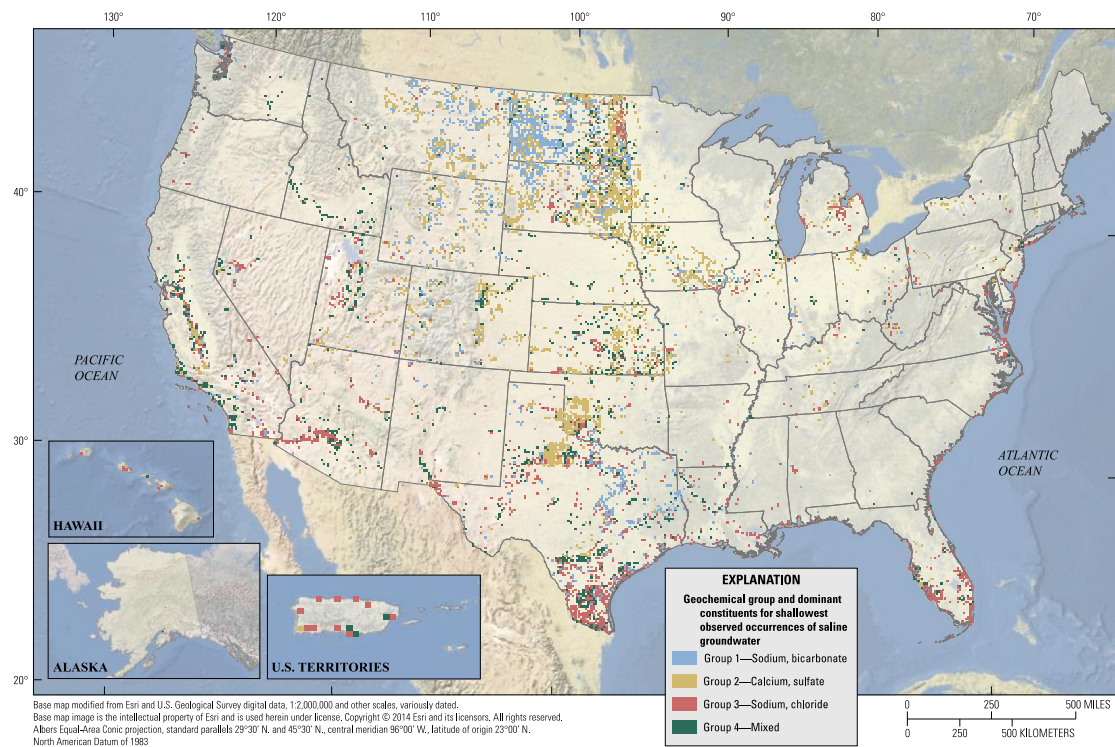


Figure 1.3 Brackish water distribution in U.S. (USGS, 2017)

As it is suggested in Table 1.1 and Figure 1.3, the most abundant type of brackish water in U.S. is Group 2, which occupies 35% of all brackish water well, and the dominant salt in Group 2 is calcium sulfate. Table 1.2 is concluded from USGS data, which shows the mean molar percentage of every ion in the four water groups.

Table 1.2 Mean molar percentage of cations (up) and anions (down) in the four groups of water (USGS, 2017)

Cations	Group 1	Group 2	Group 3	Group 4
Calcium	5.5	42.7	13.2	37.1
Magnesium	4.1	27.8	9.3	10.4
Sodium	89.7	28.6	76.4	39.6
Potassium	0.7	0.9	1	1.4
Silica	0.5	0.7	0.5	1.7

Anions	Group 1	Group 2	Group 3	Group 4
Bicarbonate	49.8	20	13.9	35.3
Sulfate	34.9	71.4	19.1	34.1
Chloride	15.3	8.7	67	30.7

As can be seen from Table 1.2, even in the groups where calcium sulfate is not the dominant salt, the concentrations of sulfate are still high. Thus, sulfate is one of the most abundant anions in groundwater all over the U.S. Plus, for one of the most common salts calcium sulfate, it has a low solubility (i.e. 2100mg/L at 20°C) (Partridge & White, 1929), therefore it can exist in large amount in saturated solution.

During the desalination process, feed water is concentrated as water recovery rate increases, the concentration of calcium sulfate will exceed the saturation point and separate out from solution. Other major salts in U.S. brackish groundwater either have high solubility (e.g. sodium chloride) or cannot exist considerably due to the low solubility (e.g. magnesium bicarbonate). The morphology of calcium sulfate crystals is in rod/needle-like shape presented in Figure 1.4.

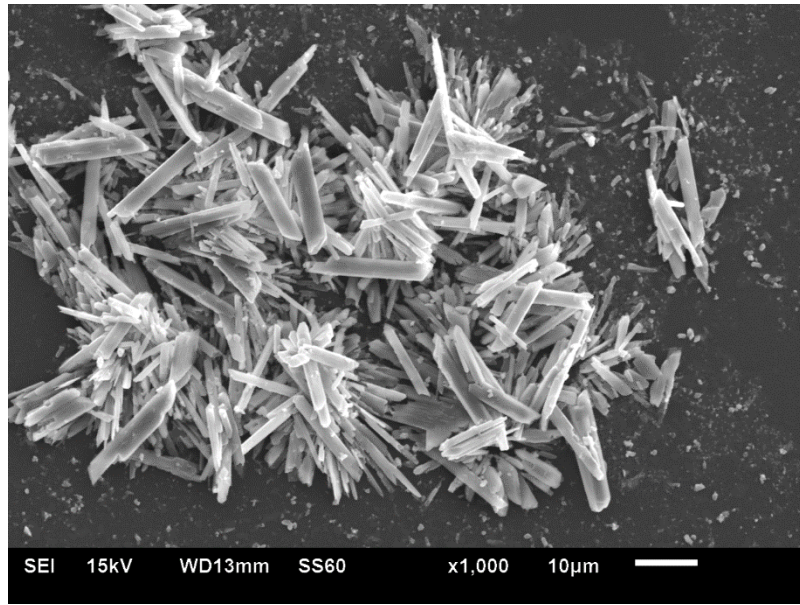


Figure 1.4 Gypsum crystals under SEM

1.2 Direct Contact Membrane Distillation

Direct contact membrane distillation (DCMD) is a thermal desalination process relying on the vapor pressure difference across the hydrophobic membrane provided by the temperature difference between the feed and permeate side (Lawson & Lloyd, 1997). The schematic graph of lab-scale DCMD module is presented as in Figure1.5.

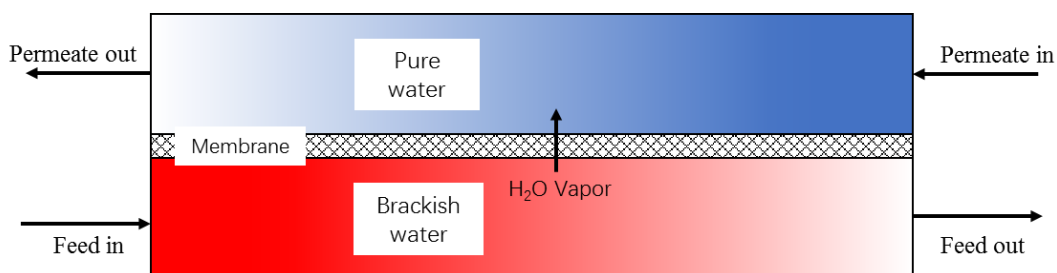


Figure 1.5 Schematic of DCMD module

Unlike pressure driven membrane desalination processes, such as reverse osmosis (RO) and nanofiltration (NF), which require significant pressure to overcome osmotic pressure generated by salinity, the thermally driven MD process is not as affected by the salinity because the impact of salinity on vapor pressure is not as significant as the impact on the osmotic pressure. Although MD has higher energy cost compared with pressure driven membrane processes, it can be integrated with solar energy or waste heat to reduce the operating cost and facilitate wider use (Cipollina, Di Sparti, Tamburini, & Micale, 2012; Deshmukh et al., 2018; Schwantes et al., 2013). Because the feed salinity has limited impact on the vapor pressure (D. Y. Hou et al., 2010), MD is uniquely positioned to offer high water recoveries. MD has been used to treat high salinity waters, including produced water from oil and gas extraction, landfill leachate and seawater RO brine (Anvari, Kekre, Azimi Yancheshme, Yao, & Ronen, 2019; Ji et al., 2010; Lokare, Tavakkoli, Wadekar, Khanna, & Vidic, 2017; Zhou, Huang, Deng, & Cai, 2017). DCMD can achieve 99.85% water recovery for the feed containing 600 mg/L sodium chloride (Cath, Adams, & Childress, 2004), and it has been used to concentrate produced water up to 300,000 mg/L TDS (Lokare, Tavakkoli, Wadekar, et al., 2017). MD faces the same problems with membrane fouling that is relevant to all membrane processes for water

purification. As the target feed solution is concentrated, the solubility limit of some salts may be exceeded, which would lead to precipitation of these salts on the membrane surface (i.e. membrane scaling) and a decrease in permeate flux due to permeability reduction (Gryta, 2008a; F. He, Sirkar, & Gilron, 2009b; Tong, Wallace, Zhao, & Wang, 2019; David M Warsinger, Swaminathan, Guillen-Burrieza, & Arafat, 2015). It is also possible that these precipitates can affect membrane hydrophobicity and lead to feed water intrusion into the membrane (i.e., membrane wetting) (Rezaei et al., 2018). Both membrane scaling and wetting have negative impact on membrane distillation and need to be mitigated to maintain stable performance and requisite water recovery.

Other merits for membrane distillation systems are: the ability of using low-grade heat as energy, the relatively compact comparing other systems and the capability of treating high salinity wastewater. These unique characteristics of membrane distillation can be further developed in the future implementation and become advantages competing with other desalination systems (Creusen et al., 2013; Swaminathan, Chung, & Warsinger, 2018; Ullah et al., 2018).

Firstly, for the low-grade heat resources, there are three main ideas for providing energy for membrane distillation: Industrial waste heat, solar thermal system and geothermal heat. Industrial waste heat as well as waste heat from power plants is abundant in this country, applying this waste energy to MD will not only save the electricity input, but also help the industries or power plants meet the heat emission standards. The shortcoming of this resource is that the temperature of heat is uncertain, and therefore it is difficult to judge which heat resource is practically useful. Solar thermal system is an economic heat source for MD for it directly convert solar energy to heat and can easily reach a practical temperature. However, the solar

thermal system occupies too much space that if a proper amount of feed water is to be heated by solar thermal system, an extreme large area of land will be required. Geothermal heat is a promising heat resource for MD, for its abundance and stability. Especially in the produced water treatment, deep wells are already drilled to get gas, only less than twice deeper depth is required to get stable geothermal heat in the continent of America.

Secondly, as mentioned above, the efficiency of MD will be competitive among thermal desalination methods only when the treatment scale is small, which means practical MD systems will always be smaller than other desalination systems and be more portable for being applied to remote areas and under-developed areas where the construction technology and electricity supply are limited.

Thirdly, the reason why MD is still popular even when it has a relatively low energy efficiency is that it has a good capability of dealing with high salinity water. According to recent research, RO system will stop working when the TDS of reject comes to 80000ppm, while MD is able to bring it to 360000ppm. Although other thermal desalination will probably reach the same result, MD is still outstanding for its lower cost due to the simple configuration and low heat requirement.

Comparing to hydraulic pressured system such as RO and NF, MD has a lower possibility of fouling because the pore size of MD membrane is bigger and the running pressure is lower. However, this merit is less obvious in real use because MD is always used to deal with much higher salinity wastewater than RO and NF, in which the concentrations of foulants and scalants are so high that even MD membranes cannot tolerate.

There are several kinds of methods to prevent MD membrane from fouling, scaling and wetting. One of the ideas is to improve the membrane characteristic. Currently there are four

kinds of MD membranes including hydrophobic, super hydrophobic and omniphobic MD membrane, for each kind of membranes, they have different resistance to polar and non-polar molecules and therefore have different trend of fouling and wetting when dealing with different foulants. Choosing the most adaptable membranes for MD in respect of the feed contents will dramatically decrease the possibility of fouling and increase the water recover of the system. However, some of the membranes are so expensive that will inevitable increase the cost of MD running.

Using anti-scalants is the most common way in practical implementation of MD desalination, anti-scalants can increase the required time for foulants and scalants forming on the membrane by disturbing the nucleation process and slow down the growths of foulant particles.

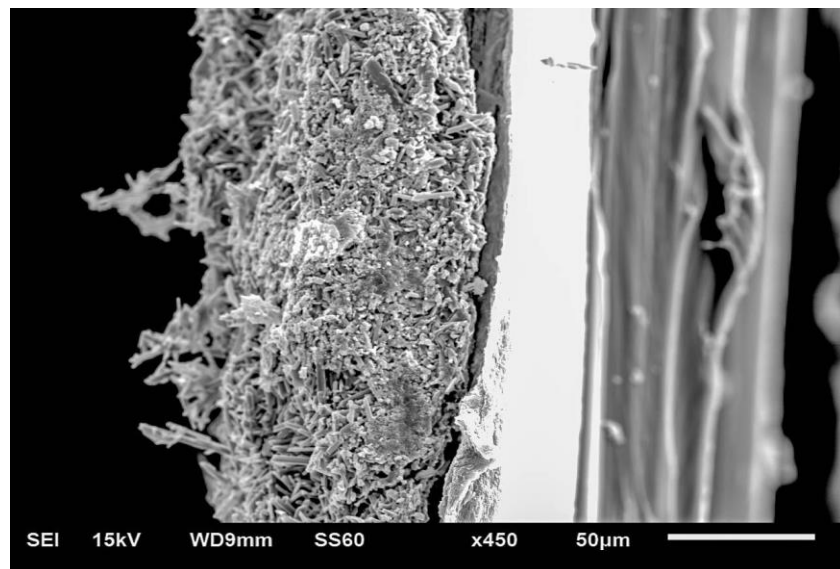


Figure 1.6 Calcium scaling on PTFE membrane

Another idea is to apply pretreatment to MD feed water, including both physical and chemical methods such as softening, coagulating, pH adjustment and ion removing. These pretreatments are highly based on the ingredients of the feed water, and thus need to be chosen carefully.

Figure 1.6 presents the calcium sulfate scaling layer formed on PTFE membrane during membrane distillation process, such scaling layer would lead to negative effects such as flux decrease, compromise of permeate quality and energy efficiency decrease. The forming mechanism, comparison of scaling in different membrane systems and potential mitigation methods will be discussed in this research.

1.3 Research Objectives and Layouts

The main objective of this study is to understand calcium scaling in water desalination processes by first comparing this process in MD systems with that observed in traditional pressure driven membrane process. Different pretreatment methods to prevent calcium scaling and enhance the water recovery in MD were evaluated based on in-depth understanding of calcium scaling process through real-time monitoring of scale evolution during the desalination process, including high salinity conditions that have not been evaluated before. Specific objectives of this study are:

Objective 1: Verification of the Pitzer model for predicting calcium precipitation in high salinity solutions to enable accurate predictions under the conditions that are relevant for MD applications (i.e., high water recovery for high salinity solutions)

The purpose of this study is to verify the Pitzer model in predicting calcium precipitation in high salinity water with Electrochemical Impedance Spectroscopy (EIS). The classic Pitzer equations were used with parameters developed by Harvie et al. (Harvie, Møller, & Weare, 1984) to predict the saturation index of CaSO_4 in NaCl solution of different salinity. EIS was used to detect the crystallization of calcium species in the synthetic water with supersaturated solution predicted by Pitzer model. The objective of this study is to provide insight into the precipitation of salts in high salinity aqueous phase and investigate the impact on the kinetics of chemical reaction on the predictions of the thermodynamic (equilibrium) model.

Objective 2: Comparison of calcium scaling in MD with that observed in pressure driven membrane desalination process

In this study, calcium sulfate and calcium carbonate scalants were tested in both MD and NF systems using the same feed concentration, temperature and crossflow velocity. The objective of this work was to investigate the differences in calcium scaling and its impact on the performance of thermal and pressure driven desalination systems and to quantify its impacts in terms of permeate flux and quality. Considering that the main difference between these two processes is the pressure on the feed side of the membrane, it can be expected that there will be differences in the form of precipitate formed and its affinity to attach to the membrane surface and associated impact on system performance. Synthetic CaSO_4 and CaCO_3 solutions with different ionic strength were utilized in lab-scale MD and NF systems to understand the impact

of feed pressure on membrane scaling. The permeate flux and quality were monitored and the shape and size of deposited crystals were analyzed to assess the impact of calcium scaling on MD and NF membrane permeability and final quality of the permeate. Scale characterization in the two systems was conducted using both microscopic (i.e., scanning electron microscopy (SEM)) and macroscopic (i.e., flux, scale weight, gas permeation) analysis.

Objective 3: Validate pretreatment approaches for MD operation in the case of inland brackish water reverse osmosis (BWRO) reject to prevent membrane scaling and enable high water recovery when treating this highly concentrated brine

The main objective of this study was to investigate the feasibility of using membrane distillation to enhance the overall water recovery of current BWRO treatment plants and reduce the cost associated with reject disposal. DCMD system was employed in this study to study system performance, including permeate flux and quality, as a function of key operating parameters. In addition, possible BWRO reject pretreatment using barium precipitation to remove potential foulants and achieve high water recovery was investigated in this study.

The three major objectives of this study listed above were to be pursued to elucidate the calcium scaling in membrane distillation and provide solutions to prevent this detrimental occurrence in realistic applications for MD technology. In-situ monitoring to understand the governing factors for calcium scaling that were to enable enhanced water recovery in inland brackish water desalination were to be utilized to achieve these objectives.

2.0 Verification of Thermodynamic Models for Gypsum Precipitation in Hypersaline Solutions with Electrochemical Impedance Spectroscopy (EIS)

This chapter, written by Zhewei Zhang and coauthored by Ritesh Pawar and Radisav D. Vidic, is ready to be submitted as manuscript to Water Research

2.1 Introduction

The prediction of solid precipitation is critical for desalination system performance since major fouling problems are caused by the precipitation of salts once the solubility limit is exceeded. Among various mineral salts, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is one of the major foulants that contributes to most of the scaling and wetting problems in membrane-based desalination systems (Chang et al., 2021; Christie, Yin, Lin, & Tong, 2020; Pawar, Zhang, Rhoades, Blotevogel, & Vidic, 2022; Xie et al., 2022; Zhewei Zhang, Wadekar, Lokare, & Vidic, 2021). The precipitation of gypsum in aqueous phase is difficult to be reversed once the crystals form and a variety of pretreatment options and antiscalants are widely adopted to prevent or delay its crystallization. Zhang et al. and Pawar et al. used barium sulfate precipitation in brackish groundwater and fracking produced water to avoid gypsum scaling in subsequent membrane distillation system operated at high water recovery (Pawar, Zhang, & Vidic, 2022; Zhewei Zhang, Lokare, Gusa, & Vidic, 2021). Yin et al. used poly(acrylic) acid as antiscalant and significantly mitigated gypsum scaling in combined system of membrane distillation and reverse

osmosis (Yin et al., 2022). Kazi et al. used gum arabic as solution additive to retard the precipitation rate of gypsum on heat exchanger surface (Kazi, Teng, Zakaria, Sadeghinezhad, & Bakar, 2015). Other methods, such as surface modification and crystallization inducing, also reduced the impact of gypsum scaling by limiting the attachment of gypsum on relevant surfaces (Chagwedera, Chivavava, & Lewis, 2022; Karanikola, Boo, Rolf, & Elimelech, 2018; Yan et al., 2021). On the other hand, controlled gypsum precipitation can benefit industrial and agricultural productions such as flue gas desulfurization, radium removal, soil nutrient loss control and heavy metal uptake (Gusa, Tomani, Zhang, & Vidic, 2020; Koralegedara, Pinto, Dionysiou, & Al-Abed, 2019; Jinman Wang & Yang, 2018; D. Zhang et al., 2019). In both cases, it is essential to accurately predict gypsum precipitation to efficiently control potential adverse effects or enhance its production.

The common method for predicting precipitation reactions with multiple salts is via Debye-Hückel limiting law. However, Debye-Hückel limiting law is only valid for dilute solutions where the electrolyte ions are assumed to be mainly affected by the long-range coulombic interactions. Previous study reported that Debye-Hückel limiting law had negligible deviation from experimental results in 0.01M solution but showed major discrepancy when the ionic strength exceeded 1M (Marshall & Jones, 1966). Therefore, Pitzer model is widely adopted in desalination research as an extension of Debye-Hückel limiting law in predicting precipitation reactions at high salinities. Based on the Pitzer model, multiple models were developed over the years, such as Aqueous model (AQ), Mixed Solvent Electrolyte model (MSE) and Mixed Solvent Electrolyte-Soave Redlich Kwong model (MSE-SRK). However, these models have not been compared and limited researches have kinetically verified gypsum crystallization and precipitation in hypersaline. Reiss et al. reported that gypsum crystallization could take more

than one month to reach equilibrium in seawater desalination brine without seeding.(Reiss et al., 2021) Ziegenheim et al. studied the reaction kinetics of 0.04-0.2M calcium and sulfate in water, and illustrated that the equilibrium could be reached between several minutes to hours.(Ziegenheim, Peintler, Pálinkó, & Sipos, 2020) He et al. reported in their seeded gypsum crystallization study that the fastest gypsum growth rate happens at salinity of 3M. (S. He, Oddo, & Tomson, 1994) In desalination area, thermodynamic precipitation may not happen in given time and has limited effect on scaling and fouling issues. To verify the prediction models, a sensitive particle detection method is required since the size of particles at early stage of crystallization could be minimal and difficult for direct observation.

Electrochemical Impedance Spectroscopy (EIS) is an electrochemical method based on the impedance of a system determined from a response to alternating current (AC) signal of varying frequency. EIS allows the detection of minimal surface changes and has been adopted in various areas, such as corrosion monitoring (Jüttner, 1990; Mansfeld, 1990), scaling detection for tubing and cooling system (D. Li, Feng, Bai, & Zheng, 2007; Tour et al., 2009), evaluation for batteries and fuel cells (Z. He & Mansfeld, 2009; S. S. Zhang, Xu, & Jow, 2006), and characterization of coatings and paintings (Collazo, Fernández, Izquierdo, Nóvoa, & Pérez, 2005; Deflorian, Fedrizzi, Rossi, & Bonora, 1999). In previous studies, EIS successfully detected minor change in membrane-based systems. Chen et al. used EIS to probe early-stage surfactant induced wetting in membrane distillation by monitoring the system impedance (Y. Chen, Wang, Jennings, & Lin, 2017). Rao et al. used EIS to induce electrophoretic mixing at concentration polarization layer of direct contact membrane distillation (DCMD) and measured multiple response signals to characterize the efficiency of scaling prevention (Rao et al., 2020).

The purpose of this study was to compare different thermodynamic models in predicting gypsum precipitation at a wide range of salinities and experimentally verify the onset of gypsum precipitation. The modeling was conducted using PHREEQC and OLI Studio software. Several techniques (e.g., dynamic light scattering, turbidity and EIS) were evaluated of their ability to detect gypsum crystallization and verify modeling results. The objective of this study was to provide insight into the precipitation of salts in very high salinity aqueous phase and investigate the impact by salinities on the precipitation kinetics

2.2 Material and methods

2.2.1 Thermodynamic models

Gypsum equilibrium was modeled using PHREEQC (United States Geological Survey) and OLI Studio (OLI Systems, Inc.). PHREEQC includes two ion-association aqueous models: (a) Pitzer specific-ion-interaction and (b) Specific ion Interaction Theory (SIT). The Pitzer model was used in this study to predict Gypsum SI in hypersaline, the Pitzer model parameters in this simulation were acquired from previous study by C.A.J Appelo (Appelo, 2015). OLI Studio includes three models: (a) Aqueous model (AQ), (b) Mixed Solvent Electrolyte model (MSE) and (c) Mixed Solvent Electrolyte- Soave Redlich Kwong model (MSE-SRK) that should all be suitable for predicting SI in high salinity solutions and were used in this study. The simulation conditions (i.e., temperature and pressure) were identically in each model used to predict gypsum

saturation index (SI) at salinities ranging from 0.5 M to 5.37 M with gypsum concentration of 3000 mg/L, 6000 mg/L and 9000 mg/L, respectively (0.022 M, 0.044 M and 0.066M).

2.2.2 EIS system

The laboratory EIS setup is depicted in Figure 2.1. An electrochemistry flask (Pyrex, PA) with a 4-outlet glass lid was used as EIS cell and was installed on a magnetic stirring hotplate in a Faraday cage to eliminate the interference from external electromagnetic waves. A 316 stainless steel electrode (Metal Samples, AL) was placed in the center outlet as a working electrode. It was well polished into a gloss finish with sand papers from 300 to 3000 grit and

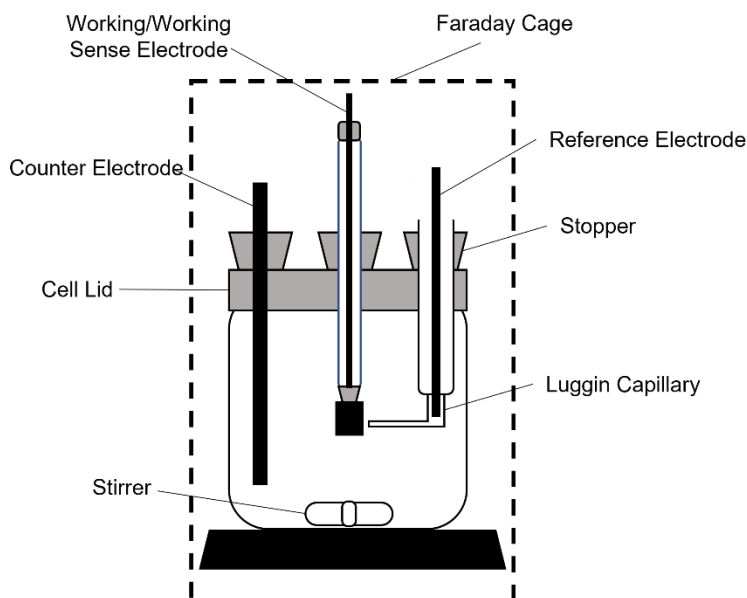


Figure 2.1 Schematic of laboratory-scale EIS system

polishing compound to minimize the solid deposition on the electrode surface during the precipitation process. A commercial silver/silver chloride electrode (930-00015, Gamry

Instruments, PA) was used as reference electrode and was inserted in a customized Luggin capillary to decrease the distance between reference electrode and working electrode and increase detection sensitivity for precipitated gypsum particles. A dense graphite electrode was used as the counter electrode to reduce the overall electrical resistance of the EIS system, and an extra lid outlet invisible from Figure 2.1 was used to add solution into the EIS cell. All electrodes were connected to a computer-based potentiostat system (Model G300, Gamry Instruments, PA) capable of scanning AC signals from 10 μ Hz to 300 kHz. Signal analysis software (Echem Analyst, Gamry Instruments, PA) was used for data acquiring, signal interpreting and model fitting.

