

A NOVEL BRINE PRECIPITATION PROCESS WITH THE AIM OF HIGHER PERMEATE
WATER RECOVERY

by

Mojtaba AzadiAghdam

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING

In Partial Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

WITH A MAJOR IN ENVIRONMENTAL ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

2016

STATEMENT BY AUTHOR

The thesis titled *A Novel Brine Precipitation Process with the Aim of Higher Permeate Water Recovery* prepared by *Mojtaba AzadiAghdam* has been submitted in partial fulfillment of requirements for a master's degree at the University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that an accurate acknowledgement of the source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: *Mojtaba AzadiAghdam*

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Thesis Director: Shane A. Snyder
Professor of Chemical and Environmental Engineering

May 4th 2016
Date

Acknowledgement

First of all, I would like to thank my thesis advisor Professor Shane Snyder. The door to Prof. Snyder office was always open whenever I ran into a trouble spot or had a question about my research or writing. He consistently allowed this research to be my own work, but steered me in the right the direction whenever he thought I needed it.

I would also like to thank Professor Jim Farrell. Without his passionate participation and input, this research could not have been successfully conducted. I am also gratefully indebted to him for his very valuable comments on the research paper that is published based on this study.

Finally, I must express my very profound gratitude to my parents and friends for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Dedication

This work is dedicated to my parents and mainly my father who passed away while I was studying in United States. He has always loved me unconditionally and whose good examples have taught me to work hard for the things that I aspire to achieve. I hope I always live with his blessings...

Table of Contents

Title page.....	1
Statement by author	2
Acknowledgement	3
Dedication	4
Table of Contents	5
List of figures	7
List of tables.....	8
Graphical Abstract	9
Abstract.....	10
Introduction.....	11
Membrane-based technology	14
Pressure driven membranes	14
Intermediate chemical softening	14
Seeded slurry precipitation and recycle	17
Pellet reactors.....	17
Electrocoagulation	18
Electrical potential-driven membranes.....	18
Impact of different parameters on multi-step brine precipitation	19
Mixing rate.....	19
Selection of chemical.....	19
Alkaline chemical dose	20
Pretreatment time	20
Antiscalant dose	20
Seeded material.....	20
Seeded material amount.....	21
Seeding time.....	21
Experimental	21
Materials.....	21
Brine generation and system description.....	23
Methods.....	24
Results and discussion	25
Ferric Chloride Addition.....	25
Carbonate Mineral Precipitation.....	28

Enhanced Barium Removal	31
Permeate water recovery estimation for the secondary membrane.....	34
Conclusions.....	35
Appendix 1: Supplementary data	36
References	39

List of figures

Figure 1 Graphical abstract.....	9
Figure 2 Conceptual illustration of steps required for achieving near-ZLD or ZLD of concentrate generated from RO processes (Subramani and Jacangelo 2014).....	13
Figure 3 CESP Illustration for precipitation of supersaturated brine with respect to CaCO_3 and CaSO_4	16
Figure 4 PB-900 Programmable Jar tester, Phipps & Bird	22
Figure 5 CAP brine supersaturation levels.....	23
Figure 6. Phosphorus removal and pH reduction as a function of FeCl_3 dose after 30 min of mixing.....	26
Figure 7. Phosphorus removal and pH change over 30 min of mixing time after addition of 0.2 mM FeCl_3	27
Figure 8. Change in concentration of solution species after ferric hydroxide precipitation.	27
Figure 9 SI values as a function of mixing time after addition of Na_2CO_3 to an initial pH value of 9.6.....	30
Figure 10 Effect of calcite dose on SI values after 30 minutes of mixing post Na_2CO_3 addition to reach a pH of 9.67	31
Figure 11 The effect of 5 g/L seeding by silica, garnet or barite on SI values after 30 min of mixing.....	32
Figure 12 Effect of barite seeding on SI values for the brine after 30 min of mixing.	33
Figure 13 Effect of mixing time on SI values after addition of 5 g/L of barite seed crystals.....	33
Figure 14 SI values for different recovery rates in the secondary membrane.....	34

List of tables

Table 1 Brine characteristics generated from CAP water at 85% recovery with an NF membrane	24
Table 2 Mineral SI values after 30 minutes elapsed after pH adjustment to 9.6 in samples with and without previous treatment with 0.2 mM FeCl ₃	28
Table 3 values and solution concentrations after 30 minutes elapsed for solutions with initial pH values of 9.6 after addition of Ca(OH) ₂ , NaOH or Na ₂ CO ₃	29

Graphical Abstract

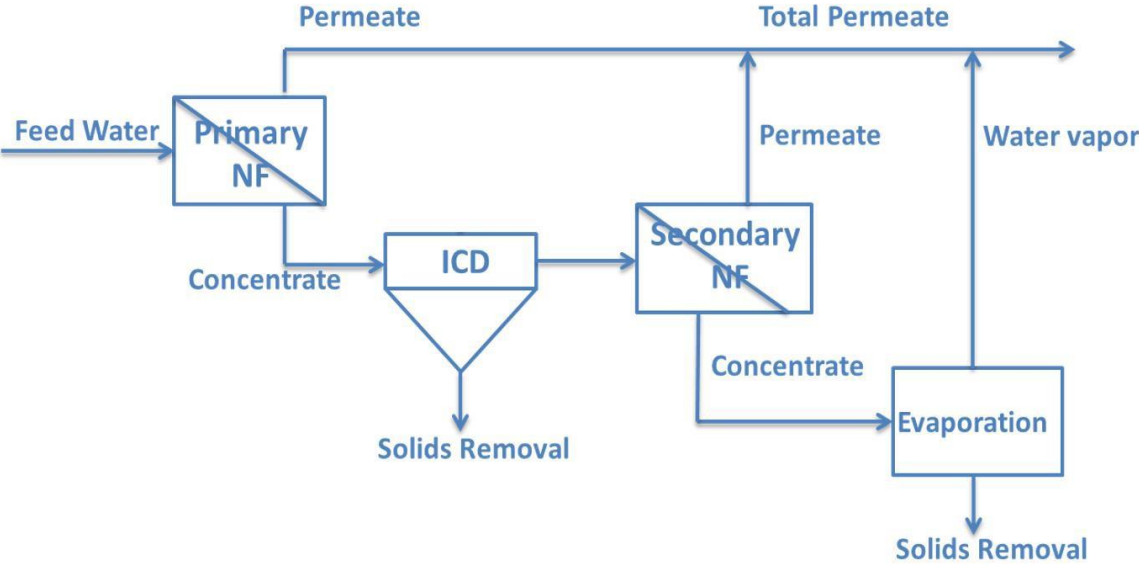


Figure 1 Graphical abstract

Abstract

This research developed a three-step demineralization process for removing scale-forming compounds from brine solutions produced during nanofiltration (NF) of potable water. The process is designed to remove compounds that would produce scale and membrane fouling during further treatment via NF or reverse osmosis (RO). Jar tests were performed to determine the most suitable dosages and mixing times for each reagent. The first step in the demineralization process employs ferric chloride for removing phosphonate scale inhibitors via co-precipitation with ferric hydroxide. The second step of the process increases the solution pH value to promote carbonate mineral precipitation. The third step involves barium sulfate precipitation promoted by barite seed crystals. Saturation indices for precipitation of mineral solids were simulated using the PHREEQC thermodynamic modeling program. Water recovery from the treated brines was modeled using the ROSA package for simulating permeate and concentrate compositions for NF processes. The three-step demineralization process allowed the recovery rate for the brine solution to be as high as the initial feed water, and achieved a total water recovery of >97%.

Introduction

Over the last few decades, potable water scarcity has become a significant issue due to increase in world population, and climate change. It is estimated that more than one billion people are without clean drinking water and almost 2.3 billion people live in regions with water shortages (Service 2006). Therefore, water reuse and recycling schemes are gaining traction as they are the most feasible method to deal with water scarcity (Gerrity et al. 2013).

High pressure membrane processes are now used because of their proven ability to reject both organic and inorganic species and produce extremely clean water (Rahardianto et al. 2007). However, one drawback is the small but highly concentrated brine stream produced that is difficult to deal with and very expensive to treat (Rahardianto et al. 2007). The volume of concentrate generated is even more critical for inland membrane plants located in areas far away from the ocean (Oren et al. 2010). There are several ways to dispose the membrane concentrate namely: surface water discharge, deep well injection, evaporation and land application (Malmrose et al. 2004). Disposal of concentrate depends on its site, water quality and quantity. Cost plays an important role in choosing the method of disposal (Malaeb and Ayoub 2011). Concentrate disposal to surface waters includes releasing the water to lakes, rivers, bays, brackish canals or oceans. However, some plants avoid surface water discharge due to extensive and costly permit reviews (S. Sethi 2005). Blending of the concentrate with other wastewaters or dilution is another option. Moreover, concentrate blended with industrial or municipal wastewaters can go through further treatments or be released to publicly owned treatment works (POTW) (S. Sethi 2005). Deep-well injection is a method of pumping the concentrate into porous subsurface rock formations with well depths from several hundred feet to several thousand feet depending on the geological conditions of the site (Nicot and Chowdhury 2005). Evaporation ponds are another feasible option for small flows and for regions with warm and dry climate with high evaporation rates and low land costs (Malmrose et al. 2004).