2.2.3 EIS principles

Preliminary EIS experiments were conducted with 4M NaCl solution and AC signal frequency from 0.1 mHz to 10 kHz. The acquired data were first evaluated by Kramers-Kronig (K-K) relations model with Echem Analyst software to exclude unreliable data points (i.e., only the data that were compliant with K-K relation were used for electrical equivalent circuit (EEC) model fitting). Different EEC models were then applied using Simplex method using the goodness-of-fit coefficient (GOF) to compare the residual errors and fit discrepancies of EEC models. Preliminary test have shown that the Constant Phase Element model (CPE) had the best GOF coefficient (i.e., 0.0203%) among all existing EEC models and was adopted for this EIS cell. Figure 2.2 (a) and (b) show the fit of CPE model with EIS cell data and CPE equivalent circuit. In this circuit, C_m is the constant phase element that behaves as an imperfect capacitor,

while R_s and R_m are resistors connected to C_m in series and parallel, respectively. R_s and R_m can be obtained by analyzing the Nyquist plot of the total system impedance.

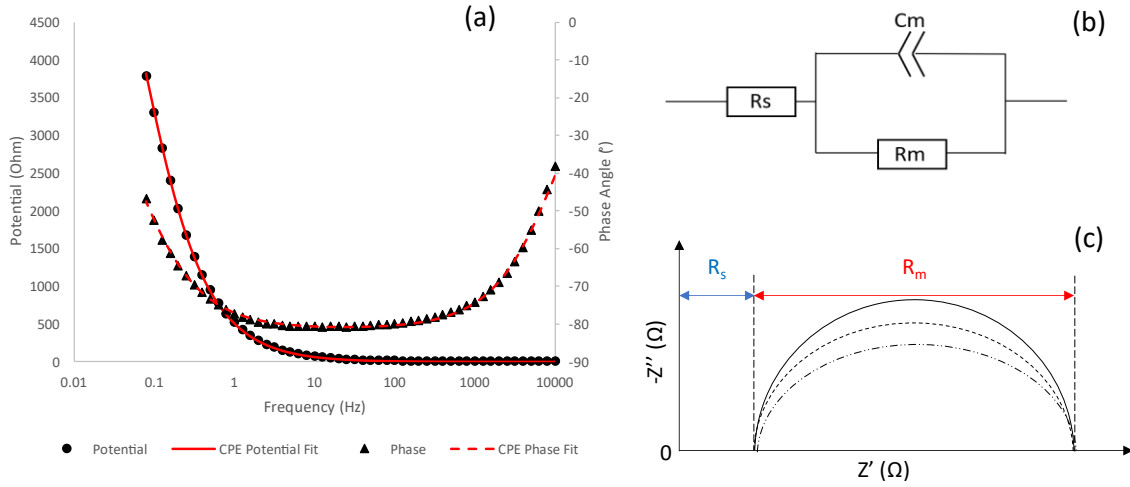


Figure 2.2 CPE model fit to EIS cell data (b) CPE equivalent circuit (c) general Nyquist plot of CPE model

The total impedance (Z) of the EIS system can be calculated using the excitation signal (E_t) and response signal (I_t) using Ohm's law:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (2-1)$$

where, Z_0 is the magnitude, E_0 is the initial amplitude of the signal, ω is the angular velocity of radial frequency, I_0 is the response signal amplitude and ϕ is the phase shift. The absolute impedance $|Z|$ as a function of $\log(\text{frequency})$ yields the Bode plot (The Bode plot was

shown in Figure 2.2(a)). Nyquist plot is obtained by converting system impedance to complex form using Euler equation:

$$\exp(j\phi) = \cos\phi + j\sin\phi \quad (2-2)$$

And the system impedance can be presented as:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \exp(j\omega t)}{I_0 \exp(j\omega t - \phi)} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi) \quad (2-3)$$

The complex number form of the system impedance contains real part and imaginary part. Nyquist plot is the relationship between the negative imaginary part, $-Z''$, and the real part, Z' . According to CPE equivalent circuit, the total system impedance can be expressed as:

$$Z = R_s + \frac{1}{\frac{1}{R_m} + j\omega C_m} = R_s + \frac{R_m}{1 + j\omega R_m C_m} \quad (2-4)$$

Thus, the real part and the imaginary part of impedance can be expressed as:

$$Z' = R_s + \frac{R_m}{1 + \omega^2 R_m^2 C_m^2} \quad (2-5)$$

$$-Z'' = \frac{j\omega R_m^2 C_m}{1 + \omega^2 R_m^2 C_m^2} \quad (2-6)$$

In Nyquist plot (Figure 2.2(b)) , R_s is the distance between zero point and the first intersection point of the semicircle or semioval curve, R_m is the distance between the two intersection points on x-axis of the semicircle or semioval curve. The calculation of C_m follows the method developed by Jovic (Jovic, 2003):

$$C_m = \frac{(Q^0 R_m)^{\frac{1}{n}}}{R_m} \quad (2-7)$$

where, Q^0 is the numerical value of the admittance ($1/|Z|$) at $\omega = 1$ rad/s, n is the EIS phase angle divided by -90° , which can be acquired from Nyquist plot analysis with Echem Analyst software.

The resistance (i.e., R_s and R_m) in this system is dominated by the electrical conductivity of solutions and EIS components (i.e., electrodes, connectors and wires). Because both hypersaline solution and metals are good conductors, the resistance does not change significantly during the precipitation process. On the other hand, the capacitance (C_m) is only impacted by the electrochemical change of the constant phase element, which is the imperfect capacitor between working electrode and reference electrode. Previous studies have shown that the capacitance change in an EIS system is a good indicator of crystallization and polymerization in the solution (Deflorian et al., 1999; H. Li, Dzombak, & Vidic, 2012). Particle deposition on the electrode would disturb the electrical double layer at the electrode-solution interface and thus change the capacitance that is defined as:

$$C_m = \frac{\varepsilon A}{d} \quad (2-8)$$

where, ε is the permittivity of dielectric between the electrodes, A is the shared area of the two electrodes and d is the distance between the electrodes. When the working electrode and reference electrode are in fixed positions, capacitance is governed by the media (dielectric) permittivity between two electrodes (i.e., hypersaline solution with or without gypsum crystals).

Because gypsum crystallization in solution would change the overall solution permittivity it can be accurately detected by the EIS system.

2.2.4 Gypsum detection with EIS

Gypsum precipitation was initiated by mixing calcium chloride and sodium sulfate solutions at different total salinities. Gypsum SI was investigated using CaSO_4 concentrations of 3000, 6000 and 9000 mg/L at salinities (as total NaCl) of 2.5M, 4M and 5M. It was reported that calcium sulfate precipitation in aqueous phase could result in 3 forms of crystals with different hydration levels, namely anhydrite (CaSO_4), bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with gypsum being the absolutely dominant product at ambient temperature and pressure (i.e., 25°C and 1 bar) and in the range of salinities investigated in this study (Freyer & Voigt, 2003; Ossorio, Van Driessche, Pérez, & García-Ruiz, 2014).

All solutions were prepared using type-1 ultrapure water (resistivity $>18\text{M}\Omega\text{-cm}$) with reagent grade $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 and NaCl salts and were filtered through 0.22 μm membrane filter (Stericup, Millipore Sigma, MA) into a sterilized flask to eliminate bacteria and any particles that may enter the solutions during preparation. EIS cell, electrodes and stirrer were cleaned or polished as needed before each experiment. CaCl_2 solution was first added to the EIS cell and stirred at 250 rpm. Na_2SO_4 solution was then slowly added (i.e., 10 ml/min) using a peristaltic pump (Masterflow, Model 7520, Thermo Fisher, PA) to prevent gypsum precipitation due to abrupt concentration increase. EIS was set to potentiostat mode with frequency scanning from 20 mHz to 10 kHz to maximize the accuracy of the subsequent fit with EEC model. Three replicate measurements at each frequency were conducted to ensure statistical significance of the

experimental data, which means that the frequency scan at each time point took approximately 12 minutes to complete. An open circuit potential (OCP) measurement was conducted for 1 minute before each scan to optimize the AC potential that would be applied between the working electrode and the reference electrode. The OCP measurement was necessary to avoid excessive AC potential and prevent electrical corrosion of the working electrode in a hypersaline solution. The solution in EIS cell was continuously stirred while conducting measurements over period of 30 hours. The acquired data were evaluated by K-K relation and then fitted to the CPE model while solution samples were taken for subsequent analysis.

2.3 Results and Discussion

2.3.1 Thermodynamic predictions

The predicted saturation index for CaSO_4 concentrations of 3000, 6000 and 9000 mg/L as a function of salinity in the range of 0.5 - 5.3 M is shown in Figure 2.3(a)~(c) using MSE-SRK, MSE, AQ and Pitzer models, respectively. All models predicted gypsum SI as a convex curve with minimum SI at the solution salinity between 2.3 - 2.6 M. The SI predictions of four

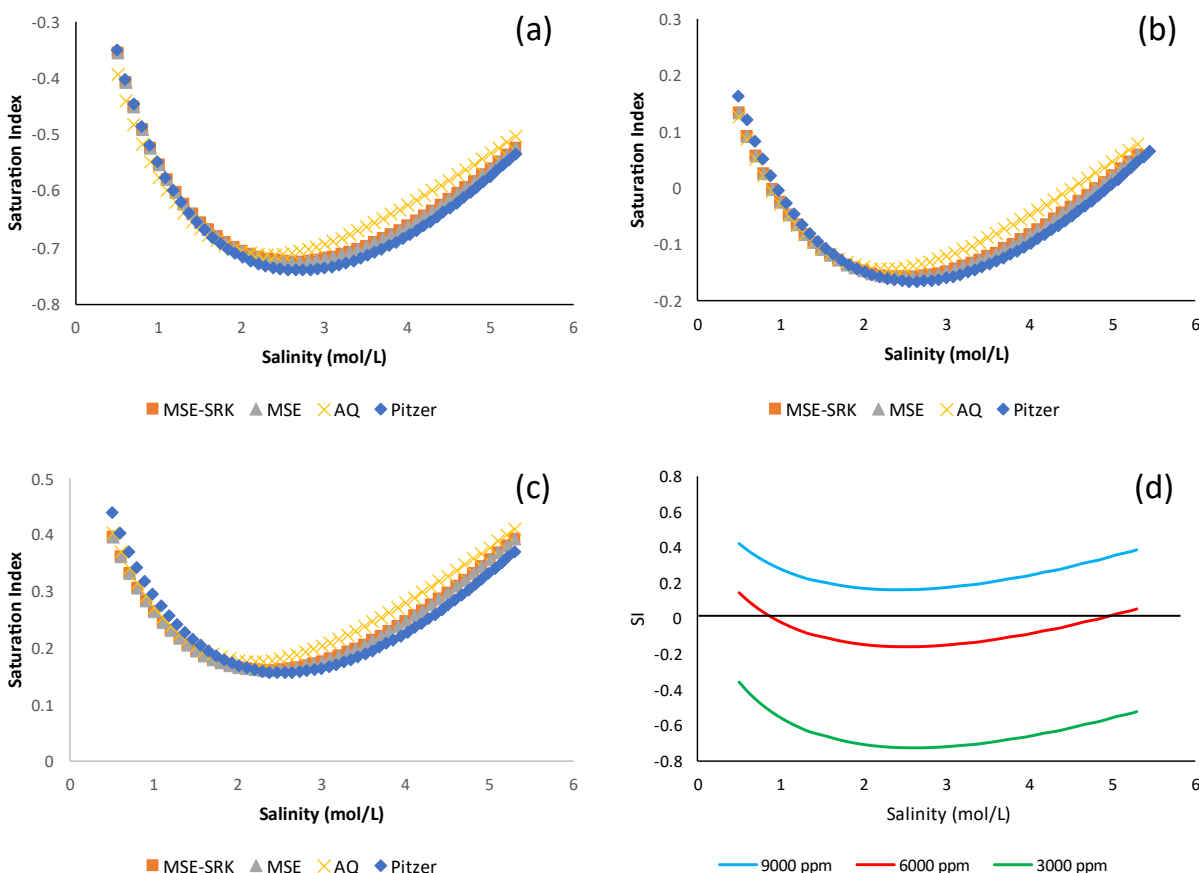


Figure 2.3 Predicted gypsum SI in hypersaline solutions containing (a) 3,000 mg/L, (b) 6,000 mg/L and (c) 9,000 mg/L CaSO_4 and (d) arithmetic means of SI predicted by the 4 models

different models were quite similar with slightly higher values predicted by AQ model. The SI values for the total CaSO_4 concentration of 3000 mg/L varied from -0.35 to -0.72 (Figure 2.3(a)), indicating that it is undersaturated regardless of the solution salinity. Thermodynamic models predicted that the CaSO_4 solution containing 6000 mg/L was supersaturated at solution salinities below 0.9 M and above 4.9 M (Figure 2.3(b)), while it is undersaturated at solution salinities in the range from 0.9 - 4.9M with a minimum SI of -0.15 at 2.4 M salinity. The solution containing 9000 mg/L of CaSO_4 was always supersaturated regardless of the background salinity (Figure 2.3(c)) and the SI ranged from 0.44 - 0.16. Figure 2.3(d) shows the arithmetic mean of the SI for each initial CaSO_4 concentration. Similar gypsum solubility trends were obtained in previous experimental studies (E. Bock, 1961; Doubra, Kamran-Pirzaman, Mohammadi, & Hassanalizadeh, 2017; S. He, Oddo, & Tomson, 1994; Shukla, Mehta, & Kumar, 2018; Trivedi, Pandya, & Kumar, 2013). One-way analysis of variance (ANOVA) was used to determine the deviation between the models. The p-values for 3000, 6000 and 9000 mg/L initial CaSO_4 concentrations were 0.6632, 0.5407 and 0.3819, respectively, which suggest no statistically significant difference among these predictions.

2.3.2 EIS results

The normalized capacitance measured by EIS at 2.5 M salinity during 30 hours of continuous mixing is presented in Figure 2.4. No significant capacitance increase was observed in the experiments with 3000 and 6000 mg/L initial CaSO_4 concentration, indicating that these

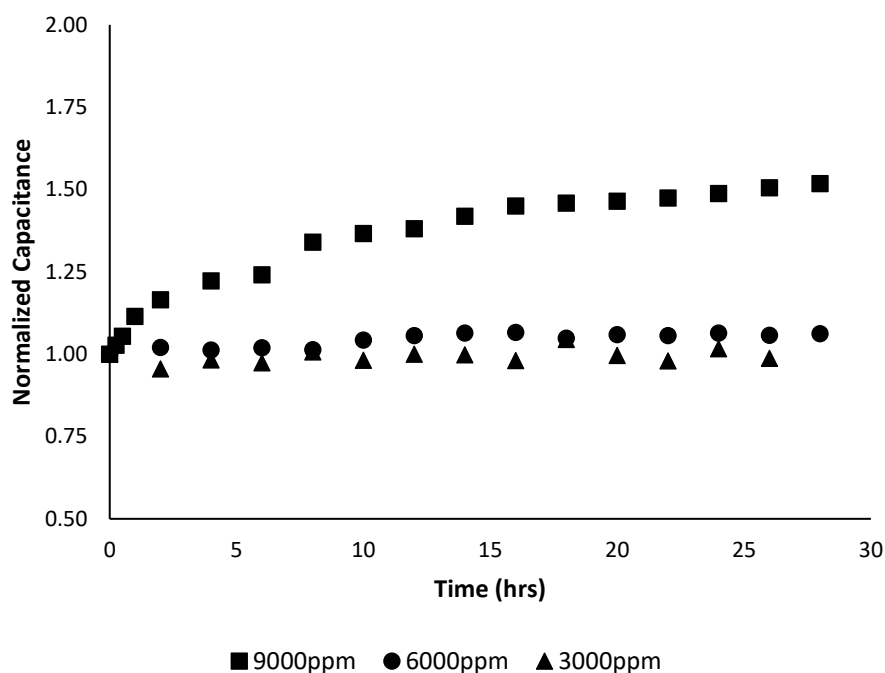


Figure 2.4 Normalized capacitance during gypsum precipitation in 2.5 M NaCl solution

hypersaline solutions were stable and no gypsum precipitation occurred within 30 hours. On the other hand, a 50% increase in normalized capacitance was observed in of 9000 mg/L solution indicating that gypsum crystallization occurred. Figure 2.3 (d) indicates that the average SI for solutions of 3000, 6000 and 9000 mg/L CaSO_4 in 2.5 M solution is -0.73, -0.16 and 0.16, respectively, which means that the only solution that is supersaturated under these conditions is

the one at 9000 mg/L. However, no particles were visible in the solution even after 30 hours of reaction time because the SI of 9000 mg/L solution is only slightly above 0 and the concentration and size of gypsum particles cannot be detected by the naked eye. The EIS results in Figure 2.4 show that the normalized capacitance of the 9000 mg/L solution keeps increasing after 30-hour observation time, thereby suggesting that gypsum precipitation may have not reached equilibrium during this time. This behavior can be explain by the low level of gypsum supersaturation (i.e. $SI = 0.16$) that results in slow rate of precipitation (Van Driessche, Stawski, & Kellermeier, 2019).

The results of EIS experiments with gypsum precipitation in 4 M hypersaline solution are presented in Figure 2.5. No significant capacitance increase was observed in 3000 and 6000 mg/L $CaSO_4$ solutions as their SIs were below 0. Approximately 30% capacitance increase was observed with 9000 mg/L solution and a white milk-like color was also observed due to the formation of massive amounts of gypsum crystals in this hypersaline solution. Previous studies have shown that higher SI in supersaturated solutions would reduce induction time and increase nucleation density and thereby increase the precipitation rate (Elduayen-Echave, Azcona, Grau, & Schneider, 2020; Kazadi Mbamba, Batstone, Flores-Alsina, & Tait, 2015). The increase in capacitance slowed down during the first 12 hours and leveled off afterwards, indicating gypsum

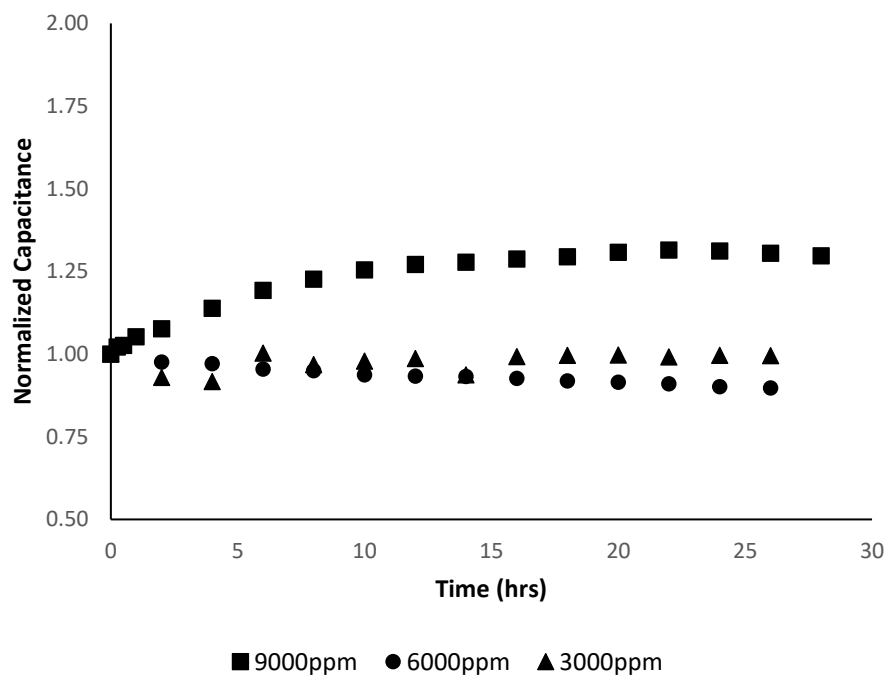


Figure 2.5 Normalized capacitance during gypsum precipitation in 4 M NaCl solution

precipitation reached equilibrium after 12 hour when precipitaton and dissolution rate of gypsum were balanced.

Figure 2.6 depicts normalized capacitance for CaSO_4 solutions in 5 M hypersaline solution. The normalized capacitance in 3000 and 6000 mg/L solutions fluctuated around 1 throughout the experiment while the normalized capacitance in 9000 mg/L solution increased by approximately 70% by the end of 30-h long experiment. This behavior suggests that gypsum precipitation only occurred in 9000 mg/L solution although theoretical calculations predicted gypsum precipitation in 5 M solution for both 9000 (SI = 0.348) and 6000 mg/L (SI = 0.019) CaSO_4 concentrations (Figure 2.3d). Previous study showed that precipitation is kinetically limited when the solution is only slightly supersaturated (Kazadi Mbamba et al., 2015), which

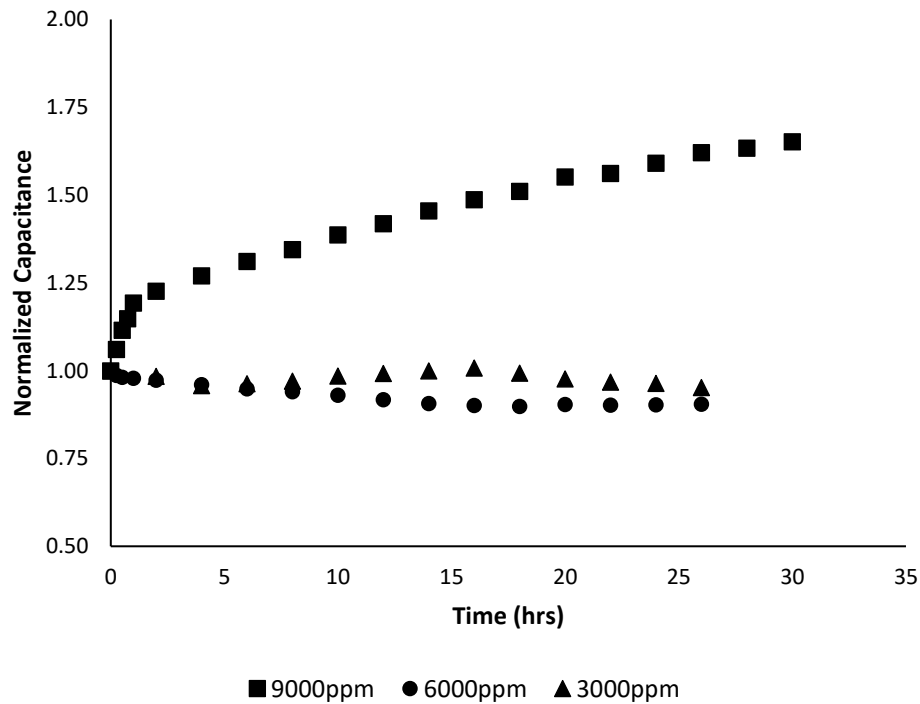


Figure 2.6 Normalized capacitance during gypsum precipitation in 5 M NaCl solution

was the case with 6000 mg/L solution. Normalized capacitance in 9000 mg/L increased rapidly in the first hour indicating fast gypsum precipitation at high SI, while the subsequent reaction rate was reduced due to the reduction in the concentration of calcium and sulfate ions. However, the reaction did not reach equilibrium after 30 hours as evidenced by the continuous increase in normalized capacitance even after 30 h of reaction.

Gypsum precipitation was detected by EIS in 9000 mg/L solution at all salinities investigated in this study but the precipitate was visible by naked eye only at 4 and 5 M salinities. While theoretical calculations predicted gypsum precipitation in 5 M solution containing 6000

mg/L of CaSO_4 , no change in normalized capacitance was observed over a period of 30 h. Subsequent analyses of experimental samples collected from these studies was conducted to provide insight into these discrepancies.

A quantitative precipitation kinetic test with 4M salinity and 9000mg/L gypsum was done to compare with the EIS result. Identical experimental conditions with EIS test were applied (i.e. temperature, vessel dimensions, loading speed, mixing speed, etc.), solution samples were taken in time order and filtered with 0.05 μm membrane to remove gypsum crystals. Filtered samples were diluted immediately to prevent further gypsum crystallization. The dissolved gypsum concentrations changing with time were shown in Fig.7.

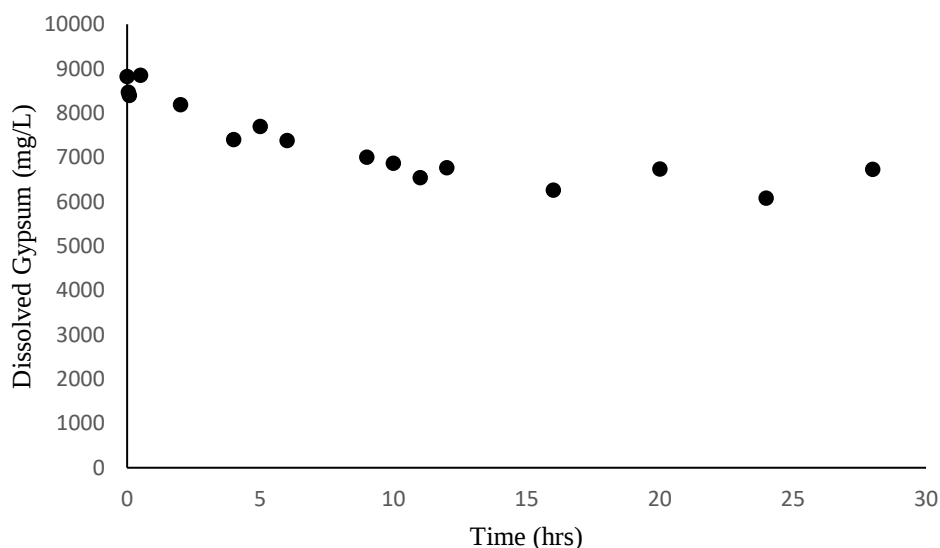
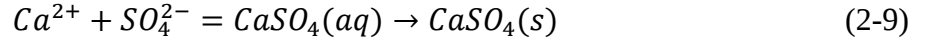


Figure 2.7 Dissolved gypsum concentration over time

It is shown in Figure 2.7 that gypsum crystallization reached equilibrium in 12 hours, which matched the result from EIS analysis in Figure 2.5. Dissolved gypsum concentration

stabilized at approximately 6400 mg/L, complying with the simulation results in this study. This precipitation kinetic results were then fitted to a second order reaction model with reaction equation as:



The relationship between concentration and reaction coefficient described as:

$$\frac{dC}{dt} = kC^2 \quad (2-10)$$

Where, C is the reactant concentration at time t, k is the reaction coefficient. The reaction concentration C in this equation represented calcium or sulfate concentration as they are equal in this experiment. The equation could be derived as:

$$\frac{1}{C} - \frac{1}{C_0} = kt \quad (2-11)$$

Where, C_0 is the initial concentration of reactant. By fitting experimental data to this model, the average reaction coefficient k yield to be $1.996 \times 10^{-6} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Normalized capacitance (C_m/C_{m0}) acquired in EIS experiment were adjusted with equation 2.12 to compared with normalized concentration (C/C_0) and normalized second order reaction model.

$$\frac{C'_m}{C'_{m0}} = -\frac{C_m}{C_{m0}} + 2 \quad (2-12)$$

The results presented in Figure 2.8. It is shown that EIS results complies with both kinetic test results and reaction predictions, illustrating that EIS is capable of accurately detecting precipitation kinetics.

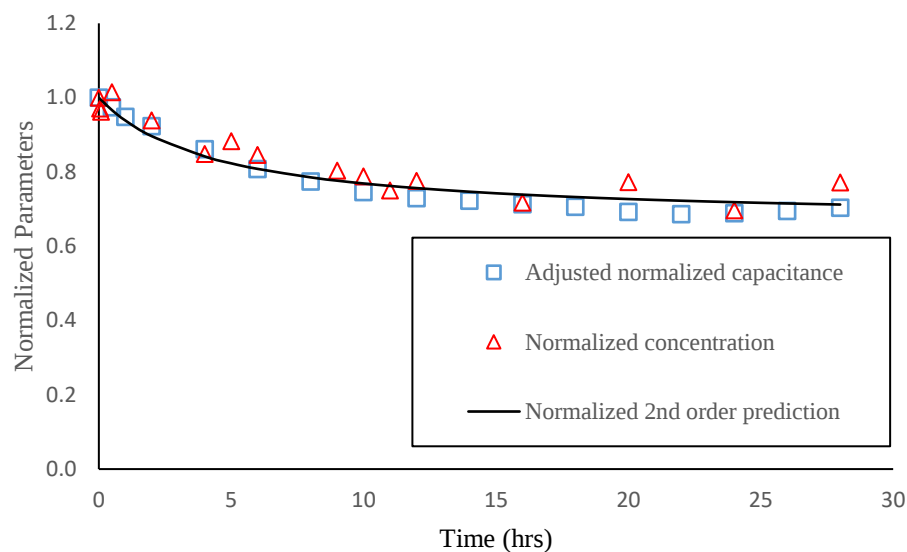


Figure 2.8 Comparison of Adjusted normalized parameters

2.4 Precipitate characterization

2.4.1 Turbidity measurement

Turbidity measurement is a fast optical method sensitive to the presence of suspended solids in solution. Samples collected after 30 h were analyzed for turbidity using a portable turbidimeter (2100p, Hach company, CO). All samples were well shaken to prevent stratification of solids in the vial and the results of turbidity measurements are included in Table.2.1.

Table 2.1 Turbidity of hypersaline CaSO₄ solutions after 30-h of mixing (Unit: NTU)

Background NaCl concentration	Initial CaSO ₄ concentration (mg/L)		
	3000	6000	9000
2.5 M	0.20±0.04	0.19±0.02	0.21±0.04
4 M	0.18±0.03	0.26±0.03	482±27
5 M	0.18±0.02	0.22±0.03	790±52

The results in Table 2.1 indicate that significant turbidity was observed in samples containing initial concentration of CaSO₄ of 9000 mg/L at 4 and 5 M background NaCl concentration while no significant turbidity was observed in other samples. These results support the findings from EIS experiments that no gypsum precipitation occurred in 5 M solution containing initial CaSO₄ concentration of 6000 mg/L and 2.5 M solution containing initial CaSO₄ concentration of 9000 mg/L, which is contrary to the predictions by thermodynamic models (Figure 2.3). Although the turbidity measurement is more sensitive than visual observation, it is still limited by instrument accuracy and particle size and concentrations and is unlikely to distinguish the nuances of limited number of particles in solution.

2.4.2 DLS measurement

Dynamic light scattering (DLS) is an optical method that analyzes particle size by measuring their diffusion speed due to Brownian motion and the accurate measurement are feasible only for particles sizes between 0.1 nm to 10 μm . Figure 2.7 (a) to (c) depict particle size distribution in 2.5 M, 4 M and 5 M hypersaline solutions measured by DLS method using Anton Paar Litesizer (Model 500, Anton Paar GmbH, Ashland, VA) . The data in these figures indicate

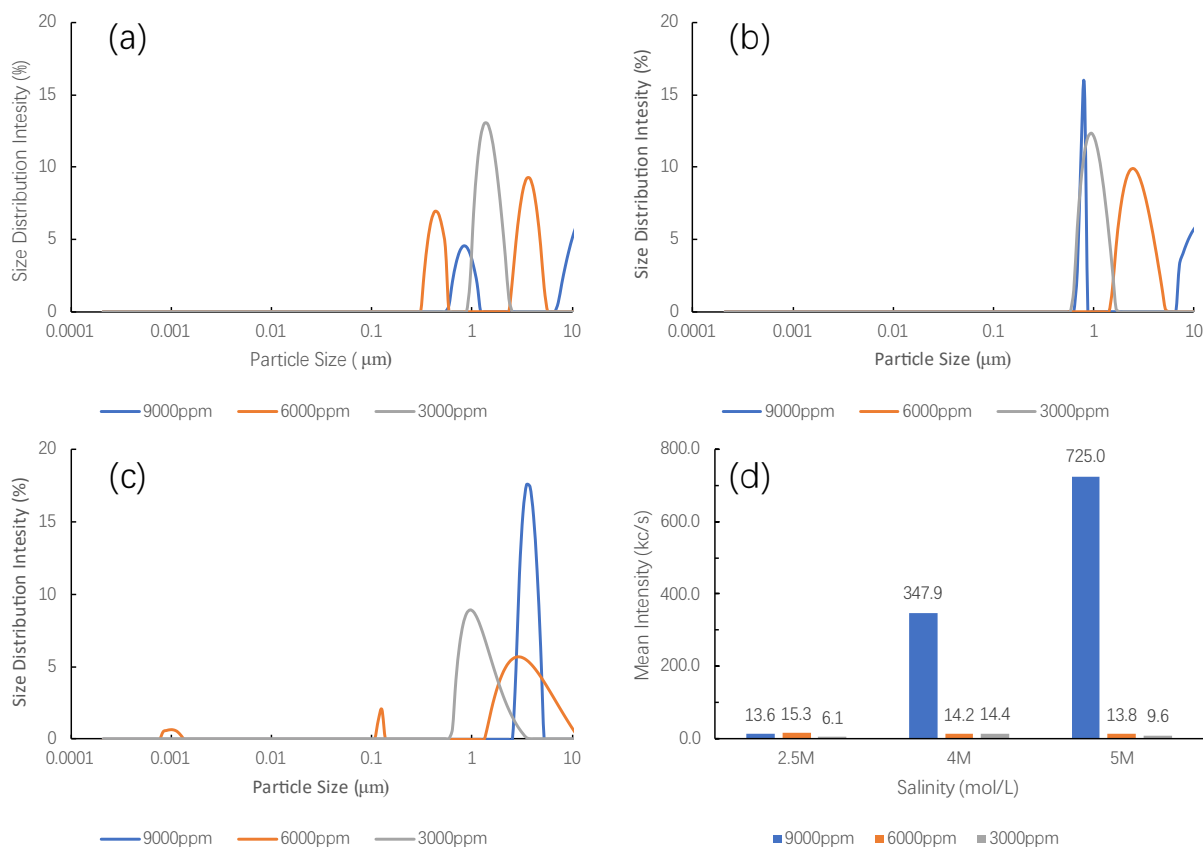


Figure 2.9 Particle size distribution between 0.1nm to 10 μm in (a) 2.5 M solution (b) 4 M solution (c) 5 M solution and (d) particle mean intensities in different groups

that most of particles were between 0.1 μm to 10 μm . Incomplete peaks reflect particles larger than 10 μm that could not be included in this analysis. However, these data indicate the presence of solid particles even in undersaturated gypsum solutions (i.e., initial CaSO_4 concentrations of 3000 and 6000 mg/L). Such behavior is due to low measurement intensities as summarized in Figure 2.7(d) that depicts mean intensity for each background salinity and each initial CaSO_4 concentration. This figure indicates that most DLS measurements had extremely low mean intensities (i.e., intensity $\leq 15\text{kc/s}$) except for the samples with the initial CaSO_4 concentration of 9000 mg/L in 4 M and 5 M NaCl concentration that had mean intensities of 347.9 and 725.0 kc/s (thousand counts per second). For comparison, a DLS measurement conducted with filtered deionized water showed likewise particle distributions similar to those with low mean intensities (data not shown). This suggests that the DLS analysis is not reliable for solutions with very low particle concentrations. It was surprising to see that the DLS analysis could not accurately characterize particle precipitated in 2.5 M NaCl solution containing 9000 mg/L of CaSO_4 that was shown to affect normalized capacitance in EIS measurements. In addition, DLS analysis can not be applied in the situation where massive precipitations result in particle sizes greater than 10 μm (e.g., 4 and 5 M NaCl solution with 9000 mg/L initial CaSO_4 concentration).

2.4.3 SEM/EDX measurement

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) (Sigma 500 VP Analytical FE-SEM with Oxford Microanalysis, Zeiss, Germany) was used to confirm gypsum precipitation and to characterize the morphology of gypsum particles. 10 ml of solution samples collected after 30 hours were filtered through 0.01 μm membranes to capture

gypsum particles. Membranes were then naturally dried and coated to be analyzed with SEM/EDX. This analysis confirmed that gypsum particles were present only in solution containing 9000 mg/L CaSO_4 and none were found in samples with the initial CaSO_4 concentrations of 3000 and 6000 mg/L. Figure 2.8 shows the SEM images of gypsum particles in (a) 2.5 M solution (b) 4 M solution and (c) 5 M solution (the images are done in same magnification of 100 times for direct comparison).

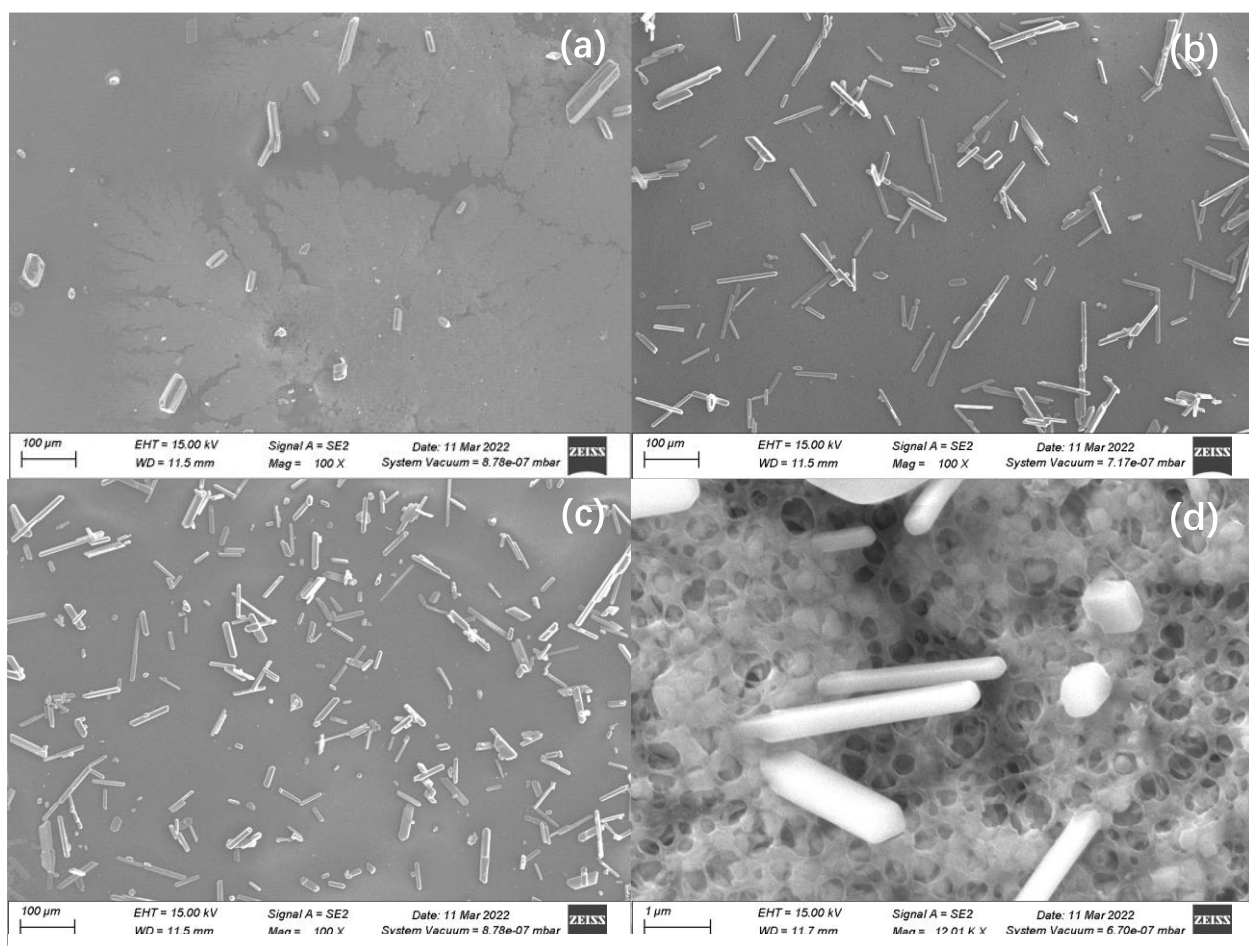


Figure 2.10 SEM images of gypsum particles in samples with 9000 mg/L CaSO_4 at 100 times magnification in (a) 2.5 M solution (b) 4 M solution (c) 5 M solution and (d) undergrown gypsum crystals in 2.5 M solution

All particles in Figure 2.8 , including those collected from a sample with 2.5 M NaCl, have a classic needle/rod-like morphology of gypsum. EDX analysis confirmed their chemical composition as gypsum. The precipitation in 2.5 NaCl solution containing 9000 mg/L CaSO_4 (Figure 2.8(a)) was detected by EIS as capacitance increase but could not be confirmed with turbidity and DLS measurement. It is also evident in Figure 2.8 (a)~(c) that as salinity increased from 2.5 M to 5 M, the gypsum particle concentration increased due to an increase in SI but there was no noticeable difference in particle shape and size. Most of the gypsum particles in these figures are larger than 10 μm but undergrown particles with sizes less than 1 μm were observed in the solutions with NaCl concentration of 2.5 M where the SI was only slightly positive (Figure 2.8 (d)). These undergrown particles represent the early stage of gypsum precipitation but further growth of gypsum particles was not possible due insufficient concentration of calcium and sulfate in solution. SEM/EDX results offer a convincing validation of the capability of EIS approach to track chemical precipitation in aqueous solutions at high salinities. The capacitance change during EIS analysis has shown to be quite sensitive to detect the presence of solid particles even when their concentration is low.

2.5 Conclusion

This study was designed to predict gypsum saturation index (SI) in hypersaline solution with multiple models and to evaluate the capabilities of electrochemical impedance spectroscopy (EIS) to detect and track gypsum precipitation. Simulations conducted using PHREEQC and OLI Studio with thermodynamic models, including Pitzer, MSE-SRK, MSE and AQ, were compared

at the initial CaSO_4 concentration of 3000, 6000 and 9000 mg/L in NaCl solutions ranging from 0.5 - 5.3 M. EIS measurement was compared with turbidity measurement, dynamic light scattering (DLS), and Scanning electron microscopy / energy dispersive x-ray spectroscopy (SEM/EDX) to assess its sensitivity and accuracy for detecting gypsum precipitation.

Simulation results showed that gypsum SI would decrease then increase with salinity increase from 0.5 - 5 M, with a minimum value at 2.3 M to 2.6 M salinity. Predictions of all four models were very similar with no statistically significant difference. The convex trend of gypsum SI in hypersaline solution showed trends that traditional water activity and ionic strength theory would not predict at these high salinities. A minimum SI value for gypsum would provide an insightful guidance regarding scaling control in heat exchange, evaporation and desalination processes.

The experimental results obtained in this study showed that the EIS has excellent sensitivity for tracking gypsum precipitation in hypersaline solutions when compared to optical methods such as turbidity and DLS as confirmed by SEM/EDX observation. The EIS cell established for the detection of gypsum precipitation complies with the constant phase element (CPE) model, allowing quantitative analysis of system parameters including resistance and capacitance. Electrochemical signal changes due to gypsum precipitation was well fitted with the CPE model and tracking normalized capacitance allowed reliable and accurate in-situ and real-time detections of gypsum precipitation. The gypsum precipitation detected by EIS was in agreement with the predictions of four different thermodynamic models.

This study revealed the trend in gypsum saturation in hypersaline solutions with comprehensive modeling and validation using electrochemical impedance spectroscopy that offers a reliable method that can be applied in other systems needing in-situ monitoring of precipitation or scaling.

3.0 Comparison of calcium scaling in direct contact membrane distillation (DCMD) and nanofiltration (NF)

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3.1 Introduction

As the global water crisis became more severe in recent decades, desalination has been developed as one of the key approaches to acquire fresh water for public and industrial use. Among several desalination processes, membrane-based technologies have been shown to be both efficient and economical for a variety of applications, including seawater, inland brackish water and shale gas wastewater.(Chang et al., 2019; Charcosset, 2009; Lokare, Tavakkoli, Rodriguez, Khanna, & Vidic, 2017; Mehdizadeh, 2006; Shaffer et al., 2012) Current membrane desalination techniques can be divided into two broad categories based on the driving force: pressure and thermally/chemically driven processes. Pressure driven processes, such as reverse osmosis (RO) and nanofiltration (NF), apply pressure on the feed side to overcome the osmotic pressure and allow water transport through membrane pores, while thermally/chemically driven desalination processes, such as membrane distillation (MD) and forward osmosis (FO), utilize vapor pressure

or chemical potential difference across the membrane for mass transfer of pure water to the permeate side.(Alkhudhiri et al., 2012; Cath, Childress, & Elimelech, 2006; Van der Bruggen, Vandecasteele, Van Gestel, Doyen, & Leysen, 2003)

The presence of dissolved organic and inorganic components in the feed water can compromise the performance of membrane desalination processes by the formation of scales on membrane surface.(David M. Warsinger, Swaminathan, Guillen-Burrieza, Arafat, & Lienhard V, 2015) Salts like calcium sulfate, calcium carbonate and silica exist in natural water bodies.(Guo, Ngo, & Li, 2012) As the feed water is concentrated by the extraction of fresh water, the dissolved inorganic salts with low solubility become supersaturated and precipitate on the feed side of membrane systems. Membrane scaling refers to the deposition of solids on the membrane surface, which can significantly increase the mass transfer resistance and hence, decrease the permeate flux across the membrane.(Antony et al., 2011; Gilron & Hasson, 1987; Lokare, Tavakkoli, Wadekar, et al., 2017) Such behavior strongly affects the desalination process by increasing energy consumption, reducing permeate quality and reducing the overall membrane service life.(Shirazi, Lin, & Chen, 2010) Formation of deposits on the membrane surface in MD systems may not only decrease the permeate flux but could also change the hydrophobicity of the membrane and lead to membrane wetting.(Chang et al., 2021; Tijing et al., 2015) Feed pre-treatment to remove potential scaling species and addition of anti-scalants to prevent scales from forming or attaching to the membrane surface are widely used to combat this phenomena that burdens all membrane-based desalination processes.(Chellam, Jacangelo, Bonacquisti, & Schauer, 1997; Jun Wang et al., 2008; Wolf, Siverns, & Monti, 2005) Cho et al. compared multiple pre-treatment systems for MD including FMX-B membrane system, flocculation-settlement system and flocculation-settlement-microfiltration system when treating shale gas produced water.(Cho, Choi, & Lee, 2018) Zhang et

al. used precipitative softening combined with walnut shell filter as pre-treatment system to achieve 82.5% water recovery with only 10% flux reduction.(Zuoyou Zhang, Du, Carlson, Robbins, & Tong, 2019) Qu et al. also reported that commercial anti-scalants could reduce or completely eliminate membrane wetting due to gypsum scaling in DCMD systems.(Qu et al., 2020) Because the feed composition and characteristics of potential scalants vary widely, the specific pretreatment and/or anti-scalant selection and dosage need to be tailored for each application.(Listiarini, Chun, Sun, & Leckie, 2009; Lyster, Kim, Au, & Cohen, 2010; Rahman, 2013; Zhewei Zhang, Lokare, et al., 2021)

Calcium is one of the most abundant elements in natural water bodies and it appears in combination with anions such as sulfate, chloride and carbonate. Calcium sulfate is the dominant salt in 35% of brackish groundwater aquifers in the USA.(Jennifer S. Stanton et al., 2017) Due to their relatively low solubility, calcium sulfate and calcium carbonate scales are common in membrane desalination processes. Precipitated calcium sulfate and calcium carbonate solids attach to the membrane surface and are resistant to cross flow shear making it very difficult to restore membrane performance once the deposit layer is formed.(Shmulevsky, Li, Shemer, Hasson, & Semiat, 2017) Feed pre-treatment (e.g., chemical precipitation) and process control (e.g., pH adjustment, anti-scalant addition) are needed to enable requisite membrane performance.(Ayoub, Zayyat, & Al-Hindi, 2014; Gusa et al., 2020; Yu, Lee, & Hong, 2010) The pre-treatment processes can efficiently counter calcium scaling but are expensive and require complex solids handling.(Gabelich et al., 2006)

MD and NF are representative of thermal and pressure driven membrane separation processes, respectively. Theoretical salt rejection of MD is 100%, which gives it a competitive edge in desalination and water purification.(Nghiem & Cath, 2011) The main driving force for MD

operation is the vapor pressure difference across the membrane. MD is capable of treating high salinity brines that are not feasible for pressure driven desalination systems due to excessive osmotic pressures. MD has higher energy requirement compared to pressure driven membrane processes but can be integrated with solar energy or waste heat to reduce operating cost and facilitate wider use.(Cipollina et al., 2012; Deshmukh et al., 2018; Schwantes et al., 2013) On the other hand, a pressure driven membrane process like NF has higher permeate flux compared to MD and lower operating pressure compared to RO.(Bowen & Mukhtar, 1996) NF can separate organics and multivalent ions due to the nanometer level pores and the presence of charged groups on the membrane surface.(S. Lee et al., 1999; Linde & Jönsson, 1995; Wadekar & Vidic, 2017, 2018, 2018)

MD and NF were chosen to represent two different membrane separation processes to evaluate the impact of calcium scaling on system performance. Calcium sulfate and calcium carbonate scalants were tested in both MD and NF systems using identical feed composition, temperature and shear conditions to compare the impact of calcium scales on membrane performance (i.e., permeate flux and quality). Besides their difference in the separation mechanisms, these membrane processes also differ in the pressure on the feed side of the membrane. Hence, it can be expected that the difference in pressure may also affect the form of precipitate and its affinity to attach to the membrane surface, which could have vastly different impact on system performance. Therefore, the shape and size of deposited crystals in the two membrane systems were monitored together with permeate flux and quality to assess the impact of calcium scaling on the performance of MD and NF systems.