Additional recovery of water from this brine stream in an efficient and cost-effective way for treatment and management of the concentrated brine has become a chief study area. One potential solution is to pass the brine through a secondary high pressure membrane and achieve more recovery of clean water. However, this method is not cost-effective and sustainable due to rapid fouling of the second membrane. To increase the lifetime of this second membrane, pre-

treatment of the brine for removal of organic and inorganic species is desired. While, organic contaminants can be attenuated in the brine stream using oxidation processes like Ozone and UV-advanced oxidation as discussed earlier, treatment of inorganic species is more challenging.

The selection of best available technology (BAT) to achieve higher recovery reaching to near zero liquid discharge (ZLD) or ZLD depends on several important parameters. A conceptual decision tree based on work from Subramani et al. for choosing the best technology to increase the overall permeate water is presented in Figure 2. As shown in Figure 2, achieving near-ZLD or ZLD can be accomplished by thermal-based or membrane-based technologies or a combination of both (Subramani and Jacangelo 2014). It is crucial to identify the pretreatment requirements prior to the use of various technologies. For instance, further treatment of RO concentrate using membrane or thermal technologies requires the removal of scale forming ions and organics to prevent scaling, fouling and foaming (Perez-Gonzalez et al. 2012). TDS content of the concentrate is the principal criterion for selection of membrane-based technologies in comparison with thermal-based technologies. Pressure-driven membranes are restricted due to the pressure limits on the vessel used for spiral wound systems. Pressure greater than 82 bar is required for concentrates with high TDS (~4 g/l) content in order to overcome the osmotic pressure and achieve clean water permeation (Subramani and Jacangelo 2014). Therefore, for RO/NF concentrates with high TDS content (such as produced water), thermal-based processes are critical in achieving further minimization of concentrate volumes to achieve near-ZLD or ZLD.

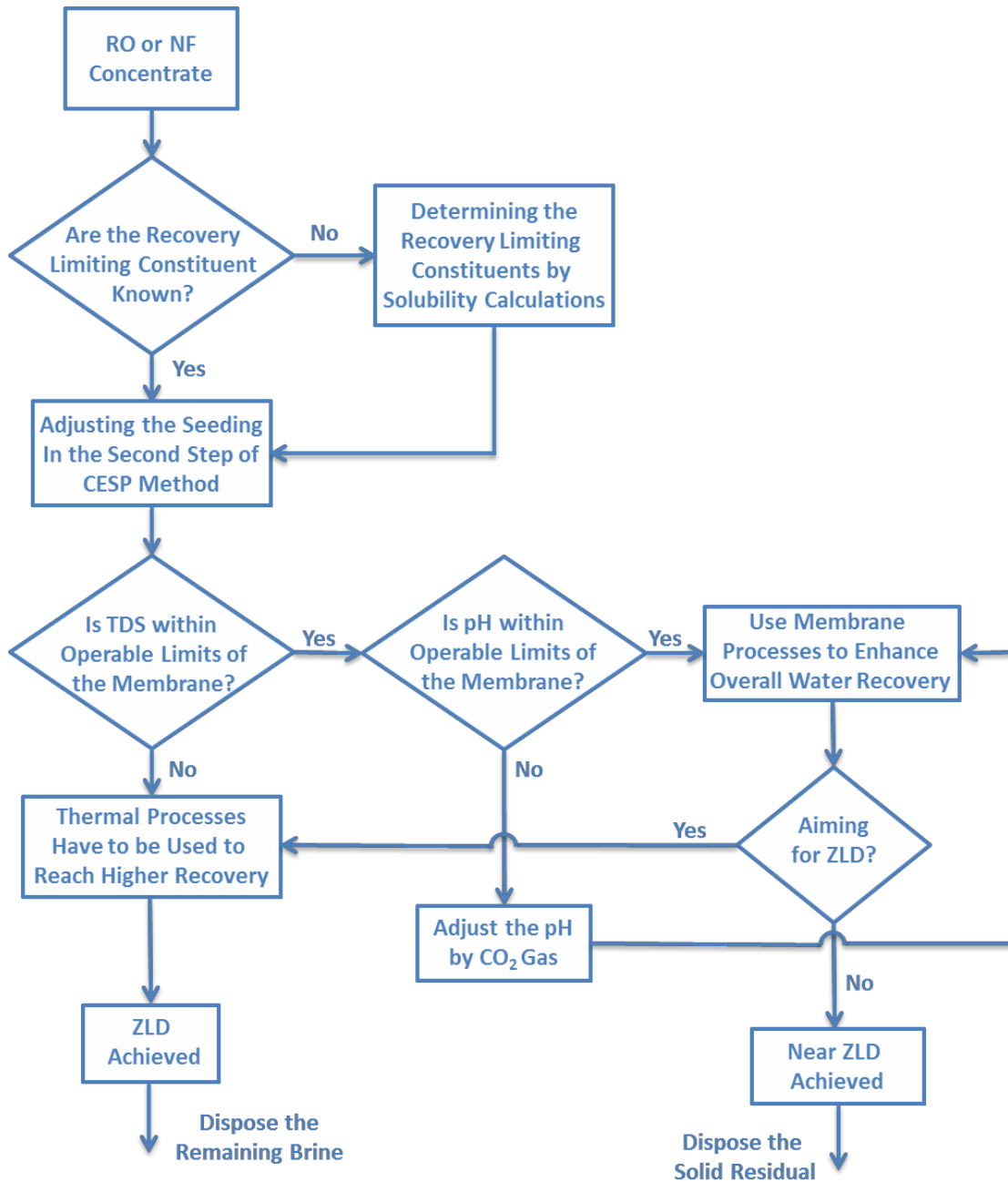


Figure 2 Conceptual illustration of steps required for achieving near-ZLD or ZLD of concentrate generated from RO processes (Subramani and Jacangelo 2014).

The next section provides a brief review of technologies for treating concentrate from municipal and industrial sites to increase the overall permeate recovery. Treatment technologies have been classified as membrane-based, thermal-based, or emerging technologies. All categories are capable of reducing membrane concentrate volume and also can achieve ZLD when operated in combination (Baudequin et al. 2011, Gabelich et al. 2007, Gabelich et al. 2010, Juby et al. 1996,

Mahvi et al. 2005, Perez-Gonzalez et al. 2012, Rahardianto et al. 2010, Subramani et al. 2012, Subramani and Jacangelo 2014, W. Shih 2013).

Membrane-based technology

Membrane-based technologies are typically used for further removal of dissolved solids in the RO/NF concentrate. But, in order to implement these technologies for RO/NF concentrate management, scaling or fouling precursors have to be removed using a pretreatment process. These processes are divided into major groups of pressure and electric potential driven mechanisms.

Pressure driven membranes

In this approach, scaling precursors (mainly calcium, barium and silica) are typically removed from the first stage RO/NF concentrate using chemical treatment techniques followed by a second stage RO/NF system (secondary RO/NF) (Gabelich et al. 2007, Gabelich et al. 2010). This type of treatment generally results in over 95% clean water recovery and can approach ZLD with thermal technologies (Gabelich et al. 2007, Gabelich et al. 2010, Rahardianto et al. 2010). There are several methods to remove scaling precursors from the primary RO/NF which are described in the following sub-sections.

Intermediate chemical softening

Chemical softening for the concentrate of the primary RO/NF can be accomplished with pellet softeners, lime softeners or fluidized bed crystallizers. Lime slurry is used for primary concentrate treatment by Gabelich et al (Gabelich et al. 2007). Gabelich et al. used a solid contact reactor for treatment of the primary RO concentrate which was then sent to the secondary RO membrane. The overall permeate recovery for the Colorado River water tested exceeded 95%. In the accelerated seeded precipitation (ASP), seed materials are added in the RO concentrate to precipitate hardness ions and therefore enable further treatment of the concentrate (Rahardianto et al. 2007). To raise the pH of the solution, an alternative to lime addition is sodium hydroxide. Alkaline chemical selection depends on the concentrate composition and the chemical cost (Gabelich et al. 2010). The advantage of using conventional softening compared to intermediate treatment of concentrate is higher removal rate of scaling precursors while its disadvantages include a larger amount of sludge and difficulties in accurate pH control in the contactor (Gabelich

et al. 2007). Despite the advantages of the conventional softening, its drawback of create a larger amount of sludge causes intermediate concentrate demineralization (ICD) methods to be more favorable.

Membrane processes draw attention because of their capability to reject inorganic and organic species while passing almost pure water (Gabelich et al. 2007). In order to reduce the inorganic species, several studies use a multi-step membrane treatment with intermediate concentrate demineralization (ICD) (Rahardianto et al. 2010). In this multi-step membrane treatment method, feed water passes through the primary membrane and maximum permeate water is achieved by avoiding the mineral scaling on the membrane. Then, the concentrate goes to ICD step in order to precipitate slightly soluble minerals and remove them by sedimentation and filtration. The resulting treated water from ICD step goes to the secondary membrane to produce additional permeate water. This process increases the permeate production and reduces the brine management costs.