3.2 Materials and Methods

3.2.1 Feed solutions

Synthetic calcium sulfate (CaSO_4) and calcium carbonate (CaCO_3) solutions were used as feed in this study and sodium chloride (NaCl) was added to explore the impact of salinity (i.e. NaCl concentration) on scaling behavior. The composition of feed solutions used in this study was selected based on the national brackish groundwater assessment report by the United States Geological Survey (USGS)(Jennifer S. Stanton et al., 2017) and is shown in Table 3.1. Samples 1 and 3 were designed to study calcium sulfate scaling at low and high feed salinity, respectively, while Samples 2 and 4 were designed to study calcium carbonate scaling at low and high feed salinity, respectively. A stable CaSO_4 feed solution was prepared by slowly adding calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) solution into sodium sulfate (Na_2SO_4) solution using a peristaltic pump (Masterflow, Model 7520, Thermo Fisher, PA) operated at a flow rate of 10 mL/min. A stable CaCO_3 solution was prepared in the same way using $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and sodium carbonate (Na_2CO_3) solutions. NaCl was added to the base solution (i.e., Na_2SO_4 or Na_2CO_3) before the addition of CaCl_2 solution to prepare Samples 3 and 4. The pH of feed solutions varied in a narrow range of 5.5 - 5.7 without any adjustment.

The solubility of CaSO_4 is 2,040 and 4,760 mg/L in 3,000 and 30,000 mg/L NaCl solution, respectively(E Bock, 1961; Meijer & Van Rosmalen, 1984) and it increases slightly with temperature increase from 20 to 40°C.(Ishikawa, 2010) The final concentration of CaSO_4 in the feed was 4,000 mg/L, which means that the it was slightly supersaturated at lower ionic strength (Sample 1) and slightly undersaturated at higher ionic strength (Sample 3). The solubility of

CaCO₃ is 15 and 35 mg/L in 3,000 mg/L and 30,000 mg/L NaCl solution at pH 7, respectively.(Coto, Martos, Peña, Rodríguez, & Pastor, 2012; J. Li, Ahmed, & Li, 2018) The solubility of CaCO₃ is influenced by solution pH, temperature, salinity and dissolved carbon dioxide (CO₂) concentration.(Chilingar, Mourhatch, & Al-Qahtani, 2008) The increase in temperature and pH and a loss of dissolved CO₂ will shift the equilibrium towards CaCO₃ precipitation(Chilingar et al., 2008) while the increase in salinity will shift the equilibrium towards CaCO₃ dissolution.(Berkowitz, Singurindy, & Lowell, 2003) The observed solubility of CaCO₃ was 3,800 mg/L at pH 6 in an open carbonate system at room temperature.(Goss, Lemons, Kerstetter, & Bogner, 2007) The final concentration of CaCO₃ in the feed was 2,000 mg/L, which means that it was undersaturated at both low and high ionic strength feed (Samples 2 and 4). Each feed solution was prepared right before the filtration experiment and stirred to ensure that it is kinetically stable (Sheikholeslami & Ong, 2003) and without any visible precipitate in the feed reservoir.

Table 3.1 Composition of feed solutions

Feed Solution	Low Salinity				High Salinity			
	Sample 1		Sample 2		Sample 3		Sample 4	
Concentration (mg/L)	CaSO ₄	4,000	CaCO ₃	2,000	CaSO ₄	4,000	CaCO ₃	2,000
	NaCl	3,431	NaCl	2,334	NaCl	30,000	NaCl	30,000

3.2.2 MD experiments

All experiments were performed using a lab-scale DCMD system shown in Figure 3.1. Commercial polytetrafluoroethylene (PTFE) membrane with a pore size of 0.2 µm, average

thickness of 120 μm and porosity of 42% on polypropylene (PP) support (Sterlitech Corporation, Kent, WA) was used in this study. The 2 x 20 cm PTFE membrane was supported by a 1 mm thick spacer with porosity of 0.77 (Delstar Technologies, PA). The feed tank was placed on a hot plate (ISOTEMP, Sterlitech, WA) to control the temperature of feed solution while a 2.4 kW chiller (M75, Thermo Fisher, Pittsburgh, PA) was used to cool down the permeate using submerged stainless-steel coil. Centrifugal pumps (UL FILE E46145, Baldor Reliance, AR) were used to deliver feed and permeate to the DCMD module. Temperature sensors (T1-4) and pressure sensors (P1-2) were used to monitor temperature and pressure on both sides of the module while the conductivity meter (Orion 145A+, Thermo Electron, Pittsburgh, PA) was used for continuous monitoring of permeate quality.

The operating temperature was 40 °C on the feed side and 10 °C on the permeate side. The membrane was conditioned with DI water to test the baseline flux. The flowrate on each side of the membrane was adjusted to 0.2 gpm (0.757 L/min) to eliminate the pressure difference across the membrane and achieve the crossflow velocity of 0.63 m/s and Reynolds number of 755 ± 17 . The system was operated in a constant concentration mode by continuously returning the permeate back to the feed tank. A 3-way valve was used to measure the permeate flux and conductivity every 15 min. These permeate samples were also returned to the feed tank to maintain constant feed concentration.

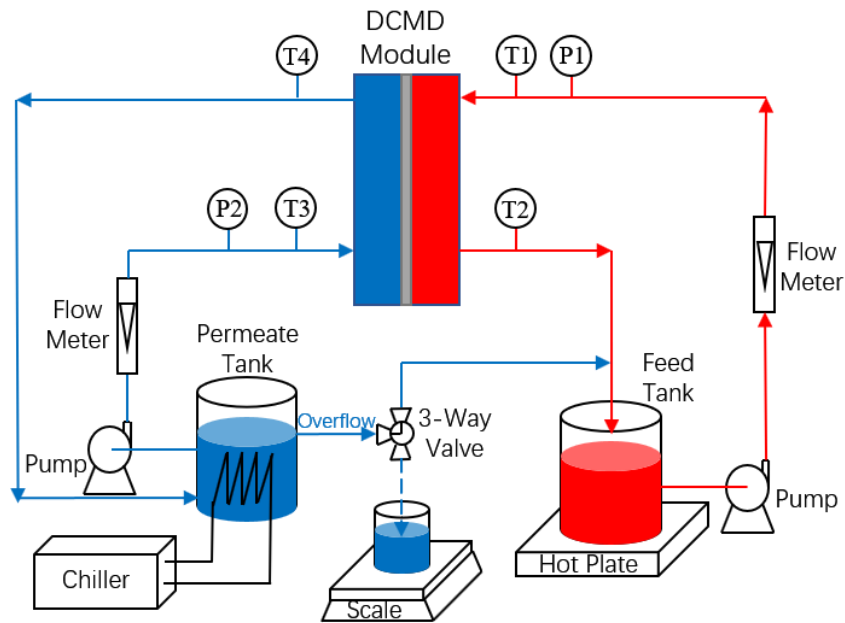


Figure 3.1 Schematic of lab-scale DCMD system

3.2.3 NF experiments

Commercial fully aromatic polyamide membrane NF270 (DOW FILMTEC) with a molecular weight cut off (MWCO) of 200 ~ 400 Da and a pore size of 0.87 nm that was characterized previously (Wadekar, Wang, Lokare, & Vidic, 2019) was used in the lab-scale NF system. The membrane was cut into 140 cm² rectangle and installed in the crossflow lab-scale SEPA-CFII test cell (GE Osmonics, Minnetonka, MN). The membrane was supported by a 0.8 mm thick spacer with a porosity of 0.9 (Sterlitech Corporation, Kent, WA). The feed was supplied by a high-pressure pump (G548, Marathon Electric, CA) and a pressure control valve was used to adjust the feed pressure (Figure 3.2). A return valve was placed between the permeate tank and the

feed tank to control the direction of permeate flow. A cooling system comprised of a 2.4 kW chiller (M75, Thermo Fisher, Pittsburgh, PA) and a submerged stainless-steel coil was used to eliminate temperature fluctuations in the feed tank induced by the high-pressure pump. Temperature and pressure sensors were used on both feed (T_f and P_f) and the permeate (T_p) side to monitor the operation of the NF system.

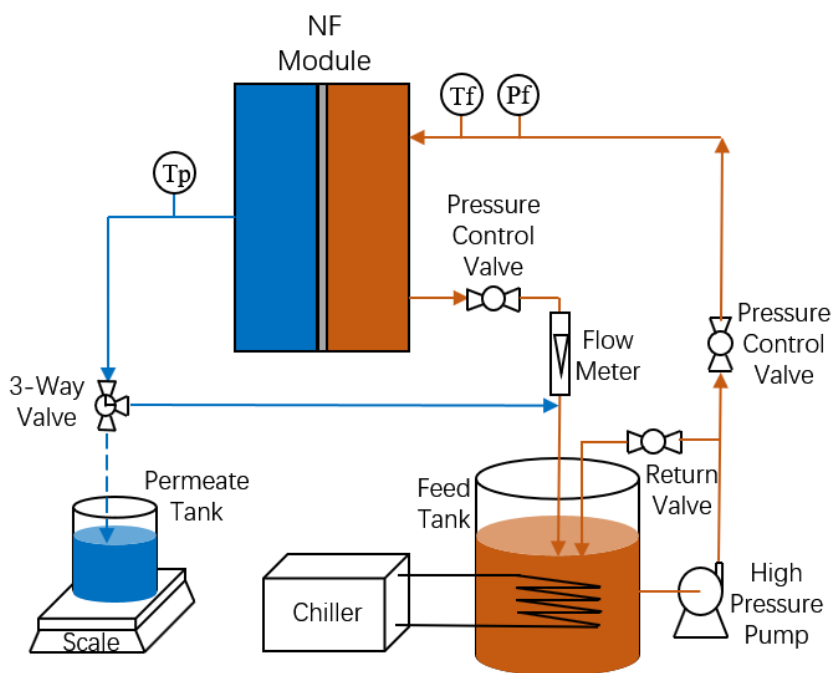


Figure 3.2 Schematic of lab-scale NF system

Prior to each experiment, 20 L of DI water was used to compact the membrane at 50 bar for 1 h. The feed pressure was then adjusted to 40 bar and the DI water was constantly recirculated for about 2 h until a stable permeate flux was achieved. The feed flowrate was adjusted to achieve the crossflow velocity of 0.63 m/s and Reynolds number of 785 ± 13 to match the conditions in the MD system. The system was operated in a constant concentration mode by continuously returning

the permeate back to the feed tank. Permeate was diverted to a graduated cylinder every 15 min to measure the flux and conductivity and was returned to the feed tank. To facilitate direct comparison of NF and MD systems, the cooling system on the feed side was used to control the temperature at 40 °C.

The membranes used in MD and NF experiments were immersed in DI water for 1 min to remove the feed solution residue on the membrane surface, air dried at room temperature for 24 h and weighed to determine the mass of accumulated scale. The membrane surface was analyzed using scanning electron microscope (SEM, JEOL brand, JSM6510) equipped with Energy Dispersive X-Ray Spectroscopy (EDS) at multiple points. Gas permeation test was conducted to determine membrane permeability before and after use according to the procedure described by Khayet et al. (Mohamed Khayet & Matsuura, 2001).

3.3 Results and Discussion

3.3.1 DCMD performance

The MD experiments with CaSO₄ solution at different salinities (Samples 1 and 3) were conducted for 720 min at feed temperature of 40 °C and permeate temperature of 10 °C and the flux and conductivity profiles are shown in Figure 3.3. The baseline flux with DI water measured prior to the experiment with Ca²⁺ solution was 21.2±0.6 LMH. Almost identical flux was measured once the feed solution was switched to Sample 1 since the total feed salinity of 7,431 mg/L had minimal impact on feed vapor pressure. The permeate flux decreased to 7.2 LMH (66% flux

reduction) after 720 min while the permeate conductivity increased from 1.5 to 275 $\mu\text{S}/\text{cm}$ during that time. The rate of permeate flux decrease gradually levelled off indicating that the scale deposition rate decreased as the total CaSO_4 in the feed solution was depleted. The continuous increase in permeate conductivity is a clear indication of membrane wetting due to scale deposition.

The MD experiment with CaSO_4 solution at high salinity (Sample 3) resulted in a constant permeate flux of 20.5 LMH while the permeate conductivity varied in a very narrow range of 1.5 - 2.7 $\mu\text{S}/\text{cm}$ throughout the test that lasted 720 min. Although the solubility of gypsum decreases with temperature increase, it is expected that 4,000 mg/L CaSO_4 used in these tests will remain fully dissolved in 30,000 mg/L NaCl solution at 40 °C. Constant permeate flux and no change in permeate conductivity indicate that virtually no scale was formed on the membrane surface under these conditions.

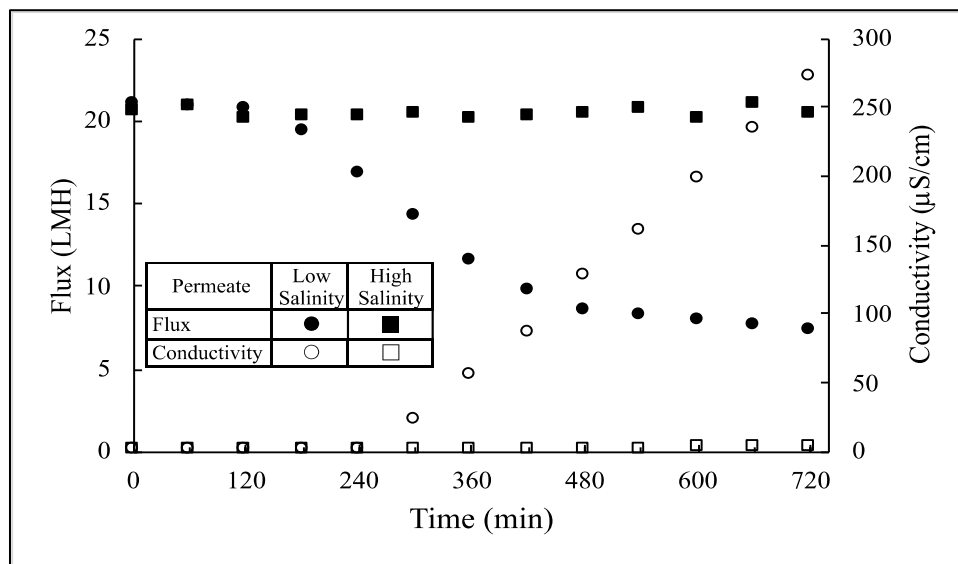


Figure 3.3 Impact of salinity on permeate flux and conductivity in DCMD treating CaSO_4 solutions (Samples 1 and 3)

MD experiments with CaCO_3 solutions (Samples 2 and 4) were conducted using identical operating conditions as in the case of CaSO_4 tests and the results are shown in Figure 3.4. The initial permeate flux for low salinity CaCO_3 solution (Sample 2) was 17.7 LMH and a constant flux of 17.2 ± 0.6 LMH was recorded during the 720 min test with a slight increase in permeate conductivity from 0.9 to 1.2 $\mu\text{S}/\text{cm}$. The decrease in permeate flux compared to the one obtained with DI water was due to precipitation of CaCO_3 that may have occurred before the first flux measurement due to heating of the feed solution. However, no further flux decline was observed throughout the experiment, which suggests that no additional membrane scaling occurred under these experimental conditions.

Similar behavior was observed in MD experiment with high salinity CaCO_3 solution (Sample 4) where the permeate flux remained stable at 17 ± 0.5 LMH for 720 min. The difference in salinity between the two CaCO_3 synthetic solutions had a small impact on the observed initial permeate flux that is driven by the difference in vapor pressure between the feed and permeate sides of the membrane.

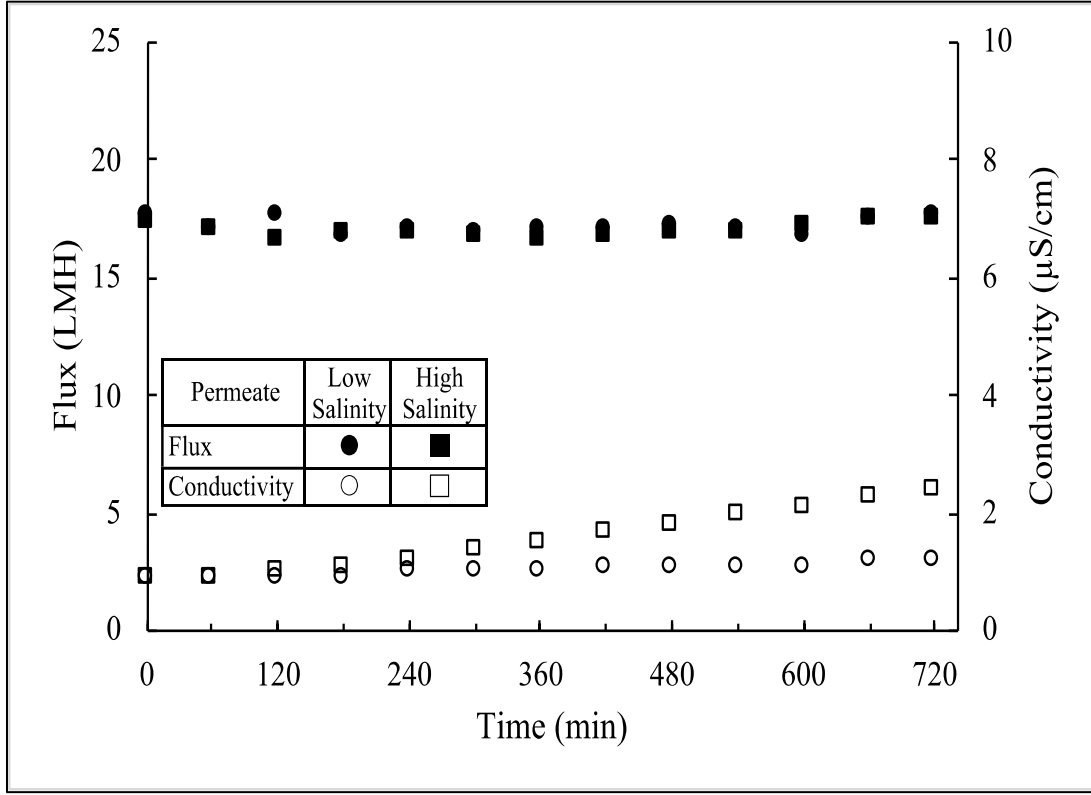


Figure 3.4 Impact of salinity on permeate flux and conductivity in DCMD treating CaCO_3 solutions (Samples 2 and 4)

The vapor pressure of a solution can be calculated as (Lawson & Lloyd, 1997):

$$p = p_0 \alpha_w = p_0 \chi_w \gamma_w \quad (3-1)$$

where, p_0 is the pure water vapor pressure, α_w is the water activity, χ_w is the molar fraction of water and γ_w is the activity coefficient. The calculation of γ_w varies with solute type and can be approximated in the case of NaCl solution as:

$$\gamma_w = 1 - 0.5 \chi_{\text{NaCl}} - 10 \chi_{\text{NaCl}}^2 \quad (3-2)$$

where, χ_{NaCl} is the molar fraction of NaCl. The water activity in 3,413 and 30,000 mg/L NaCl solution is 0.998 and 0.986, respectively. This 1.2% difference in water activity between low and high salinity solutions explains slightly higher initial flux at low salinity as compared to that observed at high salinity.

Figure 3.4 also reveals that the permeate conductivity increased from 0.9 to 2.4 $\mu\text{S}/\text{cm}$. With no observable flux decrease and negligible conductivity increase during the desalination process, it can be concluded that negligible scale accumulated on the feed side of the membrane in either MD experiment with CaCO_3 solution.

3.3.2 NF performance

The NF experiments with CaSO_4 feed solutions (Samples 1 and 3) were performed for 720 min at the feed pressure of 40 bar. The baseline permeate flux with 3,000 and 30,000 mg/L NaCl solution was 520 ± 24 and 346 ± 31 LMH, respectively. The permeate flux measurements shown in Figure 3.5 revealed that the presence of CaSO_4 had a much more dramatic impact in the case of low salinity feed when compared to that observed with high salinity feed. The initial flux of 80 LMH with low salinity feed (Sample 1) gradually decreased to 20 LMH (75% flux reduction) at the end of the test, whereas the flux declined from 340 LMH to 272 LMH (20% flux reduction) in the experiment with high salinity feed (Sample 3). The observed flux profiles clearly indicate membrane scaling for both low and high salinity CaSO_4 solution. Severe membrane scaling occurred in the case of low salinity CaSO_4 feed as evidenced by the initial flux (i.e., 80 LMH) that is about 15% of the permeate flux observed with pure NaCl solution. On the other hand, the initial permeate flux in the case of high salinity CaSO_4 feed was not statistically different from that

observed with pure NaCl solution. Significantly lower impact of scaling on NF performance observed with high salinity feed can be explained by the higher CaSO_4 solubility than in the case of lower salinity feed.

Similar impact of background salinity on permeate flux profile was observed in the experiments with CaCO_3 as shown in Figure 3.6. The permeate flux with low salinity CaCO_3 solution (Sample 2) started at 295 LMH and gradually decreased to 130 LMH (56% flux reduction) after 720 minutes. The initial permeate flux in the experiment with high salinity CaCO_3 solution (sample 4) was 370 LMH and it decreased to 323 LMH within 120 minutes and stabilized at around 315 LMH (2.5% flux reduction) towards the end of the test. The flux decline with CaCO_3 feed at low salinity (2,334 mg/L NaCl) was significantly higher than that observed with high salinity (30,000 mg/L NaCl) feed, suggesting that the deposition of CaCO_3 on membrane surface was much more pronounced in the case of low salinity feed.

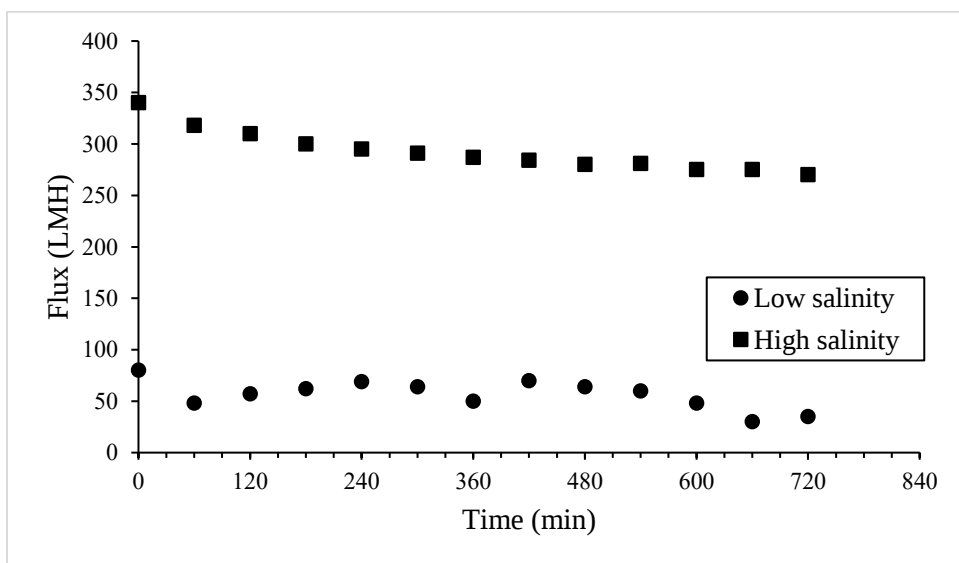


Figure 3.5 Impact of salinity on permeate flux for NF270 membrane treating CaSO_4 solutions (Samples 1 and 3)

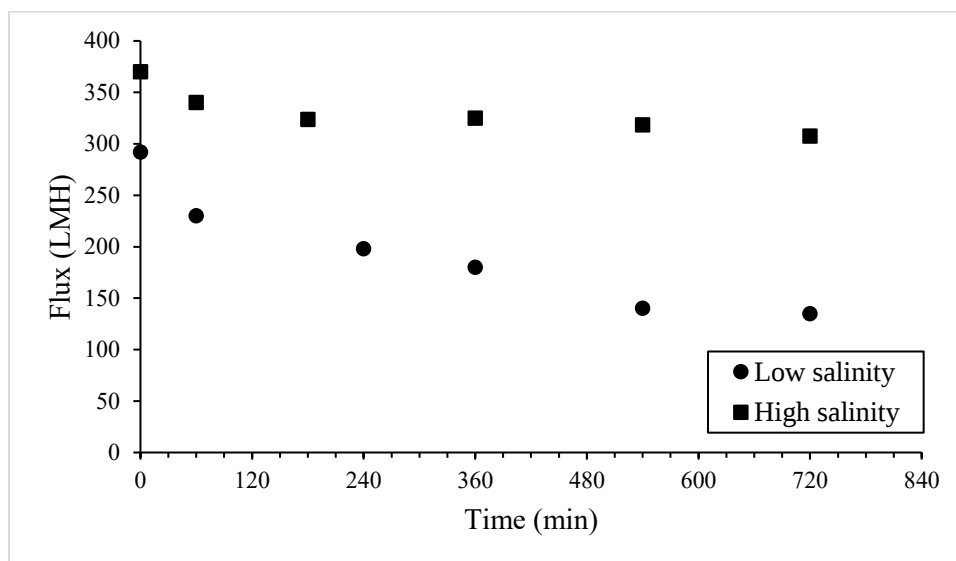


Figure 3.6 Impact of salinity on permeate flux for NF270 membrane treating CaCO_3 solutions (Samples 2 and 4)

The severity of NF membrane scaling by both calcium solutions is evident from the initial permeate flux loss and the observed decline in permeate flux during the filtration experiments. The initial permeate flux was higher for the high salinity solutions than for the low salinity solutions, which can partially be explained by the difference in the time between the start of the filtration experiment and the first flux measurement because of the difference in feed preparation protocol.

3.3.3 Characteristics of membrane scales

The mass of calcium scale deposited on MD and NF membranes used in different experiments is shown in Table 3.2.