Rahardianto et. al. studied a brine which was supersaturated with respect to gypsum and calcium carbonate. As illustrated in Figure 3, Chemically-enhanced seeded precipitation (CESP) consists of two sequential steps: (1) alkaline chemical dosing in order to scavenge antiscalant with CaCO_3 precipitation followed by (2) seeded precipitation (SP) for brine precipitation (Rahardianto et al. 2010). In the first step, alkaline chemical (i.e. Soda ash, lime and caustic soda) is added in order to increase the pH of the brine and deprotonate the bicarbonate ions in it. This causes an increased carbonate concentration in the brine making it supersaturated with respect to CaCO_3 . The purpose of this step is to promote the fast nucleation and growth (both precipitative and aggregative) of CaCO_3 particles (Liao and Randtke 1986, Naka et al. 2006). Second step of CESP process is to introduce the effluent of the first step to seeds (e.g. CaSO_4 or BaSO_4) which increase the supersaturation level of the brine with respect to added seeding crystals. The overall aim of this process is to co-precipitate the antiscalant with CaCO_3 in the first step and precipitate other supersaturated compounds (e.g. CaSO_4 or BaSO_4) with minimal retardation in the second step.

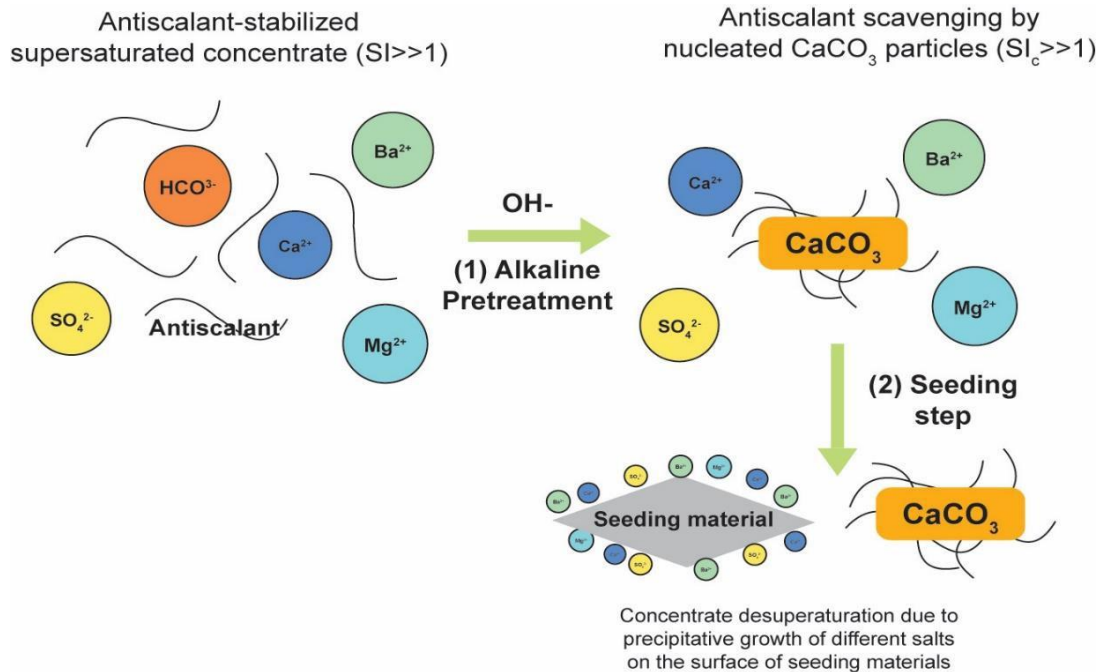


Figure 3 CESP Illustration for precipitation of supersaturated brine with respect to $CaCO_3$ and $CaSO_4$

Antiscalant removal in the first step is due to the entrapment of its particles which are adsorbed to the surface of the $CaCO_3$ precipitates. The entrapment happens because of epitaxial particle overgrowth on the surface and its aggregation on $CaCO_3$ particles (Liao and Randtke 1986, Naka et al. 2006). Antiscalant scavenging is proportional to its initial concentration and also to the surface area provided by $CaCO_3$ precipitates. Provided surface area depends on the rate of nucleation of $CaCO_3$ particles. It also depends on precipitative and aggregative growth rates which are proportional to $CaCO_3$ supersaturation level. Therefore, with a fixed antiscalant concentration, its removal depends on the dose of alkaline chemical added and treatment time of the first step. In the second step, gypsum precipitation depends on the supersaturation level of $CaSO_4$ (which is the driving force for precipitation) and amount of gypsum seeding material (which is the area available for surface reaction and epitaxial surface growth) added to the brine (C. N. Alpers 2001, J. Garside 1992).

There are several ICD methods to precipitate the brine with respect to scaling minerals such as chemical precipitation (precipitation softening) (Rahardianto et al. 2007, Rahardianto et al. 2010) and seeded precipitation softening (Bremere et al. 1998, Bremere et al. 1999, Yang et al. 2008a). Using alkaline chemicals (e.g. lime, lime-soda ash, and caustic soda) to increase the pH

and favor the CaCO_3 and $\text{Mg}(\text{OH})_2$ precipitation is an effective but chemically intensive method. Moreover, precipitation of $\text{Mg}(\text{OH})_2$ is not easy due to its poor settling characteristics (Rahardianto et al. 2010). Adding seed crystals to the brine enables its precipitation via precipitative seed crystal growth (Bremere et al. 1998, Bremere et al. 1999, Yang et al. 2008a). However, presence of antiscalant in the brine with the aim of keeping the supersaturated salts stable and dissolved in it will significantly retard the precipitation and thus lower the precipitation rate (Yang et al. 2008a).

The use of polymeric coagulants, chemical/electrochemical oxidation or organic chelants for disrupting antiscalant action by degradation or antiscalant scavenging have been proposed as pretreatment methods for precipitation by seeded precipitation (Barthrope 1994, Yang et al. 2007, Yang et al. 2008a, Yang et al. 2008b). A serious concern in the utilization of these methods, however, is the carryover of residual additives and their byproducts such as micro contaminants or oxidation byproducts into secondary membrane operation and into the final residual secondary membrane concentrate. Several studies have demonstrated that coagulants and coagulation byproducts can adversely affect antiscalant treatment and cause membrane fouling (Gabelich et al. 2005, Gabelich et al. 2006, Kim et al. 2009).

Seeded slurry precipitation and recycle

Seeded slurry precipitation and recycle (SPARRO) uses seed crystals for the precipitation of CaSO_4 from the concentrate. According to Juby et al., more than 90% feed (mine wastewater) recovery was achieved using this method (Juby et al. 1996). In this method, seed crystals are introduced to a tubular RO membrane to precipitate scaling precursors (mostly CaSO_4) on the seeds. A slurry of the seed crystals circulate within the system and CaSO_4 precipitates on these crystals instead of the membrane surface (Juby et al. 1996, Juby et al. 2008). This process has approximately half the electrical power consumption compared to previous designs which significantly improves its cost-efficiency. However, Membrane performance was generally unsatisfactory due to both fouling and hydrolysis dominating at several time periods according to previous literature.

Pellet reactors

Pellet reactors have several advantages compared to conventional methods such as lower chemical usage, less waste sludge production and smaller footprint (Subramani and Jacangelo

2014). Therefore, they are an alternative for conventional chemical softening. In this method, CaCO_3 particles precipitate on the seed crystals. pH of the concentrate is increased before feeding the reactor in order to favor the precipitation of calcium species (Mahvi et al. 2005). Shih et al. used a pellet reactor to treat the primary RO concentrate. In this study, the test water (brackish groundwater of Chino groundwater basin, CA), had increased recovery from 83.5% to 95% using a secondary RO membrane after pellet reactor use as a pre-treatment. More than 98% of the hardness and 65% of silica was removed from the concentrate (W. Shih 2013). Pellet reactors have several advantages compared to conventional methods such as lower chemical usage, less waste sludge production and smaller footprint (Subramani and Jacangelo 2014).

Electrocoagulation

Electrocoagulation (EC) is another method to remove divalent metals and ions from the concentrate. This method uses an electrolytic reactor with electrodes such as aluminum, iron or stainless steel that the concentrate passes through the reactor. The anode electrode dissolution is accompanied by hydrogen gas bubble formation at the cathode which can float the suspended solids to the surface and then it can be easily removed (Baudequin et al. 2011). Subramani et al. used EC for the treatment of primary concentrate of mining contaminated water and they were able to remove more than 90% of the barium, calcium, magnesium, strontium and silica. Overall water recovery after using a secondary RO membrane reached 93% in their study (Subramani et al. 2012). Higher scaling precursors' removal and less sludge production are the main advantages of the EC and high maintenance and operation costs and high energy consumption are the main disadvantages of this method (Subramani and Jacangelo 2014).