Table 3.2. Mass of calcium scale on MD and NF membranes

Sample	Characteristics	Total (mg)		Per unit area (g/m ²)	
		MD	NF	MD	NF
1	CaSO ₄ - low salinity	205.7	331.2	51.4	23.7
2	CaSO ₄ - high salinity	1.7	38.8	0.4	2.8
3	CaCO ₃ - low salinity	46.2	64.4	11.6	4.6
4	CaCO ₃ - high salinity	18.3	23.3	4.6	1.7

It is evident from the data in Table 3.2 that less scale was deposited on MD and NF membranes treating high salinity feed solutions, which can be explained by the solubility increase with an increase in the ionic strength of the feed solution. The amount of scale accumulated on the membrane surfaces accounted for approximately 3.5%-19.7% of the total potential precipitate that could form in these systems. In general, less scale was deposited per unit surface area of NF membranes than MD membranes except in the case of CaSO₄ feed solution at high salinity. However, scales deposited on the membrane surface had much more pronounced impact on the permeate flux reduction in the case of pressure driven than thermally driven membrane system. Such behavior can be explained by the porosity of the scale layer formed in MD process that does not have as significant impact on the transport of water vapor compared to compacted scale deposited on the membranes used in the pressure driven filtration processes.(Gryta, 2008a, 2011; Lokare, Tavakkoli, Wadekar, et al., 2017)

Precipitation of CaSO_4 usually occurs in the needle/rod shape where the length of a single crystal can vary from several to tens of micrometers depending on the solution conditions. (Quddus & Al-Hadhrani, 2009; Yang et al., 2011) In membrane processes, the form of CaSO_4 precipitation can be influenced by factors such as pH, temperature, pressure and water flowrate. (Y. Wang, 2005) Crystals deposited on the membrane surface in MD and NF experiments at different salinities are depicted in Figure 3.7.

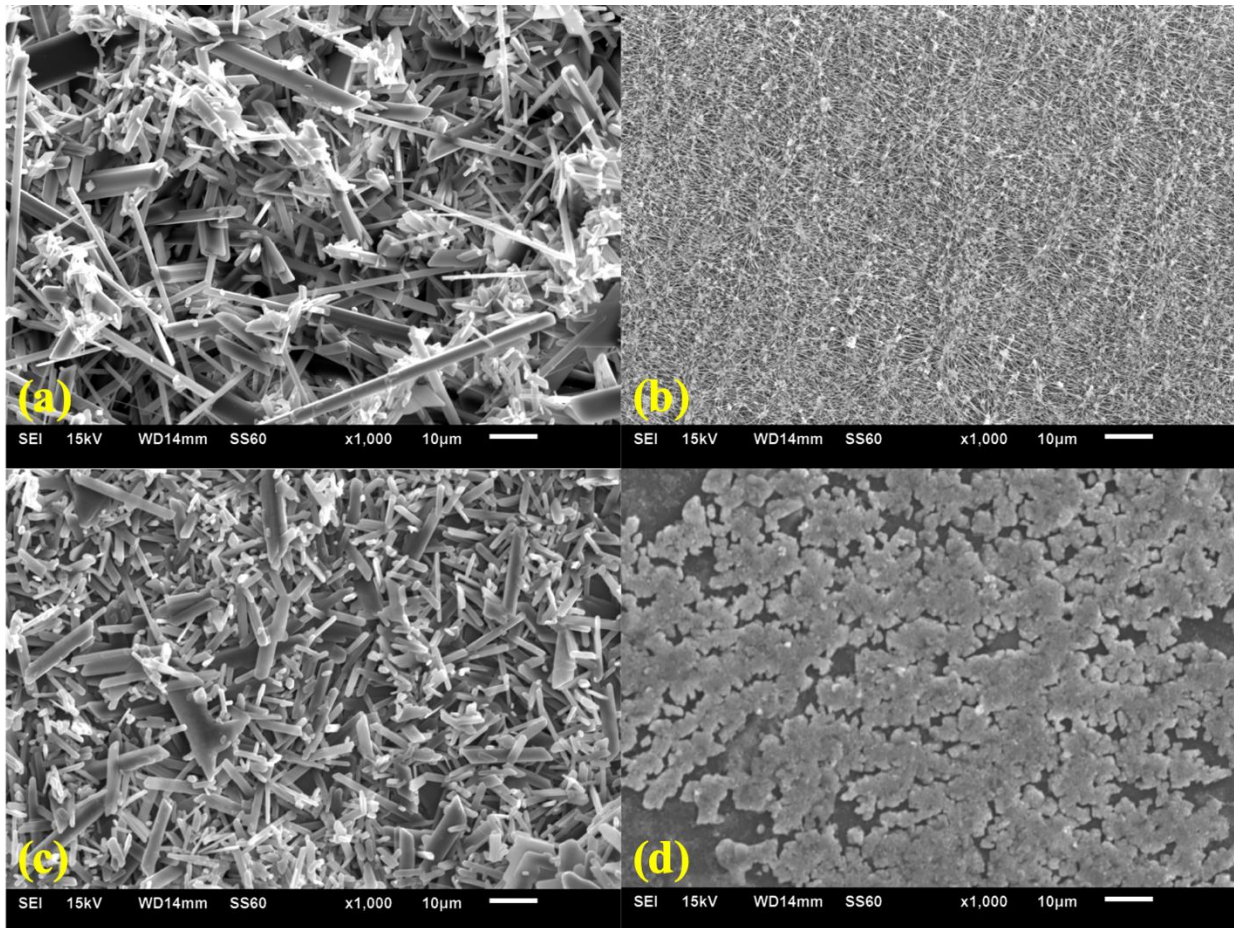


Figure 3.7 Morphology of CaSO_4 scale formed on MD membrane used in experiments with (a) low salinity feed solution and (b) high salinity feed solution (no scale is evident) and NF membrane used in experiments with (c) low salinity feed solution and (d) high salinity feed solution.

All SEM images were taken at identical magnification (i.e., 1000X) to facilitate direct comparison. The CaSO_4 scale in MD and NF systems formed at low salinity exhibited the characteristic shape but the length of the crystals in the two systems were different. The average length of one hundred randomly selected CaSO_4 crystals from Figures 3.7(a) and 7(c) was 44.8 ± 5.2 μm and 16.4 ± 3.0 μm , respectively. While there was no scale formed on MD membrane used in the experiment with high salinity CaSO_4 solution (Figure 3.7(b)), the morphology of the CaSO_4 scale observed on the surface of NF membrane used in this experiment (Figure 3.7(d)) was very different than that observed in the experiment with low salinity CaSO_4 solution. No distinct crystals are evident on Figure 3.7(d) and it appears that the scale is comprised of flat and dense solids rather than the rod-shaped crystals observed in Figure 3.7(c).

The difference in scale morphology in MD and NF systems can be attributed to the difference in solution properties near the membrane surface. In MD process, the precipitation on membrane surface is mainly affected by the sheer force and crystal growth follows the pattern of hydrodynamic precipitation in the form of needles and rods.(Gryta, 2009; Quddus & Al-Hadhrani, 2009) The impact of concentration polarization on the scale formation will be discussed together with the results obtained with CaCO_3 solutions.

The CaCO_3 precipitates can take multiple shapes, including rhombic/hexagonal, half-moon, sand-rose, flower and prismatic needles/rods(Koyuncu & Wiesner, 2007; Quddus & Al-Hadhrani, 2009) with rhombic/hexagonal cube as the most commonly observed in membrane systems.(Antony et al., 2011; Gryta, 2008a; C. Tzotzi, T. Pahiadaki, S. Yiantsios, A. Karabelas, & N. Andritsos, 2007a) The morphology of CaCO_3 scales formed on the membrane surfaces under the experimental conditions used in this study are shown in Figure 3.8.

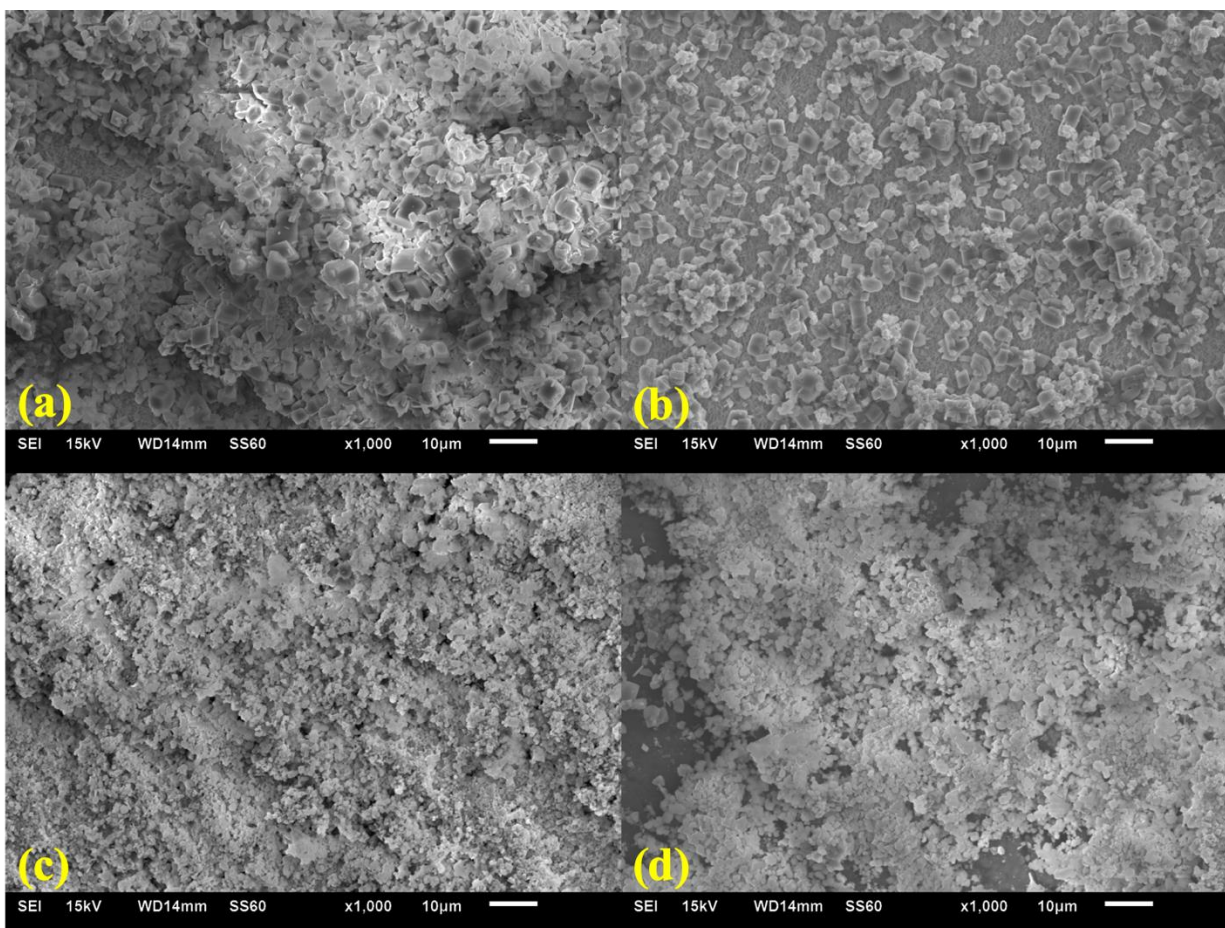


Figure 3.8 Morphology of CaCO_3 scale formed on MD membrane used in experiments with (a) low salinity feed solution and (b) high salinity feed solution and NF membrane used in experiments with (c) low salinity feed solution and (d) high salinity feed solution

CaCO_3 precipitation was observed on the surfaces of MD and NF membrane used in experiments with both low and high salinity feed solutions. Visual inspection suggests that the scales formed in the low salinity feed solutions (Figures 3.8(a) and (c)) are more porous than those formed in the high salinity feed solutions (Figures 3.8(b) and (d)). The size of CaCO_3 precipitates formed in thermally driven and pressure driven systems was analyzed using one hundred randomly selected rhombic/hexagonal-shape crystals from Figures 3.8(a) and (c). The average diameter of

crystals formed in the MD system was $3.8 \pm 0.4 \mu\text{m}$ while that formed in the NF system was $0.9 \pm 0.2 \mu\text{m}$. The difference in the crystal size could be explained by the higher salt flux towards the NF membrane, which resulted in higher level of supersaturation and greater number of smaller crystals on the membrane surface.(C. He, Zhang, & Vidic, 2016) While the shape of CaCO_3 crystals was similar in MD and NF systems for both low salinity and high salinity feed solutions, it is important to note that the mass of deposits per unit membrane area was lower in the NF system than in the MD system (Table 3.2). However, the presence of the scale in MD system had much less impact on the permeate flux for both low and high salinity feed solution compared to the NF system. Such behavior can be explained by the larger size of CaCO_3 crystals formed in the MD system, which created more porous scale that does not significantly affect the resistance to vapor transfer from the feed to the permeate side.

The difference in scale morphology in MD and NF system could also be explained by the difference in the initial concentration polarization (CP) in these two systems. Table 3.3 illustrates the theoretical concentration polarization coefficients (CPC) at the initial stages of MD and NF experiments that were calculated using the first available permeate flux measurement and the methods developed by Martínez-Díez et al.(Martínez-Díez & Vázquez-González, 1999) and Giacobbo et al.(Giacobbo, Moura Bernardes, Filipe Rosa, & De Pinho, 2018), respectively.

Table 3.3. Initial concentration polarization coefficient (CPC) in MD and NF experiments

System	CaSO_4		CaCO_3	
	Low salinity	High salinity	Low salinity	High salinity
MD	1.210	1.205	1.182	1.178
NF	1.746	10.787	7.642	13.312

As indicated by the results in Table 3.3, the NF membranes exhibited significantly higher initial CPC in all cases compared to MD membranes. The higher initial CPC resulted in higher solute concentration on the membrane surface and faster precipitation of calcium salts, which explains the smaller crystals observed in the NF experiments compared to MD experiments. Smaller crystals and higher feed pressure lead to the formation of denser scales in NF than in MD experiments that are evident from the comparison of Figures 3.7(a) and 3.7(c) and Figures 3.8(a) and 3.8(c)).

3.3.4 Membrane permeability

Gas permeation tests were conducted on pristine and used membranes to evaluate the impact of calcium scales on membrane permeability. Used MD membranes were cut into 10 mm diameter circles to perform these tests and the results are shown in Figure 3.9. The MD membranes used in the experiments with high salinity CaSO_4 solution and both high and low salinity CaCO_3 solutions exhibited almost identical permeability as the pristine membrane. A one-way analysis of variance (ANOVA) for these four data sets revealed no statistically significant difference among the experimental results obtained with these membranes. The only used MD membrane that deviated from this trend was the one used in the experiment with low salinity CaSO_4 solution. As shown in Figures 3.3 and 3.4, low salinity CaSO_4 solution was the only feed solution that resulted in significant permeate flux decline and membrane wetting. The gas permeability of the membrane used in this MD tests decreased from $4.95 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{pa}^{-1}$ to $1.65 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{pa}^{-1}$ (i.e., 3 times lower).

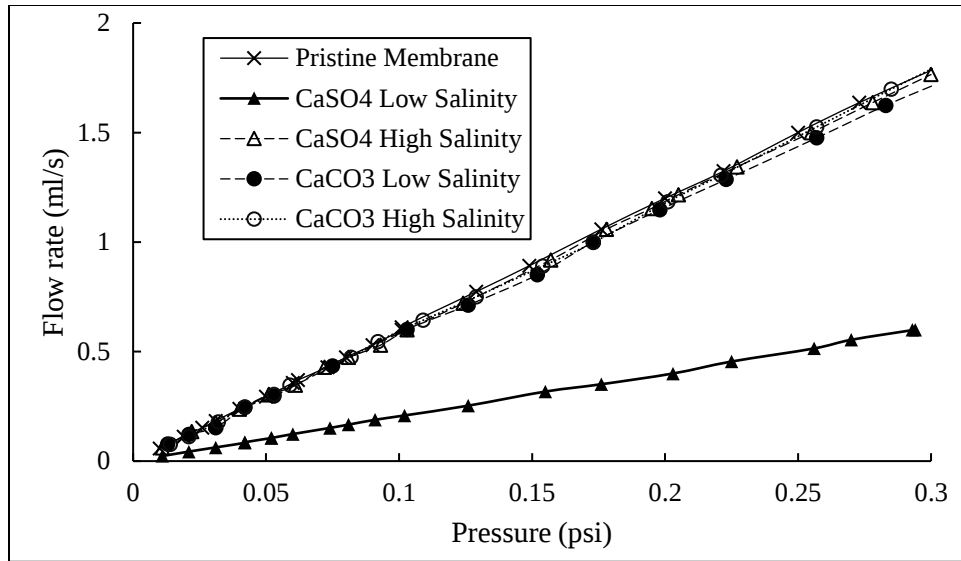


Figure 3.9 Gas permeability of pristine and used MD membranes

NF membranes were cut into 45 mm diameter circles to perform gas permeation tests and the results are shown in Figure 3.10. Contrary to the results observed with MD membranes, all used NF membranes exhibited much lower gas permeability compared to the pristine membrane. The gas permeability of pristine NF membrane was $8.15 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{pa}^{-1}$ while that of the used NF membrane ranged between $1.63 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{pa}^{-1}$ to $4.88 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{pa}^{-1}$ (i.e., 20-60 times lower). This dramatic reduction in gas permeability can be explained by the hydraulic pressure used in the NF experiments that lead to crystal formation inside the membrane pores (Shih, Rahardianto, Lee, & Cohen, 2005) and irreversible reduction in membrane permeability. Such behavior was not observed with MD membranes because only water vapor is transported through these membranes and because the porous scale formed on the membrane surface had much less impact on gas permeability.

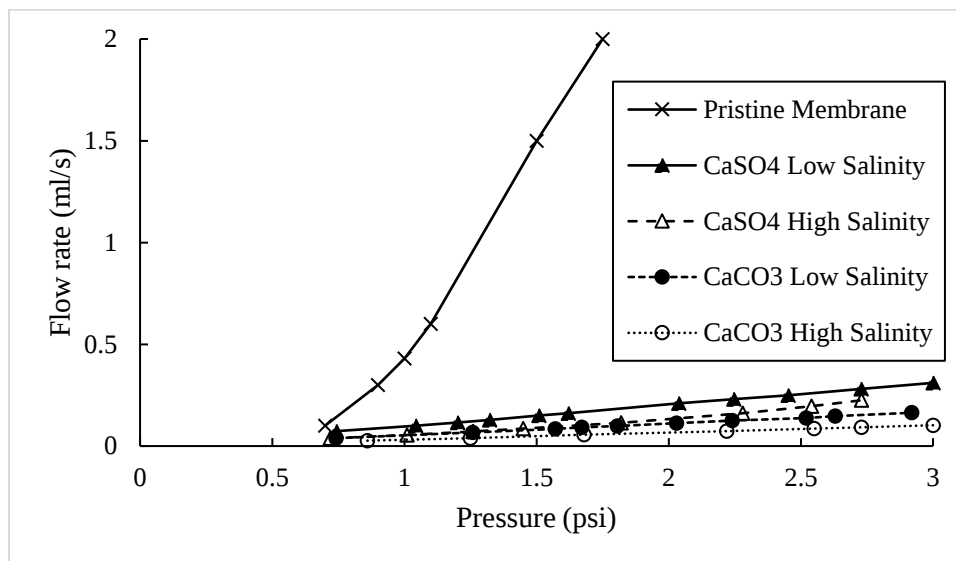


Figure 3.10 Gas permeability of pristine and used NF membranes

3.4 Conclusion

The study was designed to compare the impact of calcium scaling on thermal and pressure driven membrane processes in the experiments where calcium sulfate and calcium carbonate scales were allowed to form on the membranes used in membrane distillation and nanofiltration systems operated under identical conditions. Experimental results showed that calcium scaling is quite different in the two membrane systems with respect to scale morphology and its impact on permeate flux and membrane permeability.

The CaSO_4 scale formed on the surface of MD membranes had an impact on permeate flux in the case of low salinity feed, but no measurable impact was observed in the case of high salinity

feed. Although the precipitation of CaCO_3 was observed on MD membranes in the case of both low and high salinity feed, it had almost no measurable impact on permeate flux and quality. On the other hand, calcium scales formed on NF membranes caused significant permeate flux decline for both calcium salts irrespective of the feed salinity.

The results of this study clearly indicate that NF membranes are more susceptible to calcium scaling than MD membranes under identical operating conditions. The crystals deposited on MD membranes were larger compared to those deposited on the surface of NF membranes. Higher permeate flux and solute transport in NF systems resulted in faster and more severe scaling of the membrane with dramatic reduction in system performance. Surface crystallization in NF systems is likely extended into the membrane pores, which lead to permanent reduction in the permeability of these membranes. Higher concentration of calcium scalants on membrane surface and significant hydraulic pressure in the NF system lead to the formation of denser scales and associated severe decline in permeate flux.

This study demonstrated that calcium sulfate and calcium carbonate scales have more pronounced impact on the performance of NF than MD systems when treating identical feed solutions. Such behavior can be explained by the difference in mass transport and separation mechanisms of pressure and thermally driven membrane processes.

4.0 Pretreatment of brackish water reverse osmosis (BWRO) concentrate to enhance water recovery in inland desalination plants by direct contact membrane distillation (DCMD)

This work has been published as:

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4.1 Introduction

Global water crisis in recent years has forced a search for alternative water sources. (Charcosset, 2009) Brackish water (BW) desalination has been increasingly utilized as an alternative for drinking water supply due to the global shortage of fresh water.(Wade Miller, 2006) Brackish water is characterized by total dissolved solid (TDS) above the drinking water standards (i.e., 500 mg/L) but below 15,000 mg/L.(Alghoul, Poovanaesvaran, Sopian, & Sulaiman, 2009) Reverse Osmosis (RO) is commonly used to recover fresh water from the high salinity brackish water because of its flexible configuration and low capital and operating costs compared to other desalination technologies.(Ahmad & Schmid, 2002; Herold et al., 1998) Some small BWRO plants integrated with solar energy can decrease the energy cost to 100 kJ/kg

permeate.(Joyce, Loureiro, Rodrigues, & Castro, 2001) However, Alghoul et al.(Alghoul et al., 2009) suggested that solar powered BWRO plants in many countries achieve water recovery below 70%, which results in RO reject with a TDS of around 8,000 ppm. BWRO plants integrated with forward osmosis (FO) and ultrafiltration (UF) can increase the water recovery to 70-90% (Turek et al., 2017) and increase the reject TDS to around 15,000ppm.

Disposal of RO reject accounts for up to 33% of the total operating cost depending on the brine volume, quality, and disposal method.(Panagopoulos, Haralambous, & Loizidou, 2019) The direct reject disposal options include blending with RO permeate/feed, surface/sewage discharge, deep-well injection and land application; other reject volume reduction strategies include evaporation ponds, wind-aid intensified evaporation and mist spray."Brackish groundwater: a viable community water supply option?" NSW Public WorksWaterlines Report Series No 66, December2011 Mickley et al.M. Mickley, "Updated and Extended Survey of U.S. Municipal Desalination Plants", Bureau of Reclamation, Denver, Colorado (2018) investigated 406 desalination plants in the U.S. and reported that 70% utilize surface/sewer discharge, 17% utilize deep-well injection and 7% use land application for reject disposal. Reject disposal for inland desalination plant is more challenging due to limited disposal optionsUrban water reuse handbook. Boca Raton: CRC Press, Taylor & Francis Group, 2016. with surface/sewer discharge of brine affecting groundwater quality, agricultural productivity and municipal sewage treatment system.M. Ahmed, "Brine Disposal from Inland Desalination Plants: Current Status, Problems, and Opportunities," 2004. Deep-well injection and evaporation have less environmental impact but relatively higher cost. United Nation (UN) reports ("ESCWA Water Development Report 3 : role of desalination in addressing water scarcity," 2009; "Water desalination technologies in the ESCWA member countries," 2001; "Water pollution in selected urban areas in the ESCWA

region (case-studies of Damascus, Gaza and Jeddah).", 1997) show that the cost of deep-well injection ranges from \$0.1 to \$0.3 per m³ of desalinated water, while the cost of evaporation pond is between \$0.3-\$0.5/m³ of feed. Besides the cost for disposal, transportation and pumping of the brine contributes significantly to the total cost. ("ESCWA Water Development Report 3 : role of desalination in addressing water scarcity," 2009) A case study by Kally et al. (Kally, Fishelson, & ha-Tikhon, 1993) showed that the cost of water transfer over 200 km distance and 75 m elevation is \$0.29/m³. Therefore, an efficient process that can enhance water recovery and reduce reject disposal cost would help to alleviate the global water shortage.

Membrane distillation (MD) is a thermal desalination process relying on the vapor pressure difference across the hydrophobic membrane provided by the temperature difference between the feed and permeate side. (Lawson & Lloyd, 1997) Because the feed salinity has limited impact on the vapor pressure (D. Y. Hou et al., 2010), MD is uniquely positioned to offer high water recoveries. MD has been used to treat high salinity waters, including produced water from oil and gas extraction, landfill leachate and seawater RO brine. (Anvari et al., 2019; Chang et al., 2019; Ji et al., 2010; Lokare, Tavakkoli, Wadekar, et al., 2017; Sardari, Fyfe, Lincicome, & Ranil Wickramasinghe, 2018; Zhou et al., 2017) Direct contact membrane distillation (DCMD) can achieve 99.85% water recovery for the feed containing 600 mg/L sodium chloride (Cath et al., 2004), and it has been used to concentrate produced water up to 300,000 mg/L TDS. (Lokare, Tavakkoli, Wadekar, et al., 2017) This example illustrates the capability of DCMD to treat RO reject to further enhance the overall water recovery at inland BWRO plants and reduce the volume of reject requiring disposal. Other advantages of MD in brackish water desalination include small footprint, low capital cost and high permeate purity, which highlight the potential for widespread application of membrane distillation in inland brackish water desalination plants

to increase the overall water recovery.(E. Ali, Orfi, Najib, & Saleh, 2018; J.-G. Lee et al., 2015; Mericq, Laborie, & Cabassud, 2010; P. Zhang, Knötig, Gray, & Duke, 2015)

MD faces the same problems of membrane fouling that is relevant to all membrane processes for water purification. As the RO reject is concentrated, the solubility limit of some salts may be exceeded leading to precipitation of these salts on the membrane surface and a decrease in permeate flux due to overall permeability reduction.(Gryta, 2008a; F. He et al., 2009b; Tong et al., 2019; David M Warsinger et al., 2015) It is also possible that these precipitates can affect membrane hydrophobicity and lead to feed water intrusion into the membrane (i.e., membrane wetting).(Rezaei et al., 2018) Both membrane scaling and wetting have negative impact on membrane distillation and need to be mitigated to maintain stable performance and requisite water recovery. The main inorganic foulants in brackish groundwater vary with geographic location and depth of the groundwater. As reported by the United States Geological Survey (USGS),(Jennifer S. Stanton et al., 2017) the most abundant salt in brackish groundwater is calcium sulfate, which is the dominant inorganic chemical in 35% of the U.S. brackish groundwater wells, especially in the Midwest area. USGS also reported that silica is observed in every brackish groundwater in the U.S. Although the amount of dissolved silica in water is small due to its low solubility, once it precipitates on membrane surface it is difficult to remove with traditional membrane cleaning methods.(D. Hou et al., 2016) Regardless of the nature and source of inorganic scalants, most have detrimental impact on MD performance in terms of productivity and permeate quality . Mitigation of membrane fouling in MD is crucial for maintaining the requisite performance and current approaches can be classified in four main categories (F. He, Sirkar, & Gilron, 2009a; Hickenbottom & Cath, 2014; Hsu, Cheng, & Chiou,

2002; Tijing et al., 2015; H. Zhang, Lamb, & Lewis, 2005): (a) feed pretreatment; (b) operating mitigation methods; (c) membrane modification and (d) antiscalant application.

The main objective of this study was to investigate the feasibility of using membrane distillation to enhance the overall water recovery of current BWRO treatment plants and reduce the cost associated with reject disposal. DCMD system was employed in this study to study system performance, including permeate flux and quality, as a function of key operating parameters. In addition, possible BWRO reject pretreatment using barium precipitation to remove potential foulants and achieve high water recovery was investigated in this study.

4.2 Materials and Methods

4.2.1 DCMD module

The schematic configuration of the DCMD system used in this study is shown in Figure 4.1. The only driving force for mass transfer is the vapor pressure difference across the membrane and the permeate flux can be expressed as:

$$J = C(P_f - P_p) \quad (4-1)$$

where, C is the membrane distillation coefficient, P_f and P_p are the vapor pressure on feed and permeate side of the membrane, respectively. The vapor pressure of pure water can be calculated by Antoine equation:

$$P_m = \exp\left(23.328 - \frac{3841}{T_m - 45}\right) \quad (4-2)$$

where, P_m is pure water pressure and T_m is the water temperature. Water salinity has adverse impact on vapor pressure but is minimal compared to the impact of temperature (Hitsov, Maere, De Sitter, Dotremont, & Nopens, 2015).

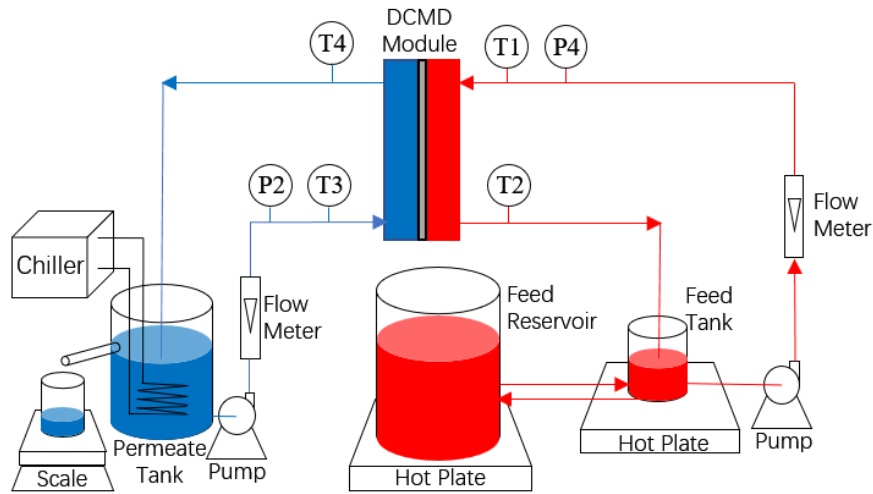


Figure 4.1 Schematic of the DCMD system

Centrifugal pumps (Baldor Reliance, UL FILE E46145) were used on both feed and permeate sides to deliver water to the DCMD module. Stainless steel coil connected to a 2.4 kW chiller (Thermo Fisher, M75) was used to maintain stable temperature in the permeate tank. Temperature (T1-T4) and pressure (P1-P2) probes connected to a computer were used to monitor the operating conditions of the system. The weight of permeate overflow was continuously monitored using a digital scale to assess the permeate flux. Permeate conductivity was also continuously monitored using conductivity meter (Thermo Electron Corp., Orion 145A+) to

detect possible membrane wetting. Unless otherwise noted, the feed and permeate temperature was maintained at 60 and 20 °C, respectively, because studies suggested that this choice of operating temperatures minimizes the specific energy cost (SEC) of DCMD (Deshmukh et al., 2018). The flow rate of both feed and permeate solution was 0.2 gpm and the feed side pressure was 166 kPa.

4.2.2 Membrane

Polytetrafluoroethylene (PTFE) membrane on polypropylene support with mean pore size of 0.21 μm , total thickness of 112 ± 17 μm , porosity of $42 \pm 0.5\%$ and contact angle of 149 ± 3 (Lokare, Tavakkoli, Wadekar, et al., 2017) was purchased from Sterlitech Corporation (Kent, WA). The membrane was cut into a 20×200 mm sheet to fit in the laboratory-scale DCMD module. Used membranes were dried at room temperature and cut in liquid nitrogen for analysis using scanning electron microscopy (SEM, JEOL brand, JSM6510). The composition of deposits on the membrane surface was analyzed using Energy Dispersive X-Ray Spectroscopy (EDS) at 5 randomly selected points. Gas permeation test (Mohamed Khayet & Matsuura, 2001) was used to assess membrane permeability before and after its use in DCMD experiments.

4.2.3 RO reject brine

Brackish groundwater sample obtained from Brackish Groundwater National Desalination Research Facility (BGNDRF, Alamogordo, NM) was concentrated 3 times by constant temperature evaporation at 30 °C to simulate the reject stream from a reverse osmosis

(RO) desalination process. The composition of concentrated groundwater characterized by ICP-OES (Agilent Technologies, Model 5100) and IC (Thermo Scientific, Model Dionex ICS-1100) is shown in Table 4.1.

Table 4.1 Concentration of main ions in simulated RO reject

Ion	Concentration (mg/L)
Sulfate	4,051
Chloride	1,478
Sodium	1,098
Calcium	489
Potassium	12
Magnesium	655
Barium	0
Silica	92

Synthetic RO reject was also prepared by adding main ions to match the BWRO reject composition outlined in Table 4.1.

4.2.4 Barite precipitation

The data in Table 4.1 suggest that the main potential scalant that would form in this water as it becomes more concentrated in the DCMD system is calcium sulfate. Ge et al.(Ge, Peng, Li, Chen, & Wang, 2014) reported that calcium sulfate was one of the main foulants in DCMD system treating RO reject containing 1,800 mg/L of sulfate while the brackish groundwater RO reject used in this study had more than 4,000 mg/L of sulfate.

Considering that Barium sulfate (BaSO_4) has an extremely low solubility product (i.e. 1.1×10^{-10}), it is expected that adding barium to this RO reject would be an efficient way to

remove sulfate ions as a pretreatment step prior to DCMD treatment. To investigate key operating parameters for this pretreatment step, barium chloride was added to the synthetic RO reject at barium to sulfate molar ratio of 120% and the solution was mixed for 240 min. The supernatant was filtered through 0.45 μm nylon membrane and used in DCMD experiment with PTFE hydrophobic membrane.

4.3 Results and Discussion

4.3.1 Equilibrium calculations

Chemical equilibrium was assessed using a computer program PHREEQC that is designed to perform a variety of aqueous geochemical calculations (e.g., speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations) and is provided by the United States Geological Survey (USGS). Major ions in RO reject with concentration above 10 mg/L were included in PHREEQC simulation to predict the effect of barium precipitation and Figure 4.2 illustrates changes in the finished water quality as a function of barium addition.

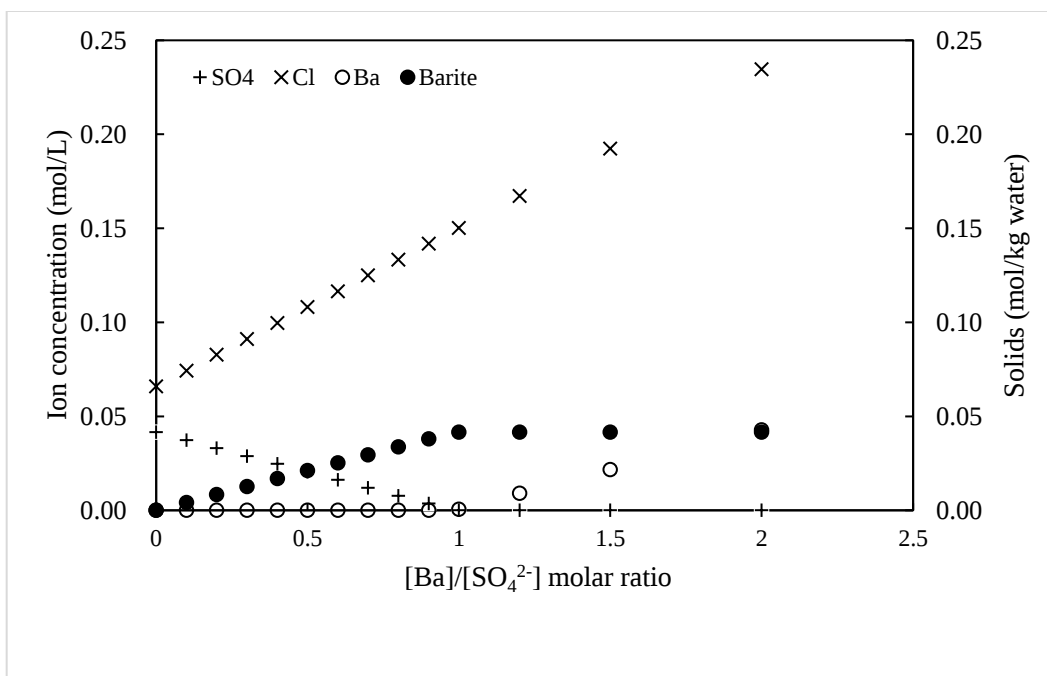


Figure 4.2 Predicted equilibrium composition of RO reject as a function of barium addition

Thermodynamic simulations indicate that the addition of barium chloride at the barium to sulfate molar ratio of 1 would precipitate 99.9% of sulfate. Kinetic experiments with simulated RO reject were conducted using different barium to sulfate ratios to verify actual sulfate removal as a function of the reaction time. These experiments revealed that the contact time of 30 min would be sufficient to remove more than 99% of sulfate when barium to sulfate molar ratio was 1.2.

PHREEQC simulation of the impact of water recovery on the composition of feed solution shown in Figure 4.3 suggests that it is possible to achieve 90% water recovery from the pretreated RO reject with minimal amount ($\sim 10^{-3}$ mol/kg water) of silica (i.e., solid/amorphous silicon dioxide) precipitation on the feed side of the DCMD module.

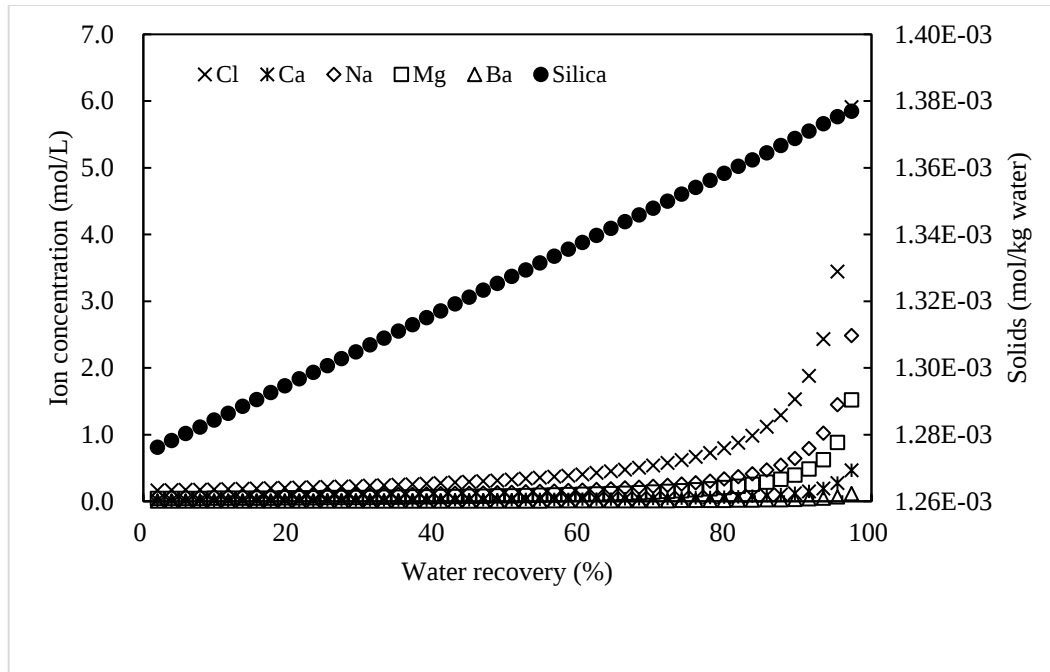


Figure 4.3 Composition of RO reject as a function of water recovery in DCMD system

Silica (silicon dioxide) is a common foulant in membrane desalination processes, especially when treating groundwater (Badruzzaman, Subramani, DeCarolis, Pearce, & Jacangelo, 2011). Bush et al. (Bush, Vanneste, & Cath, 2019) used saturated silica solution in DCMD system and observed severe membrane scaling in a long-term operation. The amount of silica predicted to form in the RO reject used in this study at 80-90 % recovery is fairly small, and it is not clear that it will affect the operation of DCMD system.

4.3.2 DCMD experiment with synthetic water

Synthetic water was prepared according to the composition outlined in Table 4.1 but without sulfate to represent the effluent from the pretreatment step that relies on barite

precipitation to remove sulfate. This water was subjected to treatment in a DCMD module operated in a batch mode at constant feed and permeate temperatures for a period of 14 hours to reach 85% water recovery. Permeate flux and conductivity during this experiment are shown on vertical axes in Figure 4.4 while the lower and upper horizontal axes represent the duration of the experiment and water recovery achieved throughout the experiment, respectively.

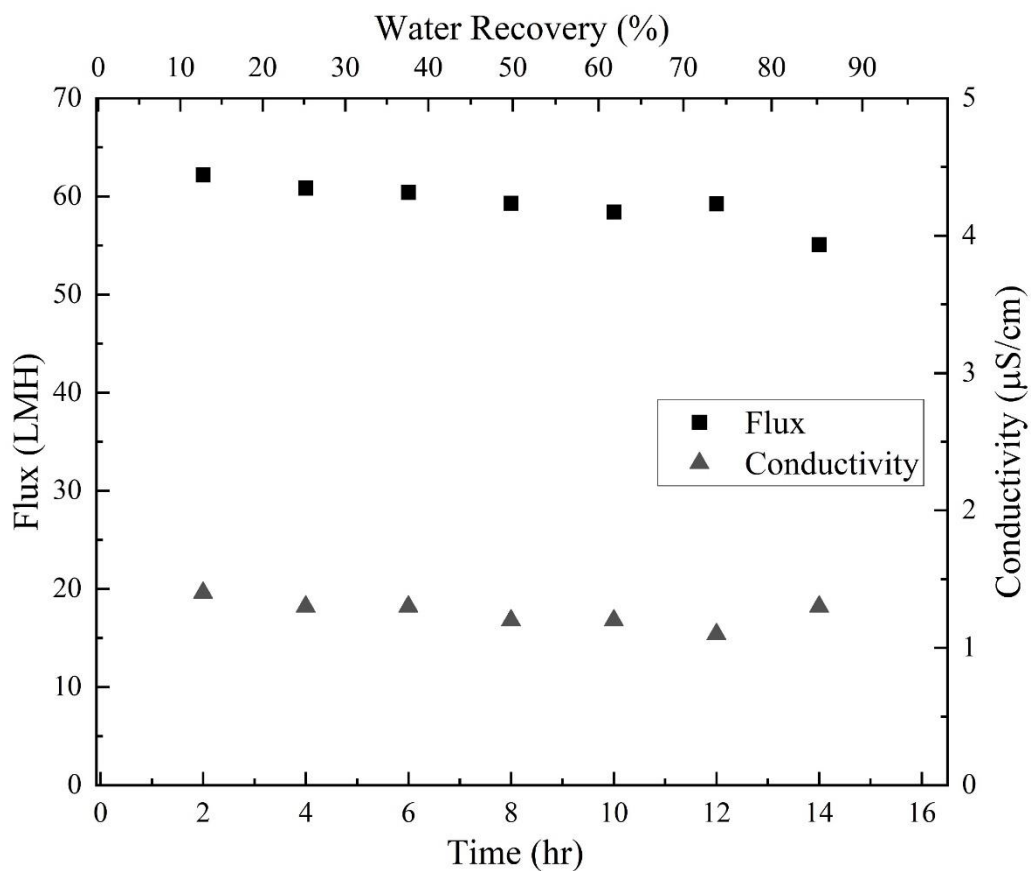


Figure 4.4 Permeate flux and conductivity in the experiment with synthetic RO reject without sulfate ($T_{\text{feed}} = 60\text{ }^{\circ}\text{C}$, $T_{\text{permeate}} = 20\text{ }^{\circ}\text{C}$; $Q_{\text{feed}} = Q_{\text{permeate}} = 0.2\text{ gpm}$)

The permeate flux at the start of this experiment was 63 LMH and it decreased to 58 LMH as the TDS in the feed solution increased from 7,341 to 49,650 mg/L and the water vapor

pressure on the feed side decreased from 19.9 to 19.4 kPa. Similar permeate flux was observed in a study with pure 600 mg/L NaCl solution.(Cath et al., 2004) The conductivity of permeate remained around 1.5 ± 0.3 $\mu\text{S}/\text{cm}$ indicating that no membrane wetting occurred in this experiment. These results suggest that it is possible to achieve 85% water recovery from the brackish water RO reject if sulfate is first removed from this wastewater, which can be accomplished through barite precipitation. However, the actual RO reject contains many other ions at low concentrations as well as organic compounds that were not present in the synthetic solution and may affect the performance of DCMD system in treating this wastewater.

4.3.3 DCMD experiment with actual brackish groundwater

Actual brackish water RO reject was pretreated by a precipitation step where barium chloride was added to achieve the initial barium to sulfate molar ratio of 1.2. The solution was mixed for 4 hours to ensure total removal of sulfate through precipitation as barite. The mixture was then filtered through 0.45 μm nylon membrane and used in DCMD test. Operation of the DCMD module continued for 14 hours with total water recovery of 87.6% and the composition of concentrate at the end of this test is shown in Table 4.2.

Table 4.2 Composition of the concentrate of actual brackish water RO reject at the end of treatment in laboratory-scale DCMD system

Ion	Concentration(ppm)
Sulfate	0
Chloride	30,247
Sodium	7,838
Calcium	3,551
Potassium	86
Magnesium	4,840
Barium	2,385
Silica	691

Both water recovery measurements and comparison of the results in Tables 4.1 and 4.2 suggest that the feed stream was concentrated about 7 times during this test. High levels of barium and chloride in the final concentrate are due to residual from barium chloride that was used as barium source to precipitate sulfate in this water prior to DCMD experiment. The permeate flux and conductivity obtained in this experiment are shown in Figure 4.5.

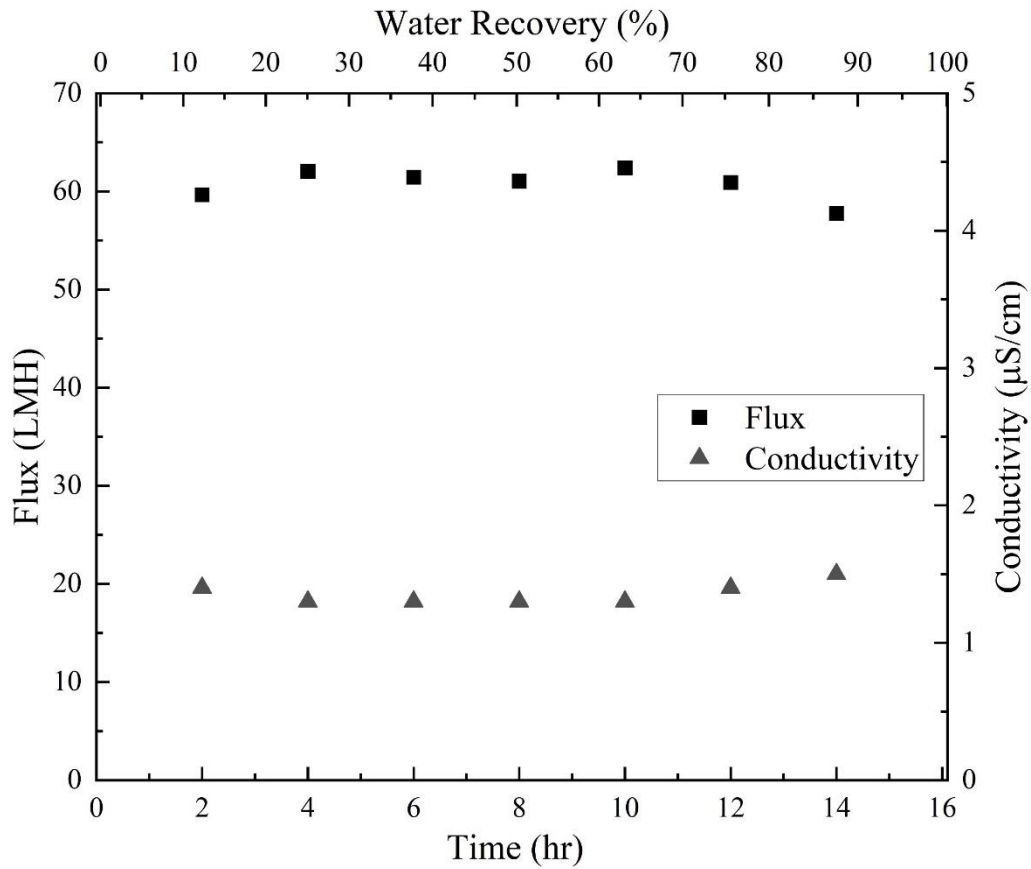


Figure 4.5 Permeate flux and conductivity in DCMD test with actual brackish groundwater

($T_{\text{feed}} = 60\text{ }^{\circ}\text{C}$, $T_{\text{permeate}} = 20\text{ }^{\circ}\text{C}$; $Q_{\text{feed}} = Q_{\text{permeate}} = 0.2\text{ gpm}$)

The results in Figure 4.5 clearly show that there was no membrane fouling in this experiment because there was no significant drop in permeate flux with actual brackish groundwater RO reject even after 87.6% water recovery was achieved in this test (permeate flux decreased from 62 to 57 LMH as the feed TDS increased from 7,011 to 56,540 mg/L). Furthermore, there was no observable membrane wetting since the permeate conductivity remained around 1.5 $\mu\text{S/cm}$. Comparison of the results shown in Figures 4.4 and 4.5 suggests

that the actual brackish groundwater does not contain any other substances that may interfere with DCMD operation. Results shown in Figures 4.4 and 4.5 also suggest that DCMD with PTFE membrane can achieve close to 90% water recovery from the RO concentrate to augment the ability of inland brackish water desalination plants to recover clean water and substantially reduce the cost of concentrate disposal by reducing its volume almost 10 times.

4.3.4 DCMD experiments at high permeate flux

To evaluate the possibility of accelerating water recovery in DCMD module, experiments with synthetic and actual brackish water samples were performed using higher temperature difference across the PTFE membrane. Previous studies suggested that higher temperature difference in a DCMD module would lead to higher permeate flux, but the concentration polarization in the module will change dramatically to affect the permeate flux (M Khayet, Godino, & Mengual, 2005; Lokare, Ji, Wadekar, Dutt, & Vidic, 2019; Lokare & Vidic, 2019). The concentration polarization coefficient can be calculated as (Martínez-Díez & Vázquez-González, 1999):

$$CPC = \frac{C_m}{C_b} \quad (4-3)$$

where, C_m and C_b are the salt concentration on the membrane surface and in the bulk, respectively. Salt concentration on the membrane surface, C_m , can be estimated based on the following equation (Schofield, Fane, Fell, & Macoun, 1990):

$$C_m = C_b \exp\left(\frac{J}{\rho K}\right) \quad (4-4)$$

where, ρ is bulk density, J is the permeate flux and K is the solute mass transfer coefficient, which can be calculated from (Martínez-Díez & Vázquez-González, 1999):

$$Sh = \frac{K \cdot d_h}{D} = 1.86 \left(Re \cdot Sc \cdot \frac{d_h}{L} \right)^{0.33} \quad (4-5)$$

where, Sh is the Sherwood number, d_h is the hydraulic diameter, D is diffusion coefficient, Re is Reynolds number, Sc is the Schmidt number, and L is the channel length. Combining Equation (4-3) and (4-4) yields the following relationship between permeate flux, J , and concentration polarization coefficient (CPC):

$$CPC = \exp\left(\frac{J}{\rho K}\right) \quad (4-6)$$

Equation (4.6) indicates that an increase in permeate flux will also lead to an increase in concentration polarization, which means that the salt concentration near the membrane surface will be much higher than in the bulk.