Electrical potential-driven membranes

There are three electrically driven pre-treatments for RO/NF concentrate minimization namely: electrodialysis (ED), electrodialysis reversal (EDR) and electrodialysis metathesis (EDM). These methods use electrical potential instead of pressure. These processes attract dissolved ions through ion exchange membranes that are impermeable to water. Movement of anions and cations without water molecules results in desalination of the water across the membrane (Malmrose et al. 2004). These methods are described in detail later in the text.

Chemical softening of RO and NF brines is made more difficult when scale-inhibiting compounds, such as phosphonate antiscalants, are present. These compounds inhibit CaCO_3 precipitation and reduce the particle size of precipitates (Greenlee et al. 2010). A recent study has found that a granular ferric hydroxide adsorbent can remove phosphonate antiscalants from RO concentrates (Boels et al. 2012, Caravelli et al. 2010). However, the kinetics of the adsorption process were considerably slower than those for ion exchange, and extended contact times were required to achieve practical adsorbent loadings.

The goal of this research was to develop a treatment scheme for removing scale-forming compounds from membrane concentrate solutions that are supersaturated with respect to multiple carbonate and sulfate minerals. To remove antiscalant compounds that interfere with mineral precipitation, ferric chloride was added to promote co-precipitation of ferric hydroxide and the phosphonate antiscalants. The effectiveness of three pH adjusting chemicals, lime, caustic soda, and soda ash, on promoting carbonate mineral precipitation was determined. The effect of mixing time and several seeding agents on precipitation rates were also investigated.

Impact of different parameters on multi-step brine precipitation

Mixing rate

Mixing rate helps in faster and better mixing of the chemicals added to a solution at first of mixing period and also helps collision and growth of precipitates which leads to greater particle size and better settling. However, too much mixing rate is also able to break the attached particle and prevent an efficient settling. Therefore, there is a need for finding an optimal mixing rate that can mix the solution very well and increase the collisions just as much as helping particles to attach to each other and not to detach them.

Selection of chemical

There are three major chemicals used to increase the pH in softening namely: Caustic soda (NaOH), Hydrated lime ($\text{Ca}(\text{OH})_2$) and soda ash (Na_2CO_3) (J. Garside 1992). The choice among these chemicals can be determined by alkalinity of feed water, increase in sodium content, production of CaCO_3 , dosage required, their effectiveness in antiscalant removal and cost. In this

research, all three chemicals are used with the aim of maximum antiscalant removal and calcium carbonate precipitation.

Alkaline chemical dose

Alkaline chemical dose is by far the most important factor for precipitating carbonate species (J. Garside 1992). There is a minimum limit of alkaline chemical dose required to overcome the antiscalant ability which stabilizes the brine and makes it favorable for precipitation of CaCO_3 . Entrapment of the antiscalant in the formed CaCO_3 particles also expedites the precipitation. Therefore, as the second optimization parameter in this research, three different pH values were selected in order to observe the effect of chemical dose on the precipitation of CaCO_3 and also on the removal of the antiscalant. A recent study used two different pH values (9 and 9.5) and found that the addition of more chemical (higher pH values) resulted in higher supersaturation levels of CaCO_3 , thereby, leading to more precipitation of CaCO_3 and calcium removal (Rahardianto et al. 2010).

Pretreatment time

Calcium carbonate precipitation consists of three steps: nucleation, growth and aggregation. Therefore, sufficient time is needed to reach the maximum aggregation within a specific alkaline chemical dose. This also affects the antiscalant removal and subsequently the BaSO_4 precipitation in the second step. Thus, Experiments were run in three different time frames: 10, 20 and 30 min in order to find out the sufficient time to reach the equilibrium range.

Antiscalant dose

The increase in antiscalant concentration causes more retardation of CaCO_3 precipitation in the first step of the process. This is due to antiscalant particles having less surface area. The resulting lower antiscalant removal affects the CaSO_4 precipitation in the second step as well.

Seeded material

In a previous study, CaSO_4 was used as seeding material due to the tested RO brine supersaturated with respect to CaSO_4 . Supersaturation level of CaSO_4 in the second step of that study was reduced to 0.04 from 0.4 (Rahardianto et al. 2010). In the current study, brine is under

supersaturated with respect to CaSO_4 . Therefore, using CaSO_4 seeding material would not be helpful. Taking this into account, garnet, silica, CaCO_3 and BaSO_4 seeding materials were chosen in order to observe the effect of them in the precipitation of generated brine. Garnet and silica will provide a precipitation surface for different supersaturated chemicals while BaSO_4 and CaCO_3 will induce the precipitation by increasing the supersaturation levels.

Seeded material amount

Optimization of the amount of seeding material is essential in the second step of the process. Increasing the amount of the seeding will lead to more surface area for precipitation in silica and garnet and also will lead to higher supersaturation levels in BaSO_4 and CaCO_3 seeding crystals. A recent study used 2.5 g/L and 4 g/L as gypsum seeding amount and determined that increasing the seeding in the second step led to more CaCO_3 precipitation (Rahardianto et al. 2010).

Seeding time

Precipitation in the second step will also require a sufficient amount of time to reach to equilibrium. A previous study used a continuous measurement of calcium concentration for 120 min in order to measure the saturation index for gypsum and calcium carbonate (Rahardianto et al. 2010). In current study, four different seeding times (30 min, 60 min, 90 min and 120 min) were implemented in order to find out the time required to maximize the precipitation of different precipitating materials.

Experimental

All of the experiments are conducted at 22° C and the mixing rate is 250 RPM.

Materials

Ferric Chloride Hexahydrate (Lumps/Certified ACS, Fisher Chemical) is procured for the step one of the process. Sodium Carbonate Anhydrous (Powder/Certified ACS, Fisher Chemical), Calcium hydroxide (98%, extra pure, ACROS Organics™) and Sodium hydroxide (ACS reagent, $\geq 97.0\%$, pellets, Sigma-Aldrich) was used as increasing pH chemicals. Calcium Carbonate (ACS AR Powder, Macron Fine Chemicals™), Barium Sulfate (Extra Pure, ACROS Organics™), Silica

and garnet (Red Flint Sand & Gravel, LLC) are used as seeding materials in the third step of the first process. PALL membrane filters with 0.45um pore size were used in between the steps for filtration of the solution (PALL GH PolyPro 50mm, PALL Life Science Division,). 2% Hydrochloric Acid (Certified ACS Plus, Fisher Chemical) was also made onsite in order to clean the vessels and paddles from precipitates. 0.1 N Sulfuric Acid (Certified ACS Plus, Fisher Chemical) is freshly made in order to measure the alkalinity. DOW FILMTEC NF270-4040 Nanofiltration Element (DOW FILMTEC™) is used for generating brine with 85% recovery rate from Central Arizona Project (CAP) water. For this purpose, 1.5 mg/l of PermaTreat 191 (PermaCare-191)— a phosphonate-based antiscalant—is added to the CAP water as antiscalant. A Mettler balance (Mettler Toledo™ Excellence Plus XPE Analytical Balances: XPE205), a Mettler pH meter (Mettler Toledo™ SevenMulti™ S50 Single Channel pH/ion Meter) and a Thermo Scientific conductivity meter (Thermo Scientific Orion™ 3 Star) are used throughout the experiments.

A laboratory-scale jar tester (PB-900 Programmable Jar tester, Phipps & Bird) as shown in the

Figure 4 is used for conducting the experiments. The jar tester system possesses 6 reaction vessels. The dimensions of the vessels are 11.5 cm × 11.5 cm × 21 cm and the capacity of them is 2 liters; however, experiments are conducted with 1 liter of the brine solution in each vessel.



Figure 4 PB-900 Programmable Jar tester, Phipps & Bird

Brine generation and system description

Water from the Central Arizona Project (CAP) as delivered to Tucson, Arizona was collected before each experiment. The water was treating using a Dow Filmtec™ (NF270-400) NF membrane operating at 85% recovery. The brine characteristics are shown in Table 1. Concentrations are given as ranges as a consequence of conducting the experiments throughout the year with different CAP water qualities. According to Figure 5, CAP water was supersaturated with respect to CaCO_3 , BaSO_4 and MgCO_3 at pH values greater than seven.