Operating a DCMD module at higher permeate flux could aggravate concentration polarization and lead to more severe membrane fouling due to enhanced opportunities for salt precipitation on the membrane (A. Ali, Macedonio, Drioli, Aljlil, & Alharbi, 2013; Gryta, 2008; Martínez-Díez & Vázquez-González, 1999). To explore the effect of concentration polarization in BWRO reject, synthetic water (Table 1) without sulfate and actual water pretreated by barite precipitation were used as feed streams to a DCMD module operated at feed temperature of 80 °C and permeate temperature of 10 °C. Other operating conditions remained identical to those in experiments depicted in Figures 4.4 and 4.5 (i.e., feed and permeate flow of 0.2 gpm and feed

pressure of 166 kPa). Permeate flux and conductivity obtained in these tests with synthetic and actual water are shown in Figures 4.6 and 4.7, respectively.

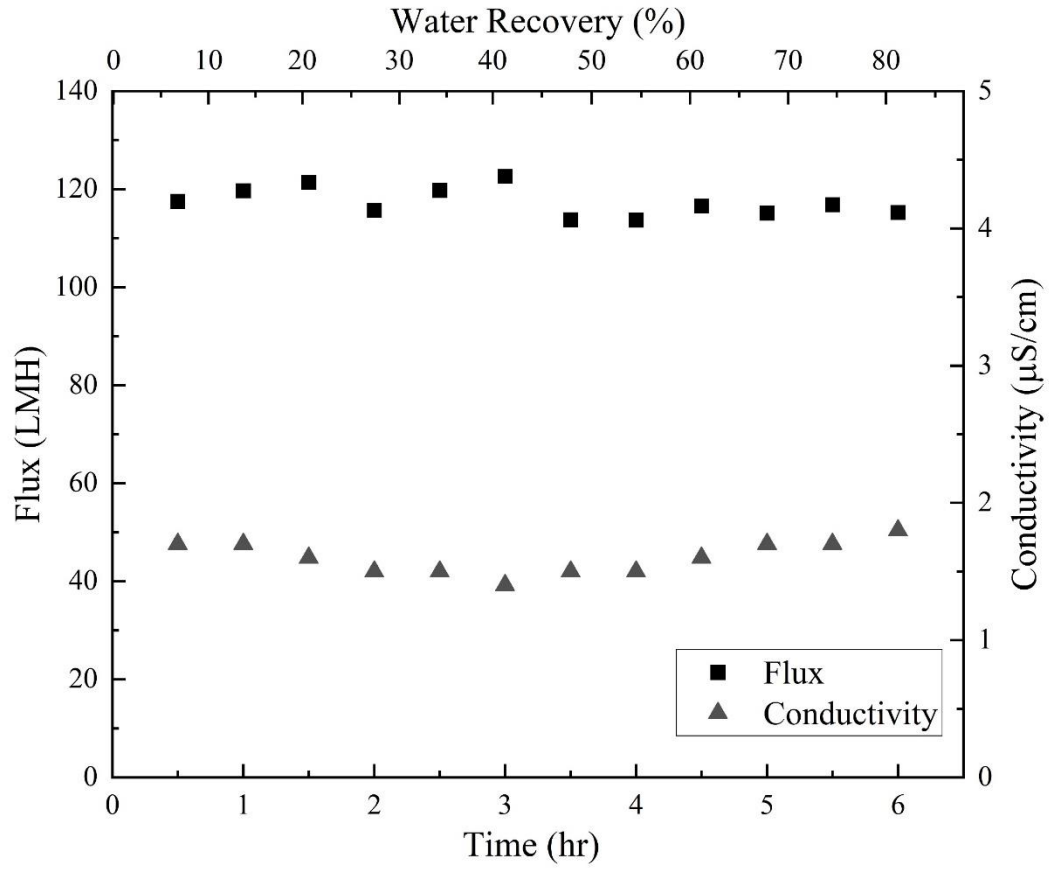


Figure 4.6 Permeate flux and conductivity in DCDM experiment with synthetic water at temperature gradient of 70 °C ($T_{\text{feed}} = 80\text{ °C}$, $T_{\text{permeate}} = 10\text{ °C}$; $Q_{\text{feed}} = Q_{\text{permeate}} = 0.2\text{ gpm}$)

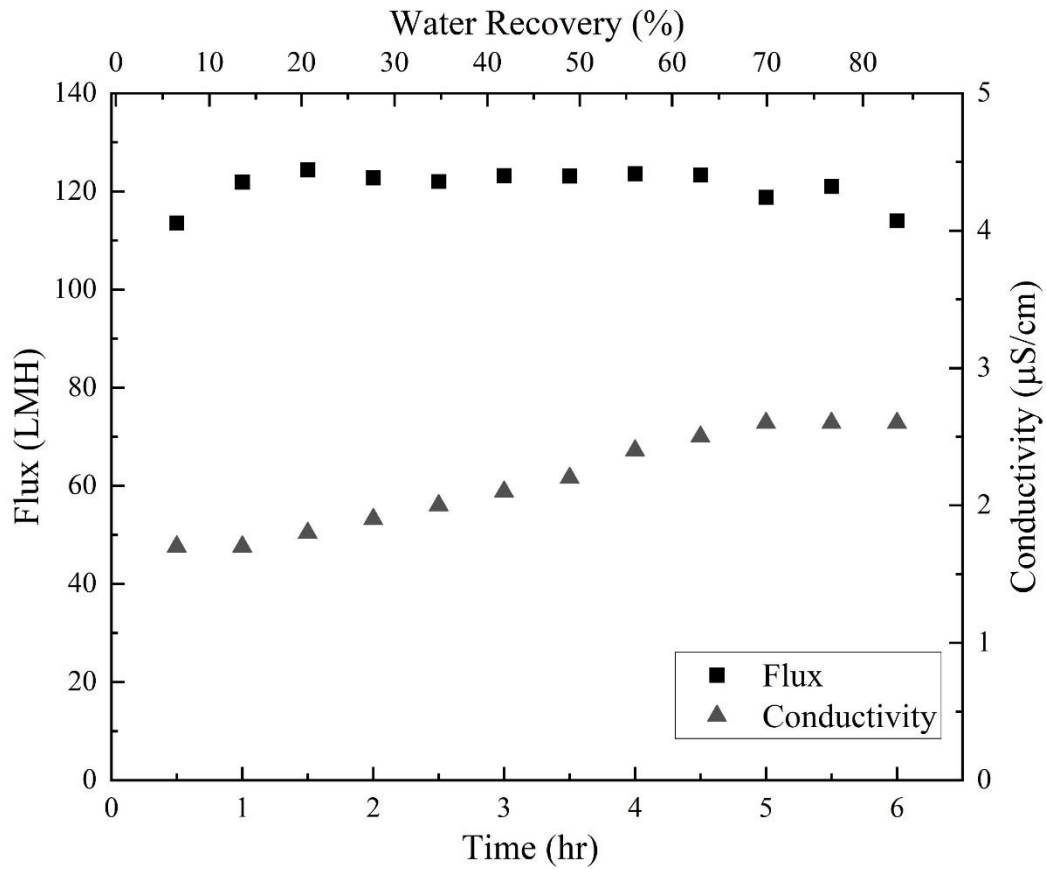


Figure 4.7 Permeate flux and conductivity in DCDM experiment with actual brackish water at temperature gradient of 70 °C ($T_{\text{feed}} = 80\text{ °C}$, $T_{\text{permeate}} = 10\text{ °C}$; $Q_{\text{feed}} = Q_{\text{permeate}} = 0.2\text{ gpm}$)

The results in Figures 4.6 and 4.7 show that the permeate flux at the temperature gradient of 70 °C with both synthetic and actual water was close to 120 LMH, which is 90% higher than the permeate flux achieved at the temperature gradient of 40 °C (Figures 4.4 and 4.5). The membrane distillation coefficient at the temperature gradient of 40 °C ($T_{\text{feed}}=60\text{ °C}$) calculated using bulk solution parameters was 3.54 LMH/kPa, while the membrane distillation coefficient at the temperature gradient of 70 °C ($T_{\text{feed}}=80\text{ °C}$) was 3.42 LMH/kPa. The membrane distillation coefficient is dependent on membrane properties and should not change with feed

temperature (Gustafson, Murphy, & Achilli, 2016; Phattaranawik, Jiraratananon, & Fane, 2003a; Singh & Sirkar, 2012). However, the concentration polarization coefficient (CPC) calculated using the method described by Martínez-Díez et al. (Martínez-Díez & Vázquez-González, 1999) shown in Figure 4.8 indicate that it increased with temperature increase. This apparent increase in CPC with temperature increase lead to a slight reduction in membrane distillation coefficient determined at higher temperature since it affected the calculations of the membrane distillation coefficient due to its impact on the vapor pressure on the feed side and apparent driving force for the mass transfer across the membrane. Figure 4.8 also indicate that there is very little difference in CPC between the synthetic and actual solutions, which means that the performance of MD process was not affected by the constituents in actual water that were not included in the composition of synthetic solution.

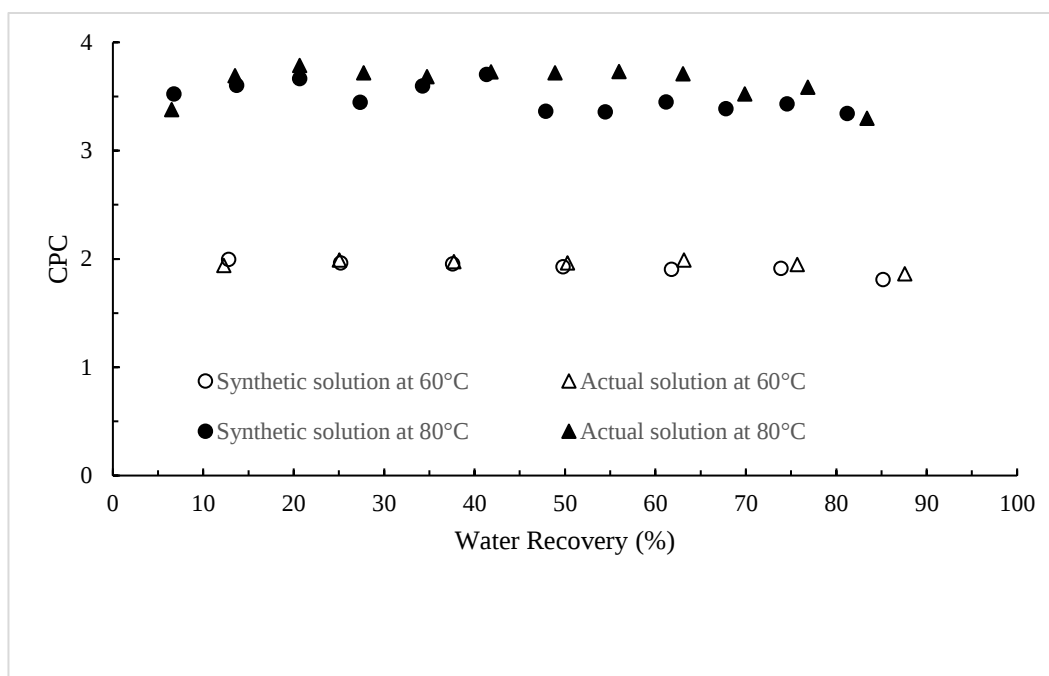


Figure 4.8 Concentration polarization coefficient in MD experiments with synthetic and actual solutions (Standard deviation in CPC is 0.055 and 0.041 for synthetic and actual solution at 60 °C, respectively and 0.121 and 0.147 for synthetic and actual solution at 80 °C, respectively)

While the permeate conductivity in the experiment with synthetic water varied in a narrow range of 1.5-2 $\mu\text{S}/\text{cm}$, the permeate conductivity in the experiment with actual groundwater varied between 1.5-3 $\mu\text{S}/\text{cm}$ within the limited duration of this experiment. No obvious membrane fouling was observed in these experiments. PTFE membrane used in this experiment was analyzed using SEM/EDX. Figure 4.9 shows SEM images of the used membrane while Table 4.3 includes chemical composition of selected areas on the membrane surface.

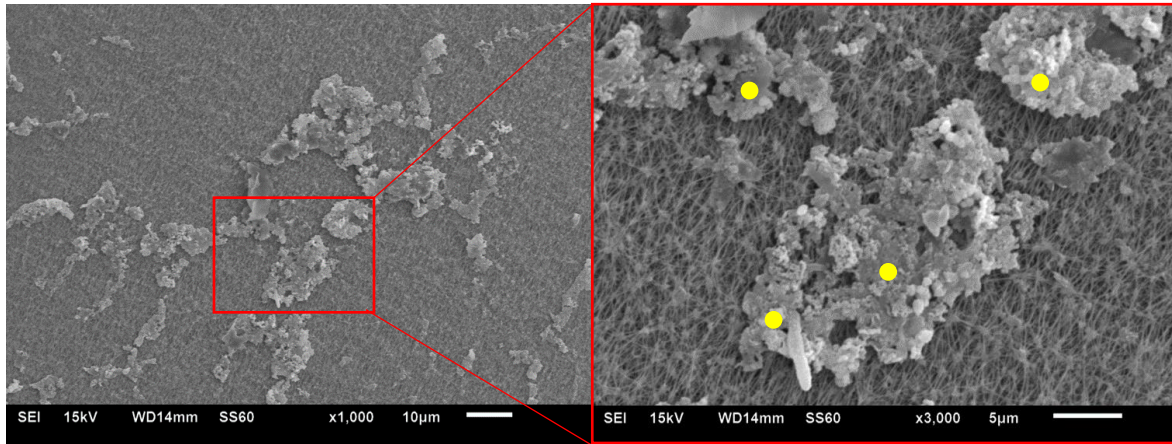


Figure 4.9 SEM images of the membrane used in DCMD experiment with actual groundwater at temperature gradient of 70 °C

Table 4.3 Chemical composition of selected locations (Unit: wt%)

Element	Position 1	Position 2	Position 3	Position 4
O	25.90	26.86	37.66	37.53
Mg	16.14	12.60	13.01	13.45
Si	32.12	27.36	24.90	27.20
Cl	18.19	26.20	18.59	15.72
Ca	7.65	6.99	5.84	6.09
Total	100.00	100.00	100.00	100.00

Figure 4.9 reveals sporadic presence of solid precipitates on the membrane surface while Table 4.3 suggest that silica is one of the main components of the observed precipitates. Other elements detected in EDX analysis, such as calcium and magnesium, are most likely due to co-precipitation with silica.(S. Chen, Chang, & Lin, 2006; Latour, Miranda, & Blanco, 2016) Under acidic or neutral condition, the main form of silica in unsaturated solution is Si(OH)_4 monomer (Ning, Tarquin, & Balliew, 2010). These monomers can combine to form amorphous polymeric silica (Bishop & Bear, 1972; Christie et al., 2020; Milne et al., 2014; Sjöberg, 1996). Although

the solubility of silica in pure water increases from 220 mg/L at 60°C to 300 mg/L at 80 °C (Alexander, Heston, & Iler, 1954; Gunnarsson & Arnórsson, 2000), the CPC calculations shown in Figure 4.8 suggest that silica concentration on the membrane surface at 80 °C will be 3.5 times that at in the bulk phase, which may lead to polymerization of amorphous silica on the membrane surface. However, Morey et al. (Morey, Fournier, & Rowe, 1964) observed that supersaturated amorphous silica can exist in solution for a long time while Kato et al. (Kato & Kitano, 1968) suggested that the increase in salinity increases silica solubility.

The amount of silica lost from the feed solution by adsorption on membrane or other surfaces in the system can be calculated as:

$$M = C_i V - (1 - \chi) V C_f \quad (4-7)$$

where, C_i is the initial silica concentration in the feed, C_f is the final silica concentration on the feed side, χ is water recovery and V is the initial volume of the feed. Using Equation (4-7) with the initial silica concentration in the feed of 92 mg/L and silica concentration in the concentrate of 594 mg/L, it can be calculated that only 10.1 mg of silica was lost from the liquid phase by adsorption on the membrane or other surfaces on the feed side of the DCMD system. If all the silica missing from the liquid phase (Equation 4.7) was deposited as a uniform layer on the membrane surface, its thickness would be 1.14 μm , which would likely reduce the permeate flux. Since that was not observed experimentally (Figures 4.6 and 4.7), it is most likely that some of the silica missing from the liquid phase was deposited on other surfaces present in the DCMD system.

If the operation of the MD system at conditions achieved at the end of the experiment depicted in Figure 4.7 (i.e., 85% water recovery) continued for a longer period of time or if the

silica concentration in the feed were higher, it is possible that the silica scale observed on the membrane surface (Figure 4.9) could extend inside the membrane pores to affect membrane characteristics and lead to membrane wetting as shown in Figure 4.10.

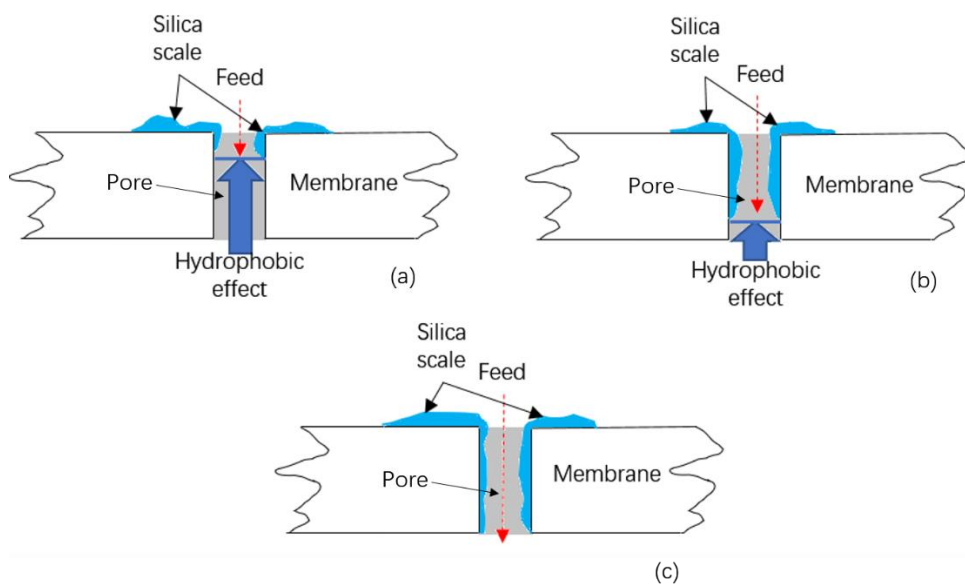


Figure 4.10 Impact of silica scale on membrane wetting: (a) Silica scale forms at the mouth of a membrane pore; (b) Silica scale grows into the membrane pore; (c) Silica scale extends through the length of the pore, leading to localized membrane wetting.

As shown in Figure 4.10, the amorphous silica scale that forms at the mouth of a membrane pore could extend throughout the length of a pore to render the pore hydrophobic and allow feed solution to pass through the membrane. It is possible that such behavior was not observed in this study because of the limited mass of amorphous silica in the feed solution.

4.4 Conclusions

This study evaluated the feasibility of using DCMD to enhance the overall water recovery by inland brackish water RO (BWRO) desalination plants and reduce the cost of concentrate disposal using DCMD to recover pure water from the BWRO concentrate. Because of high sulfate concentration in the concentrate, it was necessary to include barite precipitation as a pretreatment step to prevent membrane scaling due to formation of various sulfate minerals as the feed solution is concentrated in the DCMD process. Laboratory-scale studies with synthetic and actual BWRO concentrate demonstrated the ability of DCMD to successfully achieve water recovery of nearly 90% without observable membrane fouling if sulfate is removed from the original wastewater. Permeate flux achieved at the temperature difference between the feed and permeate sides of the membrane of 40 °C was about 60 LMH and it increased to almost 120 LMH when the temperature difference increased to 70 °C. The permeate flux remained virtually unchanged even when water recovery approached 90% indicating no significant scaling on the membrane surface.

No membrane fouling was observed even when the DCMD module was operated at very high permeate flux. SEM/EDX analysis of the membrane used in this experiment revealed a presence of silica on membrane surface. Equilibrium calculations suggested that amorphous silica could be formed on the feed side at high water recoveries. However, limited quantity of silica available under the experimental conditions evaluated in this study may have prevented severe membrane fouling.

This study demonstrated that membrane distillation is a promising technology to enhance the overall water recovery by inland brackish water RO plant and reduce potential environmental impacts and cost of concentrate disposal. However, it is necessary to ensure proper pretreatment of the BWRO concentrate to enable requisite performance of this technology.

5.0 Summary, Conclusions and Future work

The research presented in this dissertation shows significant meaning to the study of calcium scaling in Direct Contact Membrane Distillation. Fundamental understanding of calcium scaling in MD system will have significant impact on the development of diverse applications for this technology. Strategies to prevent calcium scaling in MD will strength the competitiveness of this technology, allowing the popularization of MD in desalination field. In the absence of mineral scaling, it would be possible to enhance water recovery by MD, which will also promote water reuse and mitigate the pressures of global water crisis.

5.1 Summary and Conclusions

5.1.1 Verification of Thermodynamic Models for Gypsum Precipitation in Hypersaline Solutions with Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a surface sensitive measurement allowing the detection of minimal surface changes and has been used in a variety of applications to study crystal formation. It uses impedance potential of a system determined from a response to an alternating current (AC) of varying frequency to detect salt crystallization. In this study, we used synthetic solution at supersaturated condition as predicted by multiple models to study scale formation at a range of ionic strengths (0.5 – 5 M). This study revealed that the predictions

of gypsum SI with Pitzer and OLI Studio are accurate. As salinity increases, gypsum SI will decrease first and then increase, the minimum SI occurs at approximately 2.5M. Electrochemical impedance spectroscopy (EIS) can accurately detect the crystallization of gypsum in solution by measuring the capacitance of the system, the measurement result shows a good match with kinetic test and reaction kinetic simulation. On the other hand, optical method such as turbidity measurement and Dynamic Light Scattering (DLS) have limitations on detecting small particles with low intensity in the solution.

5.1.2 Comparison of calcium scaling in direct contact membrane distillation (DCMD) and nanofiltration (NF)

Direct contact membrane distillation (DCMD) and nanofiltration (NF) were selected to study calcium scaling impact on thermal and pressure driven membrane processes. Calcium sulfate (CaSO_4) and calcium carbonate (CaCO_3) solutions with salinity in the range from 3,000 to 30,000 mg/L were used as the feed. All DCMD and NF tests were performed at identical feed temperature (i.e., 40 °C) and shear conditions (i.e., $\text{Re} = 771 \pm 28$). The average size of CaSO_4 and CaCO_3 crystals formed in the DCMD system was larger and the scale was more porous than in the NF system. The permeate flux in NF system was impacted by both calcium scales regardless of the feed salinity, while only CaSO_4 scale formed at low salinity affected the performance of DCMD system. Surface crystallization in NF systems is likely extended into the membrane pores, which lead to permanent reduction in membrane permeability. This study demonstrated that the impact of calcium scaling is affected by both feed salinity and separation driving force, and is much less severe in thermal than pressure driven membrane processes.

5.1.3 Pretreatment of brackish water reverse osmosis (BWRO) concentrate to enhance water recovery in inland desalination plants by direct contact membrane distillation (DCMD)

Inland brackish water desalination plants typically rely on reverse osmosis (RO) for the production of drinking water. However, the usual water recovery in these plants (i.e., 50 - 75%) results in fairly large quantities of the reject (concentrate) stream that needs to be disposed at considerable cost and with significant adverse environmental impacts. Membrane distillation (MD) offers a unique opportunity to improve the performance of these brackish water reverse osmosis (BWRO) plants by recovering additional clean permeate and reducing the volume of concentrate for disposal. In this study, barite precipitation was utilized to remove about 4,000 mg/L of sulfate from actual BWRO concentrate to prevent interference with MD operation. The effect of barium concentration and mixing condition was evaluated for its impact on the removal of sulfate as the key ingredient of inorganic scales that would form in BWRO concentrate with increased water recovery. The pre-treated BWRO concentrate was used as feed in direct contact membrane distillation (DCMD) system operated at 60°C to achieve at least 85% water recovery. The impact of concentration polarization on the performance of MD explored in a system operated at 80°C revealed a potential for amorphous silica fouling of the membrane.

5.2 Key Contributions

The research presented in this dissertation contributed to fundamental understanding of calcium scaling in Direct Contact Membrane Distillation at high salinities and provide alternative solutions to current calcium scaling problems and challenges associated with membrane processes treating inland brackish water.

Crucial factors that could impact calcium crystallization and scaling such as calcium sulfate saturation index, crystallization kinetics and crystal morphology in high salinity solutions were predicted and analyzed. Multiple thermodynamic prediction models were compared, a detailed and accurate prediction of gypsum SI was thus yielded. Crystallization kinetics were monitored with in-situ electrochemical impedance spectroscopy and were confirmed by both kinetic tests and reaction models. This study provided further insight to calcium crystallization in high salinity solutions that could be extended to calcium scaling in membrane desalination process with hypersaline.

Calcium scaling in different membrane systems could deviate significantly due to the desalination mechanisms. Nanofiltration and direct contact membrane distillation were selected to represent pressure and thermally driven membrane desalination process. The comparison of these most common desalination systems revealed the impact of desalination driving force on calcium scaling performance. Other parameters such as temperature and shear force were controlled to be the same in both systems. It is shown that calcium scaling has more severe and permanent impact to pressure driven membrane systems. The morphology of calcium crystals in the two systems also presented differently.