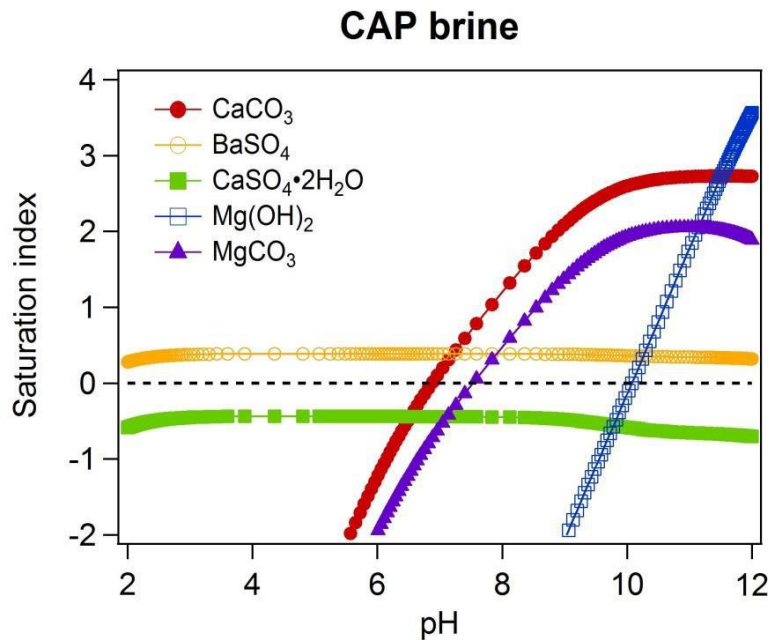


Figure 5 CAP brine supersaturation levels

The supersaturation level of brine, shown in Table 1, with respect to a mineral is assessed in terms of a thermodynamic saturation index (SI) shown in equation 1:

$$S_x = \log \frac{IAP_x}{K_{sp}} \quad (1)$$

where IAP is the ion activity product and K_{sp} is the solubility product for the mineral.

Table 1 Brine characteristics generated from CAP water at 85% recovery with an NF membrane

Analyte	Concentrations (mg/L)	
pH	8.3-8.4	
Alkalinity (as CaCO ₃)	270-330	
Sodium	287-321	
Magnesium	145-162	
Potassium	14-16	
Calcium	339-346	
Barium	0.7-0.8	
Phosphorous	0.5-0.8	
Chloride	108-118	
Sulfate	1770-1899	
	SI values	Log K _{sp} values
CaCO ₃ (Calcite)	1.5-1.54	-8.48
BaSO ₄ (Barite)	1.75-1.81	-9.97
CaMg(CO ₃) ₂ (Dolomite)	2.95-3.06	-17.09
CaSO ₄ (Gypsum)	-0.26	-4.58
CaMg ₃ (CO ₃) ₄ (Huntite)	1.42-1.73	-29.97
MgCO ₃ (Magnesite)	0.84-0.94	-8.03

Methods

Anions were analyzed using Metrohm Professional IC. Metrohm ASUPP7-250 column is used for this purpose. All reagents and standards were prepared in ultrapure water (18 MΩ cm). The eluent solution was 3.2 mM of sodium carbonate and the MSM (Metrohm Suppression Module) solutions were 1% nitric acid and ultrapure water. Cations were analyzed using Agilent 7900 ICP-MS. All of the reagents and tune solutions were procured from Agilent. Samples were prepared in 2% nitric acid before analysis. Alkalinity was measured using Gran Function Plot Method available in USGS online free software.

Scaling indices were calculated using the PHREEQC aqueous phase thermodynamic modeling package from the U. S. Geological Survey. The PHREEQC model uses extended Debye-Huckel and the Davies equation (Parkhurst 2013) for modeling solution phase activity coefficients. The scaling potential of the treated brine solutions was evaluated using the ROSA software package from DOW Filmtec™. The ROSA software simulates membrane treatment operations by applying empirical separation factors for different ions and operating conditions.

Results and discussion

Ferric Chloride Addition

The effect of ferric chloride dose on removal of the phosphonate antiscalant is shown in Figure 6. The phosphorous concentration in solution was used to track antiscalant removal, since its exact structure is proprietary information and is not known. Ferric chloride addition results in hydrolysis reactions that produce ferric hydroxide, according to (Caravelli et al. 2010):



The declining solution pH values with increasing FeCl₃ dose is indicative of ferric hydroxide precipitation. Phosphorous removal was a near linear function of the FeCl₃ dose until ~90% removal was attained, as illustrated in Figure 6. Removal below the detection limit of 1.7 µg/L was observed for doses of 0.2 and 0.4 mM. The high phosphorous removal in solutions containing high concentrations of other anions, such as SO₄²⁻, suggests that the removal mechanism involves inner sphere complexation via formation of a Fe-O-P bonds. This mechanism was reported by Boels et al (2012) for removal of the phosphonate scale inhibitor NTMP (methylenephosphonic acid) by a ferric hydroxide adsorbent.

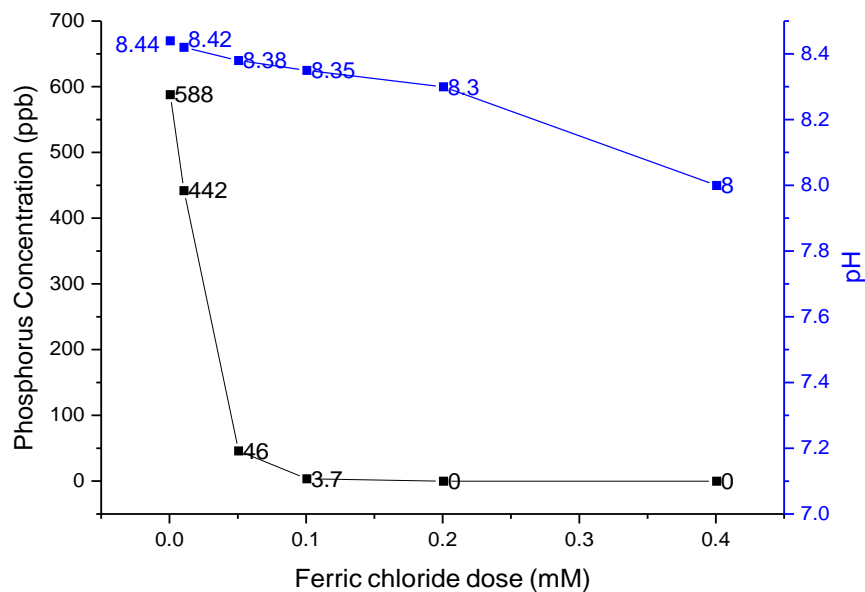


Figure 6. Phosphorus removal and pH reduction as a function of FeCl_3 dose after 30 min of mixing.

The kinetics of phosphorous removal are illustrated in Figure 7 which shows a near linear decrease with mixing time. The drop in solution pH value over the first 5 minutes is indicative of ferric hydroxide precipitation. The slowly increasing pH values between 5 and 30 minutes elapsed can be attributed to inner sphere complex formation where an OH^- ligand is replaced by phosphonate ligand. This effect on pH has been observed for arsenate complexation with ferric hydroxide (Jain et al. 1999). Inner-sphere complexation reactions with ferric hydroxide are known to proceed slowly due to high activation energies for breaking the bond between the OH^- ligand and Fe (Farrell and Chaudhary 2013). The continued pH rise after all the phosphorous has been removed from solution is indicative of a multistep adsorption process wherein a physically adsorbed compound is converted to a chemically adsorbed compound via replacing an OH^- ligand (Farrell and Chaudhary 2013).

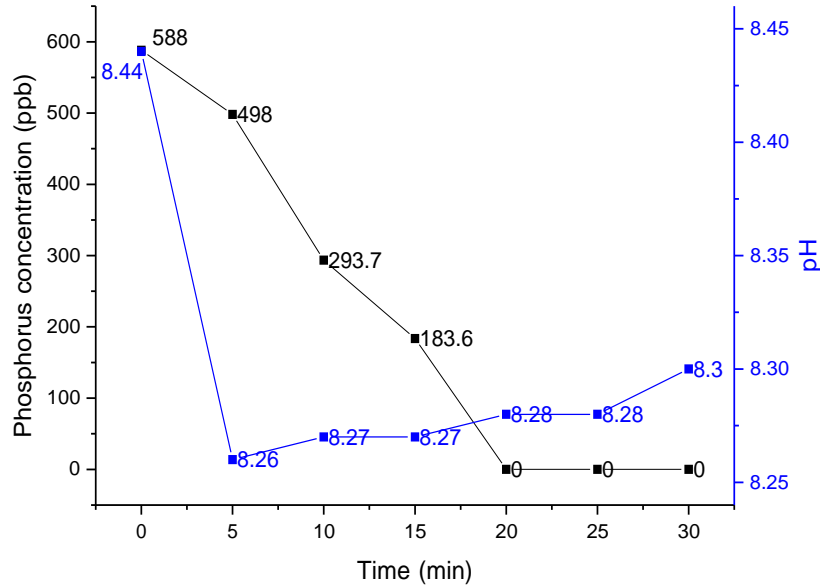


Figure 7. Phosphorus removal and pH change over 30 min of mixing time after addition of 0.2 mM FeCl₃.

In addition to removing phosphorous from solution, ferric chloride addition resulted in precipitation of CaCO₃ and BaSO₄, as indicated by the change in solution composition shown in Figure 8. Precipitation of these compounds can be attributed to two effects, removal of the antiscalant compound and the high surface energy of the small ferric hydroxide precipitates that promotes nucleation of supersaturated solids.