Among all industrial desalination processes, inland brackish water desalination is the most influenced one by calcium scaling due to the high content of calcium sulfate in brackish water. This study enables the possibility of reusing the brackish water reverse osmosis reject and achieve higher water recovery by membrane distillation. Barite precipitation was used as a novel pretreatment method to remove the sulfate in brackish water and thus prevent calcium sulfate scaling during the membrane distillation process. The optimized dose of barium input was analyzed, high water recoveries was achieved based on reverse osmosis reject with different temperature gradients across the membrane. Potential scaling problem with silica was also revealed and discussed in this study.

5.3 Future Directions

Future researchers should focus on expanding this research and provide more data and information that could be used for more comprehensive understanding of calcium scaling mechanisms in membrane desalination processes. Based on the studies in Chapter 2, 3 and 4, the following topics could be beneficial for the fundamental science of calcium crystallization and the mitigation of calcium scaling in desalination industry.

- The kinetics of calcium crystallization was observed with in-situ electrochemical impedance spectroscopy and showed good match with kinetic tests in a relatively long time period in Chapter 2. The principle of EIS measurement determines that it cannot measure the crystallization in a small scale of time, a new method that could investigate crystallization both accurately and quickly is needed for expanding this research.

- During the experimental kinetic tests with calcium sulfate crystallization in hypersaline in Chapter 2, an induction time period was observed. Researches that could accurately ascertain the induction time is needed, the relationship between solution salinity and calcium crystallization induction is also needed to be established.
- Chapter 3 compared the differences of calcium scaling in pressure and thermally drive membrane systems regarding the crystal morphology. A fundamental research of the reason why the crystals showed discrepancy on the shape and length is needed, the impact of different crystal morphology on the characteristic of scaling layer is also need.
- Pretreatment strategy was used in Chapter 4 to prevent the calcium scaling in brackish water desalination, it also revealed the silica scaling potential with the same water. Since silica is very common in natural water body, it is important to investigate silica scaling mechanism and mitigation methods

Appendix A: Equations and Models

A.1 Major equations and models

A.1.1 Calculations of MD flux

The only driving force for mass transfer is the vapor pressure difference across the membrane and the permeate flux can be expressed as:

$$J = C(P_f - P_p) \quad (A-1)$$

where, C is the membrane distillation coefficient, P_f and P_p are the vapor pressure on feed and permeate side of the membrane, respectively. The vapor pressure of pure water can be calculated by Antoine equation:

$$P_m = \exp\left(23.328 - \frac{3841}{T_m - 45}\right) \quad (A-2)$$

where, P_m is pure water pressure and T_m is the water temperature. Water salinity has adverse impact on vapor pressure but is minimal compared to the impact of temperature (Hitsov et al., 2015). The vapor pressure of a solution can be calculated as (Lawson & Lloyd, 1997):

$$P = P_m \alpha_w = P_m \chi_w \quad (A-3)$$

where, α_w is the water activity, χ_w is the molar fraction of water and γ_w is the activity coefficient. The calculation of γ_w varies with solute types and can be approximated in the case of NaCl solution as:

$$\gamma_w = 1 - 0.5\chi_{\text{NaCl}} - 10 \quad (\text{A-4})$$

where, χ_{NaCl} is the molar fraction of NaCl.

A.1.2 Calculations of concentration polarization

The concentration polarization coefficient can be calculated as (Martínez-Díez & Vázquez-González, 1999):

$$\text{CPC} = \frac{C_m}{C_b} \quad (\text{A-5})$$

where, C_m and C_b are the salt concentration on the membrane surface and in the bulk, respectively. Salt concentration on the membrane surface, C_m , can be estimated based on the following equation (Schofield et al., 1990):

$$C_m = C_b \exp\left(\frac{J}{\rho K}\right) \quad (\text{A-6})$$

where, ρ is bulk density, J is the permeate flux and K is the solute mass transfer coefficient, which can be calculated from (Martínez-Díez & Vázquez-González, 1999):

$$\text{Sh} = \frac{K \cdot d_h}{D} = 1.86 \left(\text{Re} \cdot \text{Sc} \cdot \frac{d_h}{L} \right)^{0.33} \quad (\text{A-7})$$

where, Sh is the Sherwood number, d_h is the hydraulic diameter, D is diffusion coefficient, Re is Reynolds number, Sc is the Schmidt number, and L is the channel length. Combining Equation (5) and (6) yields the following relationship between permeate flux, J, and concentration polarization coefficient (CPC):

$$\text{CPC} = \exp\left(\frac{J}{\rho K}\right) \quad (\text{A-8})$$

Equation (6) indicates that an increase in permeate flux will also lead to an increase in concentration polarization, which means that the salt concentration near the membrane surface will be much higher than in the bulk.

A.1.3 Calculations and plots of EIS

The excitation signal of EIS can be described as:

$$E_t = E_0 \sin(\omega t) \quad (\text{A-9})$$

Where, E_t is the potential at time t, E_0 is the initial amplitude of the signal, ω is the angular velocity of radial frequency.

The response EIS signal with phase shift can be expressed as:

$$I_t = I_0 \sin(\omega t + \phi) \quad (\text{A-10})$$

Where, I_t is the response signal at time t, I_0 is response signal amplitude and ϕ is the shifted phase.

The relationship between frequency f and angular signal velocity in equation (A-9) and (A-10) is described as:

$$f = \frac{\omega}{2\pi} \quad (\text{A-11})$$

Applying Ohm's law to Equation yields the impedance of the system as:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (\text{A-12})$$

Where, Z is the system impedance and Z_0 is the magnitude. Plotting absolute impedance $|Z|$ with log frequency $\lg f$ yields the Bode plot.

For Nyquist plot, applying Euler equation:

$$\exp(j\phi) = \cos\phi + j\sin\phi \quad (\text{A-13})$$

The excitation signal and response can be written as:

$$E_t = E_0 \exp(j\omega t) \quad (\text{A-14})$$

$$I_t = I_0 \exp(j\omega t - \phi) \quad (\text{A-15})$$

Impedance will thus be expressed in complex number form:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \exp(j\omega t)}{I_0 \exp(j\omega t - \phi)} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi) \quad (\text{A-16})$$

The complex number form of Impedance contains real part and imaginary part, plotting negative imaginary part $-Z''$ against real part Z' yields Nyquist plot.

A.1.4 Calculations of circuit elements

In this research, solution resistance (R_s) and membrane resistance (R_m) were acquired by analyzing Nyquist plot, for CPE circuit, the relationships between system impedance and circuit element impedances in series and parallel are:

$$Z_{series} = \sum_{i=1}^n Z_i \quad (A-17)$$

$$Z_{parallel} = \frac{1}{\sum_{i=1}^n \frac{1}{Z_i}} \quad (A-18)$$

The complex number form of impedance can be written as:

$$Z = R_s + \frac{1}{\frac{1}{R_m} + j\omega C_m} = R_s + \frac{R_m}{1 + j\omega R_m C_m} \quad (A-19)$$

Where, C_m is membrane capacitance. Thus, the real part and imaginary part of impedance can be described respectively as:

$$Z' = R_s + \frac{R_m}{1 + \omega^2 R_m^2 C_m^2} \quad (A-20)$$

$$-Z'' = \frac{j\omega C_m R_m^2}{1 + \omega^2 R_m^2 C_m^2} \quad (A-21)$$

In Nyquist plot, R_s is the distance between zero point and the first intersection point of the semicircle curve, R_m is the distance between the two intersection points on x-axis of the semicircle curve.

The calculation of C_m follows the method developed by Jovic(Jovic, 2003):

$$C_m = \frac{(Q^0 R_m)^{\frac{1}{n}}}{R_m} \quad (\text{A-22})$$

Where, where Q^0 is the numerical value of the admittance ($1/|Z|$) at $\omega = 1$ rad/s, n is the EIS phase angle divided by -90° , which can be acquired from Nyquist plot analyzation.

A.1.5 Calculations of Pitzer model

The activity coefficient for cation and anion in Pitzer model can be calculated with equations:

$$\begin{aligned} \ln \gamma_X = & (|Z_+|)^2 \left\{ -A_\phi \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I}) \right] + \sum_c \sum_a m_c m_a \beta_{ca}'' + \sum_c \sum_{c'} m_c m_{c'} \phi_{cc'}'' + \right. \\ & \left. \sum_a \sum_{a'} m_a m_{a'} \phi_{aa'}'' \right\} + \sum_a m_a \left\{ 2\beta_{Xa} + \frac{1}{2} (\sum_c m_c |Z_c| + \sum_a m_a |Z_a|) C_{Xa} \right\} + \sum_c m_c (2\phi_{Xc} + \\ & \sum_a m_a \psi_{Xca}) + \sum_a \sum_{a'} m_c m_{a'} \psi_{Xca} + |Z_+| \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (\text{A-23})$$

$$\begin{aligned} \ln \gamma_Y = & (|Z_-|)^2 \left\{ -A_\phi \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I}) \right] + \sum_c \sum_a m_c m_a \beta_{ca}'' + \sum_c \sum_{c'} m_c m_{c'} \phi_{cc'}'' + \right. \\ & \left. \sum_a \sum_{a'} m_a m_{a'} \phi_{aa'}'' \right\} + \sum_c m_c \left\{ 2\beta_{cY} + \frac{1}{2} (\sum_c m_c |Z_c| + \sum_a m_a |Z_a|) C_{cY} \right\} + \sum_a m_a (2\phi_{Ya} + \\ & \sum_c m_c \psi_{Yca}) + \sum_c \sum_{c'} m_c m_{c'} \psi_{cc'Y} + |Z_-| \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (\text{A-24})$$

Where, I is ionic strength, the parameters with subscript X and c represent cation parameters, the parameters with subscript Y and a represent anion parameters. The calculations of the major parameters are presented in equations:

$$A_\phi = 0.3770 + 4.684 \times 10^{-4}(T - 27.15) + 3.74 \times 10^{-6}(T - 273.15)^2 \quad (\text{A-25})$$

$$\beta_{ij} = \beta_{ij}^{(0)} + \beta_{ij}^{(1)} \left\{ \frac{2}{(1.4\sqrt{I})^2} [1 - (1 + 1.4\sqrt{I}) \exp(-1.4\sqrt{I})] \right\} + \beta_{ij}^{(2)} \left\{ \frac{2}{(12\sqrt{I})^2} [1 - (1 + 12\sqrt{I}) \exp(-12\sqrt{I})] \right\} \quad (\text{A-26})$$

$$\beta_{ij}'' = \frac{\beta_{ij}^{(1)}}{I} \left\{ \frac{2}{(1.4\sqrt{I})^2} \left[1 - \left(1 + 1.4\sqrt{I} + \frac{(1.4\sqrt{I})^2}{2} \right) \exp(-1.4\sqrt{I}) \right] \right\} + \frac{\beta_{ij}^{(2)}}{I} \left\{ \frac{2}{(12\sqrt{I})^2} \left[1 - \left(1 + 12\sqrt{I} + \frac{(12\sqrt{I})^2}{2} \right) \exp(-12\sqrt{I}) \right] \right\} \quad (\text{A-27})$$

$$C_{ij} = \frac{c_{ij}^\phi}{2(|Z_i Z_j|)^{0.5}} \quad (\text{A-28})$$

$$I = 0.5 \sum_i m_i Z_i^2 \quad (\text{A-29})$$

The parameters not shown above are either constant or obtained by experiments and will not be discussed here.

A.1.6 Calculations of saturation index

The saturation index (SI) can be expressed as:

$$SI = \log \left(\frac{IAP}{K_{sp}} \right) \quad (A-30)$$

Where, IAP is the ionic activity product and K_{sp} is the solubility product, the calculation of IAP can be show as:

$$IAP = \gamma_X m_X \gamma_Y m_Y \quad (A-31)$$

Where, γ is the activity coefficient, m is the molar concentration of ion. The calculation of ionic activity product is determined by water activity and salt concentration.

Appendix B: Polarization and Scaling in DCMD

Temperature polarization is a phenomenon happens near the surface of membrane which the temperature distribution shows gradient towards the membrane(Schofield, Fane, & Fell, 1987). The temperature polarization in DCMD can be presented in Figure B.1.

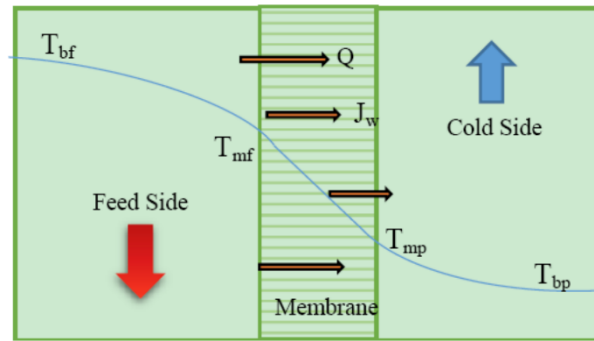


Figure B.1 Temperature polarization in DCMD (Phattaranawik, Jiratananon, & Fane, 2003b)

Temperature polarization may severely influence the efficiency of heat and mass transfer through the membrane in DCMD and VMD. The only driving force in membrane distillation system is the vapor pressure difference across the membrane. Therefore, the mass transfer can be expressed as(Hitsov et al., 2015):

$$J = C(P_{m,f} - P_{m,p}) \quad (\text{B-1})$$

Where $P_{m,f}$ and $P_{m,p}$ are the vapor pressure on the membrane from feed and permeate side, C is the mass transfer coefficient. For pure water, the vapor pressure can be calculated with Antoine equation:

$$P_m = \exp\left(23.328 - \frac{3841}{T_m - 45}\right) \quad (\text{B-2})$$

Thus, mass transfer equation (1) can be converted to:

$$J = C \left(\frac{dP}{dT}\right)_{T_m} (T_{m,f} - T_{m,p}) \quad (\text{B-3})$$

where $T_m = \frac{T_{m,f} + T_{m,p}}{2}$.

In DCMD, feed side and permeate side are all water, temperature polarization will decrease the temperature difference across membrane ($T_{m,f} - T_{m,p}$) hence decrease the vapor pressure difference and drop the flux.

The mass transfer efficiency is not widely mentioned in existing papers, but it can be assumed from the heat transfer efficiency that the mass transfer efficiency is the ratio of measured flux calculated by the temperature difference across the membrane to the expected flux calculated by the temperature difference from the feed and permeate bulk, which can be demonstrated as:

$$\eta_M = \frac{C(P_{m,f} - P_{m,p})}{C(P_{b,f} - P_{b,p})} = \frac{P_{m,f} - P_{m,p}}{P_{b,f} - P_{b,p}} \quad (\text{B-4})$$

Temperature polarization will decrease the temperature difference across the membrane and thus decrease the vapor pressure difference across membrane, which means ($P_{m,f} - P_{m,p}$)

will decline, and $(P_{b,f} - P_{b,p})$ will be constant due to the same temperature difference in the bulk. Therefore, the mass transfer efficiency will drop due to the temperature polarization.

The scaling of membrane can be understood as salt solids precipitated on the surface of membrane or inside the pore of membrane as shown in Figure B.2(Ramezaniapour & Sivakumar, 2014) and Figure B.3(L. Wang et al., 2014).

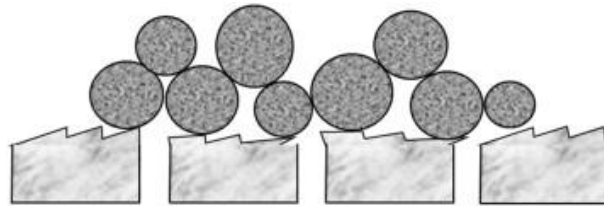


Figure B.2 Scaling on the surface of membrane (Ramezaniapour et al., 2014)

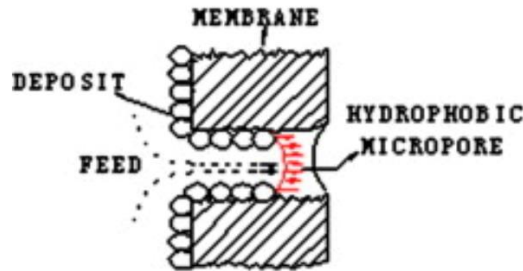


Figure B.3 Scaling inside the membrane pore (Wang et al., 2014)

The clog of membrane pores by scalant will make the pore lose the ability of vapor transfer, which leads to the formation of inactive membrane area(G. Chen, Lu, Yang, Wang, & Fane, 2014). The inactive area of membrane can be estimated as:

$$A_{in} = \frac{\sum_{i=0}^n \frac{1}{4} \pi \bar{d}^2}{\phi} \quad (B-5)$$

where $\bar{d}$ is the mean pore size, ϕ is the porosity of membrane. The total membrane area is fixed, so the functional membrane area will decrease due to the increasement of inactive membrane area during the scaling process, shown as:

$$A_f = A_{total} - A_{in} \quad (B-6)$$

The functional membrane flux which determined by membrane coefficient (C) and vapor pressure (P_m) difference can be calculated as:

$$J = C(P_{m,f} - P_{m,p}) \quad (B-7)$$

The measured permeate mass that can be measured:

$$M_{measured} = J A_f t = J(A_{total} - A_{in})t \quad (B-8)$$

The flux after scaling can be acquired by the definition equation of flux as:

$$J' = \frac{M_{measured}}{A_{total}t} = \frac{J(A_{total} - A_{in})t}{A_{total}t} = \left(1 - \frac{A_{in}}{A_{total}}\right)J \quad (B-9)$$

According to equation (5), it can be concluded that the scale formation on membrane will cause flux drop, which is also a common performance indicator of membrane scaling. The drop of flux also means membrane scaling has the effect on the decline of mass transfer through the membrane.

The effect of scaling on heat transfer is corresponded to the drop of permeate flux, which will influence the heat transfer through the membrane according to the following equation (Qtaishat, Matsuura, Kruczek, & Khayet, 2008):

$$Q_m = H_m(T_{mf} - T_{mp}) + J_w H_v \quad (\text{B-10})$$

where H_m is heat transfer coefficient, J_w is the permeate flux and H_v is vapor enthalpy. As can be seen from this equation, heat transfer can be divided to two parts, conductive heat which is controlled by temperature difference and latent heat which depends on the flux, membrane scaling will cause the reduction of latent heat transfer and thus diminish the total heat transfer through membrane. Wang et al. (L. Wang et al., 2014) also described that membrane scaling can change the heat transfer coefficient because the scale layer on the membrane can alter the original membrane characteristic, the new coefficient can be calculated as:

$$H'_f = \alpha H_f + \beta H_{f-fouling} \quad (\text{B-11})$$

in which α and β are the proportions of pristine membrane and foulant.

Membrane scaling will also influence the temperature polarization, the parameter which can display the level of temperature polarization is called temperature polarization coefficient (TPC), which can be calculated as(Gryta, 2008):

$$TPC = \frac{T_{mf} - T_{mp}}{T_{bf} - T_{bp}} \quad (B-12)$$

where T_{bf} and T_{bp} is the temperature of feed and permeate bulk. The existence of scaling layer will decrease the temperature difference across the membrane as it shows in Figure B.4(Gryta, 2008)

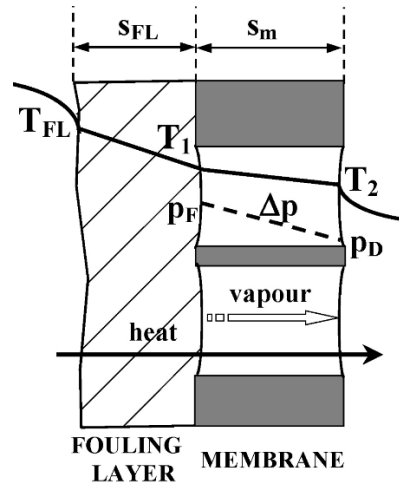


Figure B.4 Temperature polarization with scale layer(Gryta, 2008)

Which means the value of $T_{mf} - T_{mp}$ will decrease and TPC will decrease consequently, showing the amplification of temperature polarization.

As for concentration polarization, membrane scaling also has influence on it due to the reducing of permeate flux. The coefficient which can measure the degree of concentration polarization can be introduced as (Martínez-Díez & Vázquez-González, 1999):

$$\zeta = \frac{C_{m1}}{C_{b1}} \quad (\text{B-13})$$

where C_{m1} and C_{b1} are the salt concentration on the surface of membrane and the salt concentration in the bulk. The calculation of C_{m1} is derived by Schofield et al. (Schofield et al., 1990) as the following equation:

$$C_{m1} = C_{b1} \exp\left(\frac{J}{\rho K}\right) \quad (\text{B-14})$$

where ρ is bulk density, K is solute mass transfer coefficient. Combine equation (9) and (10), the relationship between flux J and concentration polarization coefficient ζ can be induced as:

$$\zeta = C_{b1}^2 \exp\left(\frac{J}{\rho K}\right) \quad (\text{B-15})$$

Therefore, when the concentration of bulk stays the same, membrane fouling will decrease the flux and hence decrease the concentration polarization.

Appendix C: Scaling Factors and Mitigation Strategies in DCMD

C.1 Scaling factors in DCMD

Both compositional and non-compositional factors could govern fouling and hence scaling in direct contact membrane distillation:

i. Composition aspects

The feed water for membrane distillation is usually brackish water or saline which contains large amount of soluble salts. Among these salts, some have solubility around several thousand part per million and their concentration in feed water are already close to the saturation limit, which makes them come out of solution and solidify in feed water or precipitate on the membrane (Antony et al., 2011).

ii. Non-compositional aspects

There are also many non-compositional factors that can influence membrane fouling, such as pH, temperature, permeate flux, feed flowrate and concentration polarization phenomenon (David M. Warsinger et al., 2015). Prihasto et al. (Prihasto, Liu, & Kim, 2009) suggested that decreasing the pH of feed water can efficiently decrease the level of scaling. Luo et al. (Luo & Lior, 2017) demonstrated that with salts whose solubilities proceed against temperature, higher running temperature of membrane distillation may cause severe scaling problem.

The concentration polarization in membrane distillation is caused by permeate flux through the membrane, the rejected solute accumulates near the surface of membrane which results in the

concentration near the membrane surface higher than the bulk. Accordingly, certain soluble salts in feed water which are below the saturation point may be supersaturated near the surface of membrane due to the concentration polarization and thus cause the scaling on the membrane.

C.2 Scaling mitigation strategies

Both the design and operation of MD could be optimized to reduce the negative impacts of fouling and scaling.

C.2.1 For the design of DCMD:

- Design the system with a higher flowrate on feed side

A higher flow rate can result in a higher flow velocity, which can decrease both the temperature and concentration polarization level and hence reduce the potential of membrane scaling.

- Design the system with spacers

The use of spacer will decrease the temperature polarization as well as concentration polarization phenomenon and hence improve the heat and mass transfer. According to the research of Phattaranawik et al.(Phattaranawik et al., 2003b), the existence of spacer in water channel will disturb the polarization boundary layer and create a better mixture near the surface of membranes shown in Figure C.1.

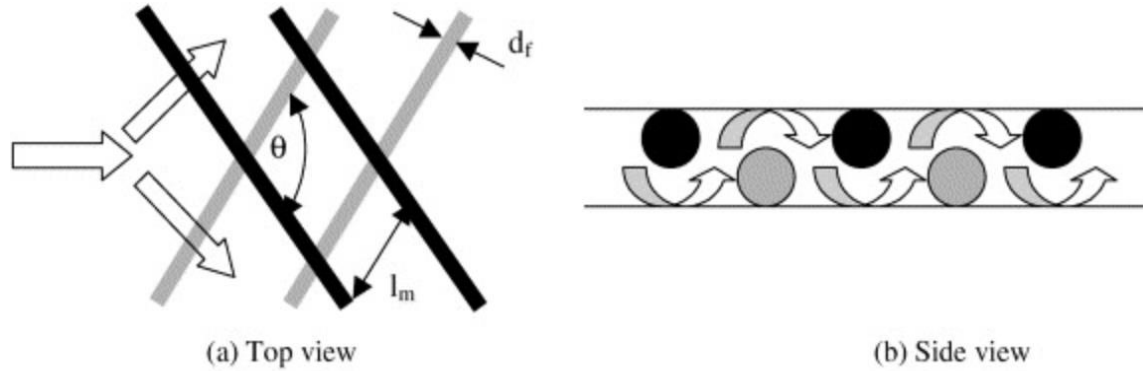


Figure C.1 The function of spacer (Phattaranawik et al., 2003)

C.2.2 For the operation of DCMD:

- Control the water recovery rate

A relatively low water recovery rate results in lower concentration factor, which means the dissolved salt may not exceed its saturation point and solidify on the membrane or the level of scaling is minor comparing to high water recovery.

- Pick reasonable operating temperature

High running temperature will cause severe concentration polarization phenomenon, causing serious scaling problem. It will also decrease the thermal efficiency. However, low running temperature is not beneficial to achieving high water flux. Therefore, find a suitable operating temperature is crucial for a high-efficiency DCMD system.

- Pretreat the feed water

Remove the potential scalants from the feed water before running on DCMD system can efficiently avoid the scaling and fouling problem. Adjusting feed pH may have the similar effect. However, pretreatment will require the cost of time and money.

- Clean the membrane periodically

Most of the scalants are soluble in acid, thus proceeding membrane cleaning with acid can effectively remove the scale on the membrane and increase the permeate flux.

- Run the system with semi-batch operation

Semi-batch operation or feed flow reversal mode, in which the supersaturated brine was diluted by undersaturated feed before the formation of scale. Consequently, scaling was mitigated and higher average flux was achieved. It is reported that Pomerantz et al.(Pomerantz et al., 2006) used fresh feed flow to reset the saturation condition before the nucleation of scale and resulted in a longer time elapse before scale began to form.

- Add antiscalants

Antiscalants are widely used in both water treatment and industrial process since last century. The major function of antiscalants is disrupting one or more processes during the nucleation and crystallization of salt solid. However, the antiscalants that specially aim to membrane distillation are still under development.

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