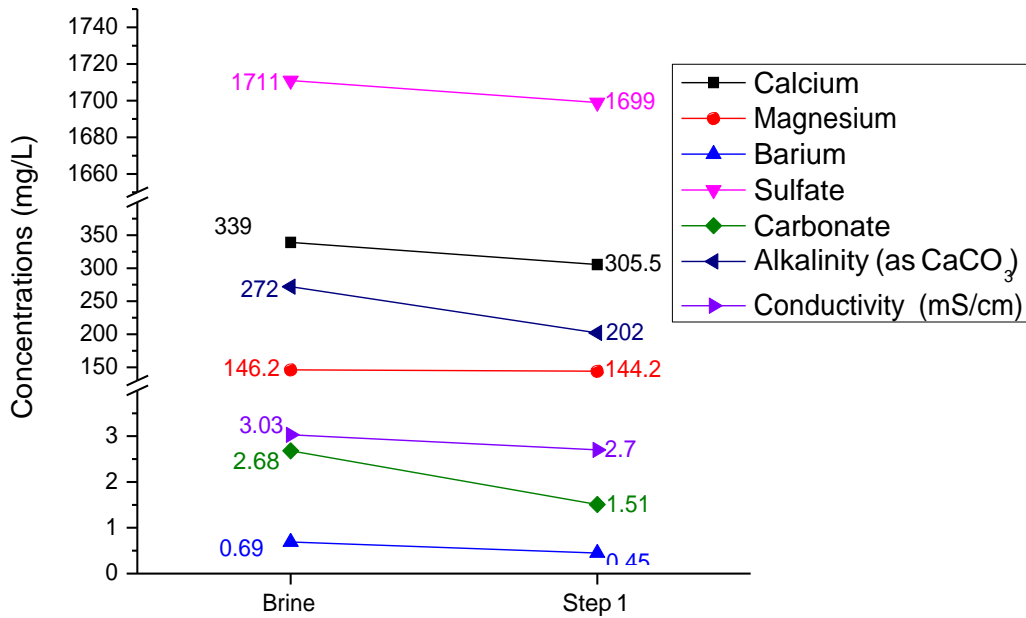


Figure 8. Change in concentration of solution species after ferric hydroxide precipitation.

Thermodynamic modeling of the solution before and after ferric chloride addition shows that the saturation indices for all five mineral solids declined, as shown in Figure S1 in the appendix 1.

The effect of removing the antiscalant compound on mineral precipitation was investigated by comparing mineral precipitation in brine solutions with and without FeCl₃ treatment. To promote carbonate mineral precipitation, the pH of two samples of brine solution was increased to 9.6 via addition of NaOH. Table 2 shows the effect of 0.2 mM ferric chloride addition on subsequent mineral precipitation. Mineral SI values for the brine sample without FeCl₃ addition ranged from 8.1 to 30.4% greater than those with FeCl₃ addition. Furthermore, final Ca²⁺ concentration was decreased by 58% by the FeCl₃ precipitation step.

Table 2 Mineral SI values after 30 minutes elapsed after pH adjustment to 9.6 in samples with and without previous treatment with 0.2 mM FeCl₃.

Saturation indices	Brine	Step two w/o ferric chloride (step 1)	Step two w ferric chloride (step 1)
Calcite	1.54	1.35	1.05
Magnesite	0.89	1.02	0.9
Barite	1.76	1.22	0.94
Dolomite	2.99	2.94	2.72
Huntite	1.55	1.76	1.35
Phosphorous (ppb)	716	81.6	0
Calcium (ppm)	346.3	163.2	95
Carbonate Activity (10 ⁻⁵ M)	4.65	6.7	8

Carbonate Mineral Precipitation

The second step in the process is aimed at carbonate mineral precipitation while avoiding precipitation of Mg(OH)₂, due to its poor settling characteristics (Rahardianto et al. 2010). The saturation pH value for Mg(OH)₂ in the brine was determined to be 9.67 using the Phreeqc software. Three pH adjusting reagents, calcium hydroxide, sodium hydroxide, and sodium carbonate, were tested for their ability to promote precipitation in solutions with pH values of 9.6. Table 3, shows the dose of each reagent and the SI values for the five mineral solids after 30

minutes stirring time. At this time, the SI values for the carbonate mineral solids increased. However, there was a 35% decline in Ca^{2+} concentration for the solution amended with Na_2CO_3 , indicating the precipitation of calcite. In the $\text{Ca}(\text{OH})_2$ and NaOH amended solutions, there was negligible calcite precipitation. Thus, Na_2CO_3 was selected for further study as the pH adjusting amendment.

Table 3 values and solution concentrations after 30 minutes elapsed for solutions with initial pH values of 9.6 after addition of $\text{Ca}(\text{OH})_2$, NaOH or Na_2CO_3 .

Saturation indices	Brine	$\text{Ca}(\text{OH})_2$	NaOH	Na_2CO_3
Calcite	1.5	2.22	2.29	2.19
Magnesite	0.89	1.58	1.68	1.76
Barite	1.81	1.79	1.79	1.38
Dolomite	2.97	4.37	4.54	4.52
Huntite	1.55	4.31	4.69	4.82
Calcium (ppm)	375.2	393.9	372.5	242
Carbonate Activity (10^{-5} M)	4.15	21.62	27.69	35.94

The effect of mixing time on mineral saturation indices after Na_2CO_3 addition is shown in Figure 9. The extended reaction time shows that there are considerable decreases in SI values for huntite and calcite up to 40 minutes elapsed. A mixing time of 40 minutes is greater than that normally used in precipitation softening where seed crystals are recirculated through the reactor (Davis 2007).

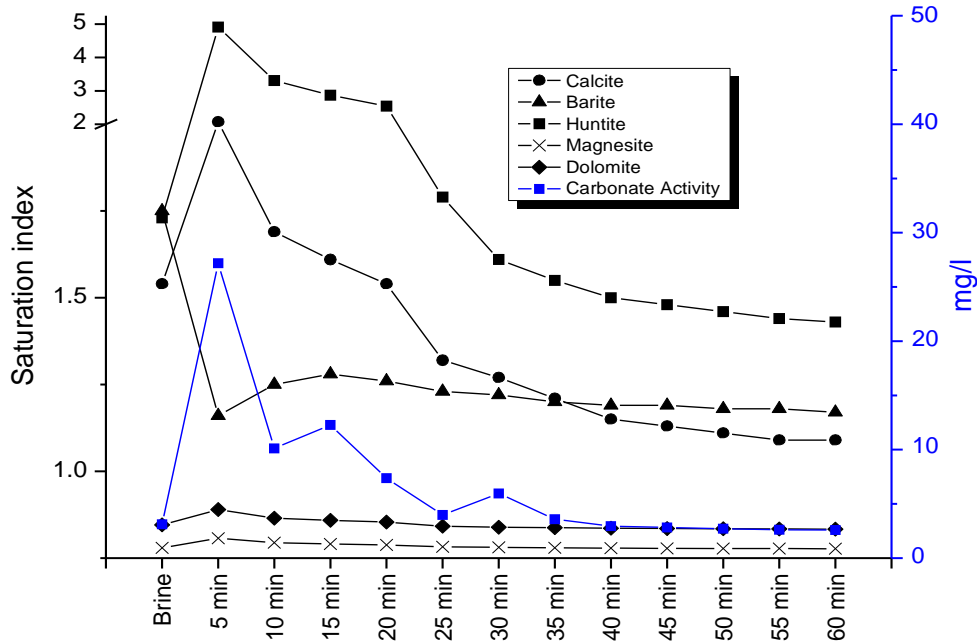


Figure 9 SI values as a function of mixing time after addition of Na_2CO_3 to an initial pH value of 9.6

To speed up the precipitation process, the effect of seeding the solutions with calcium carbonate crystals was investigated. Figure 10 shows the effect of calcite dose on the SI values. In nearly all cases, there was a monotonic decrease in SI value with increasing calcite dose. Calcite seeding avoids the high energy barriers associated homogeneous nucleation, and greater calcite doses increase the surface area available for heterogeneous crystallization. With a calcite dose of 7.5 mg/L, 57% of the Ca^{2+} was removed and the solution pH value dropped to almost the initial brine pH, as illustrated in Figure S2 in the appendix 1.

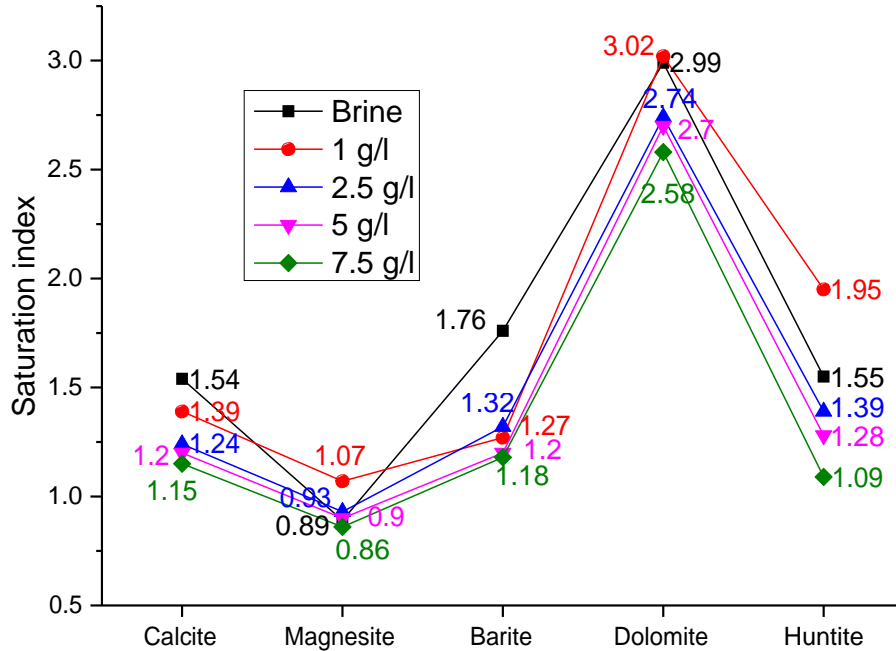


Figure 10 Effect of calcite dose on SI values after 30 minutes of mixing post Na_2CO_3 addition to reach a pH of 9.67

Enhanced Barium Removal

In many instances, Ba^{2+} precipitation is especially problematic in NF and RO treatment of groundwater, seawater and ocean as it is sparingly soluble in water (Bonny and Jones 2008, Greinert et al. 2002, Griffith and Paytan 2012, Hein et al. 2000, Shen et al. 2009). Thus, it may be desirable to remove as much Ba^{2+} as possible prior to second stage membrane treatment. Table 2 and Figure 8 show that Ba^{2+} removal occurs during the ferric hydroxide precipitation step and also during the carbonate mineral precipitation. This may result from Ba^{2+} being co-precipitated with these mineral solids, or from the solids serving as nucleation sites for BaSO_4 precipitation. The ability of a solid surface to promote crystallization of a particular mineral species depends on several factors, such as, the chemical composition of the surface, the surface roughness and the charge on the surface. Thus, there may be more suitable nucleating agents for BaSO_4 precipitation than ferric hydroxide or calcite. To address this question the effectiveness of silica, garnet and barite as nucleation agents for Ba^{2+} removal was investigated.

Figure 11 shows the effect of 5 g/L doses of silica, garnet and barite crystals on the SI values for the five supersaturated mineral solids. The seeding had very little effect on any of the carbonate minerals, but did promote further Ba^{2+} removal. The most effective seeding agent was

the barite crystals, which reduced the barite SI value down to 0.27 and removed >90% of the dissolved Ba²⁺.

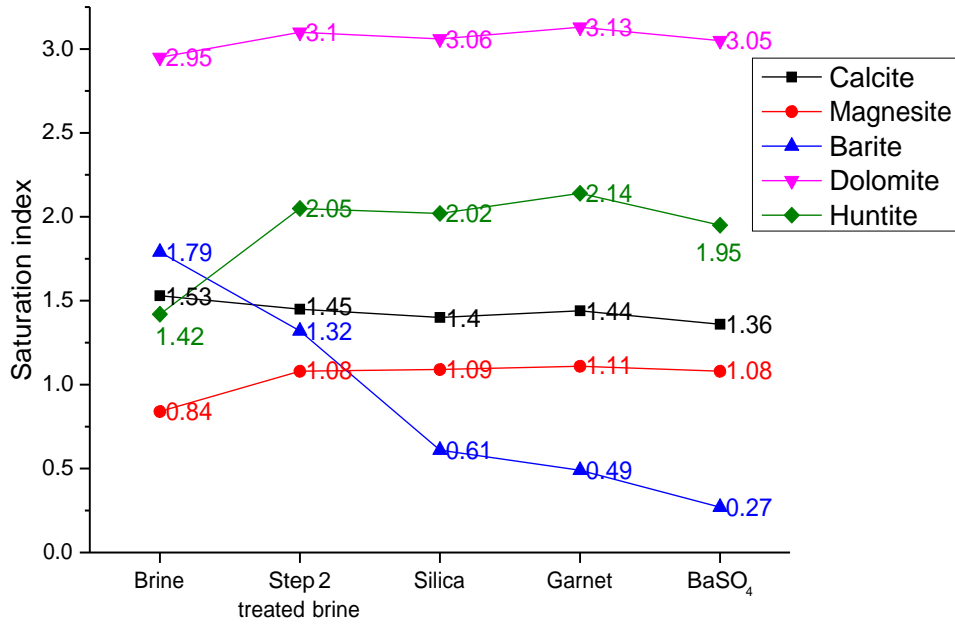


Figure 11 The effect of 5 g/L seeding by silica, garnet or barite on SI values after 30 min of mixing.

The effect of barite seed dose on barium removal is shown in Figure 12. The most dramatic impact on the SI for barite was achieved with the lowest dose, and higher doses had very small effects. This indicates that the most significant limitation to barium removal was the high energy barrier associated with homogeneous nucleation. The small effect of barite dose indicates that mass transfer limitations to barium removal were small with a 30 minutes mixing time. However, at shorter mixing times, there may be mass transfer limitations on Ba²⁺ removal.

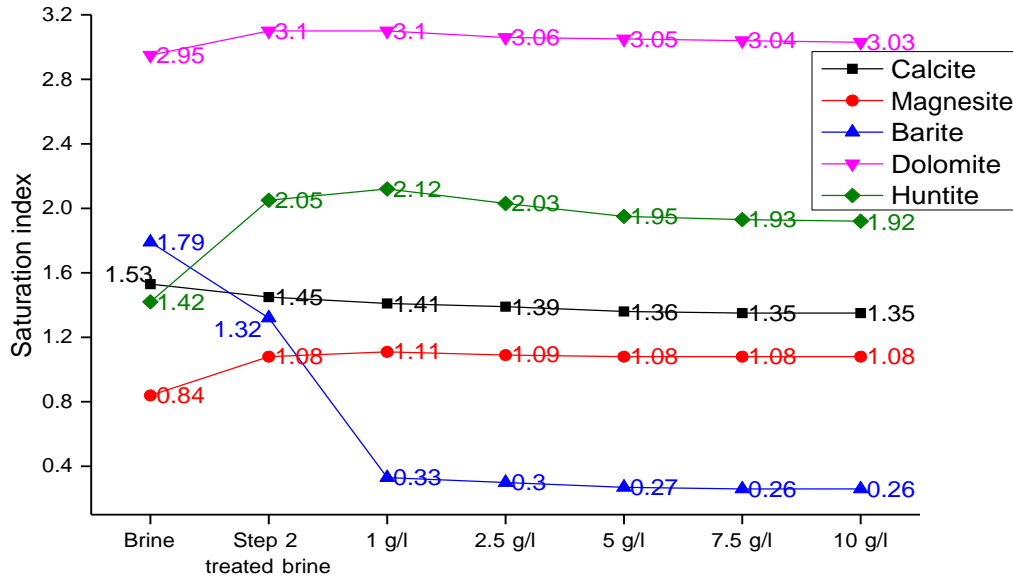


Figure 12 Effect of barite seeding on SI values for the brine after 30 min of mixing.

The effect of mixing time on barite removal was investigated to determine if a period shorter than 30 minutes could be used for the enhanced Ba^{2+} removal step. Figure 13 shows the effect of mixing time on the SI value for barite. Increasing the mixing time from 15 to 30 minutes substantially increased barium removal. Thus, it appears that a mixing time as long as 30 minutes is needed.

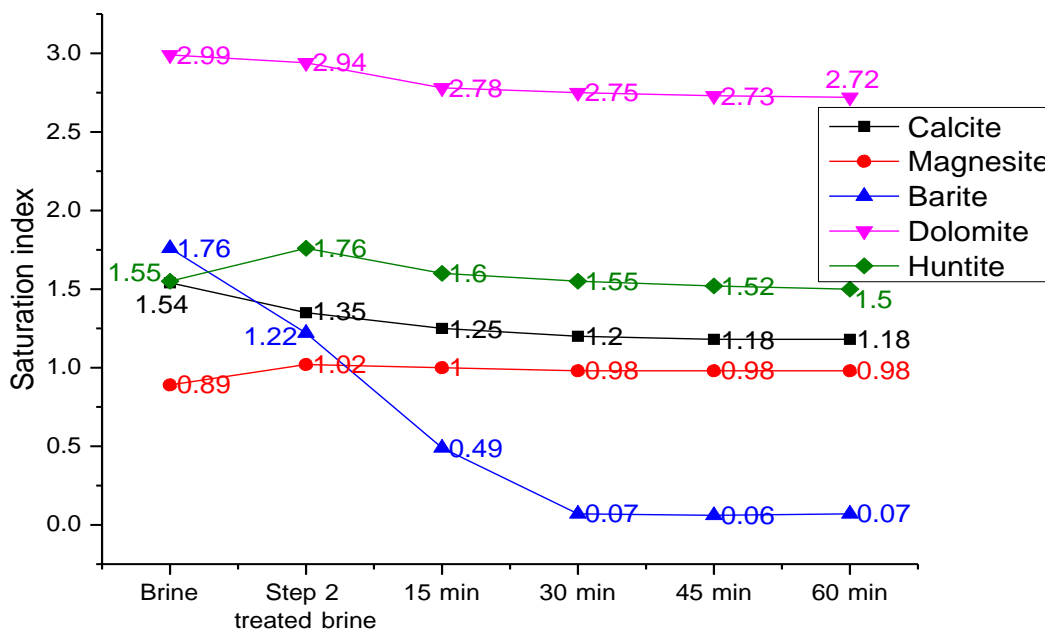


Figure 13 Effect of mixing time on SI values after addition of 5 g/L of barite seed crystals.

Permeate water recovery estimation for the secondary membrane

Changes to the composition of the brine after the three-step treatment process are summarized in Figure S3 in the appendix 1. Significant decreases in Ca^{2+} (82%), alkalinity (61%), Ba^{2+} (98%), and conductivity (31%) were observed. Furthermore, the pH that was increased to 9.67 in step two of the process dropped to less than initial brine pH at the end of step 3. In order to determine the effectiveness of the treatment, the SI values for the concentrate of a second NF membrane were modeled using ROSA software.

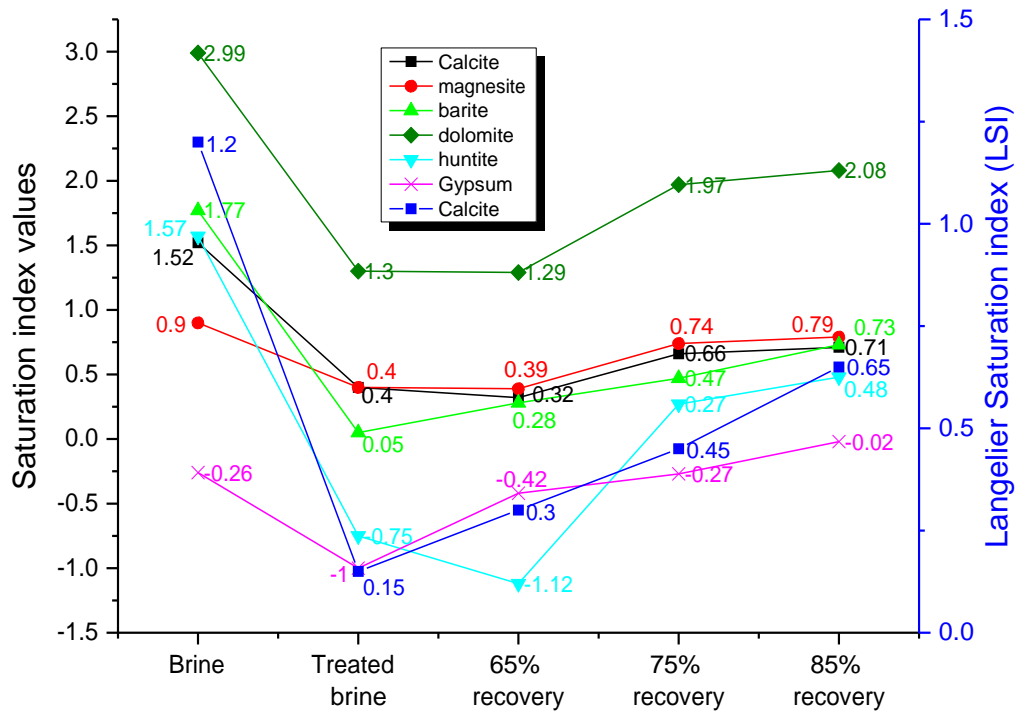


Figure 14 SI values for different recovery rates in the secondary membrane

Figure 14 shows that the SI values for all recovery ratios are lower than the initial brine produced at 85% recovery. Therefore, 85% recovery for the treated brine can be achieved in a secondary membrane, thereby increasing the overall recovery to >97%. Since an antiscalant was used in producing the initial brine, the same antiscalant dose should be used in the second stage NF.

Conclusions

This research developed a new brine treatment process that is applicable to brines that are supersaturated with respect to barite, and to multiple calcium carbonate and magnesium carbonate mineral solids. Effective precipitation of carbonate mineral solids first required removal of a phosphonate scale inhibitor via co-precipitation with ferric hydroxide. When Na_2CO_3 was used for promoting carbonate mineral precipitation, substantial amounts of calcite can be precipitated even when the pH is kept below the $\text{Mg}(\text{OH})_2$ saturation value. Although Ba^{2+} is removed in the first two steps of the process via nucleation on other solids, high levels of Ba^{2+} removal can only be achieved via homoepitaxial templating using barite itself as a seed crystal. The overall process allowed the same 85% recovery in the second state NF as was used in the first stage. The kinetics of the proposed process may be improved via implementation in fluidized bed crystallization reactor (Subramani and Jacangelo 2014) or using membrane assisted crystallization (Sluys et al. 1996).

Appendix 1: Supplementary data

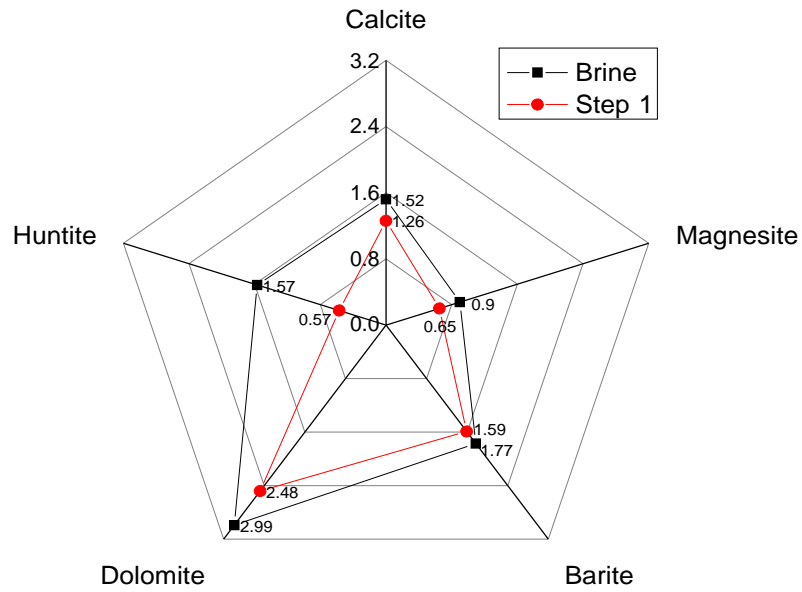


Figure S1. Saturation indices for supersaturated mineral solids before and after ferric chloride addition

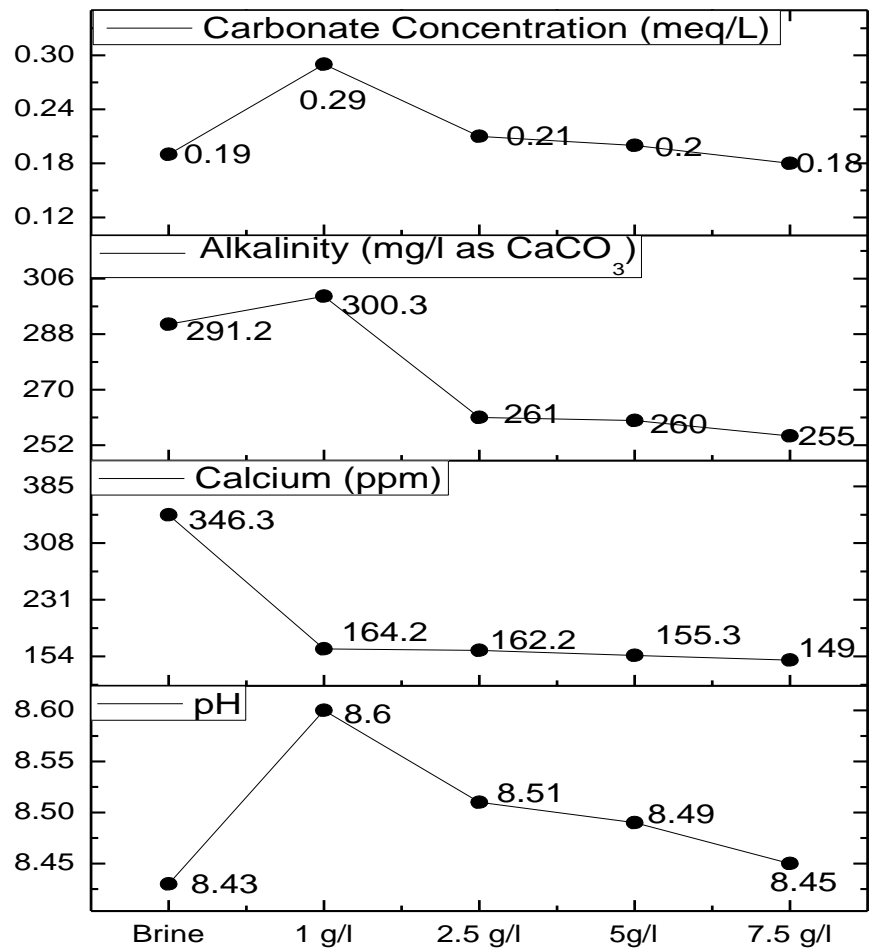


Figure S2. Concentrations of carbonate, alkalinity, and Ca²⁺ and final pH values for the data in Figure 10.

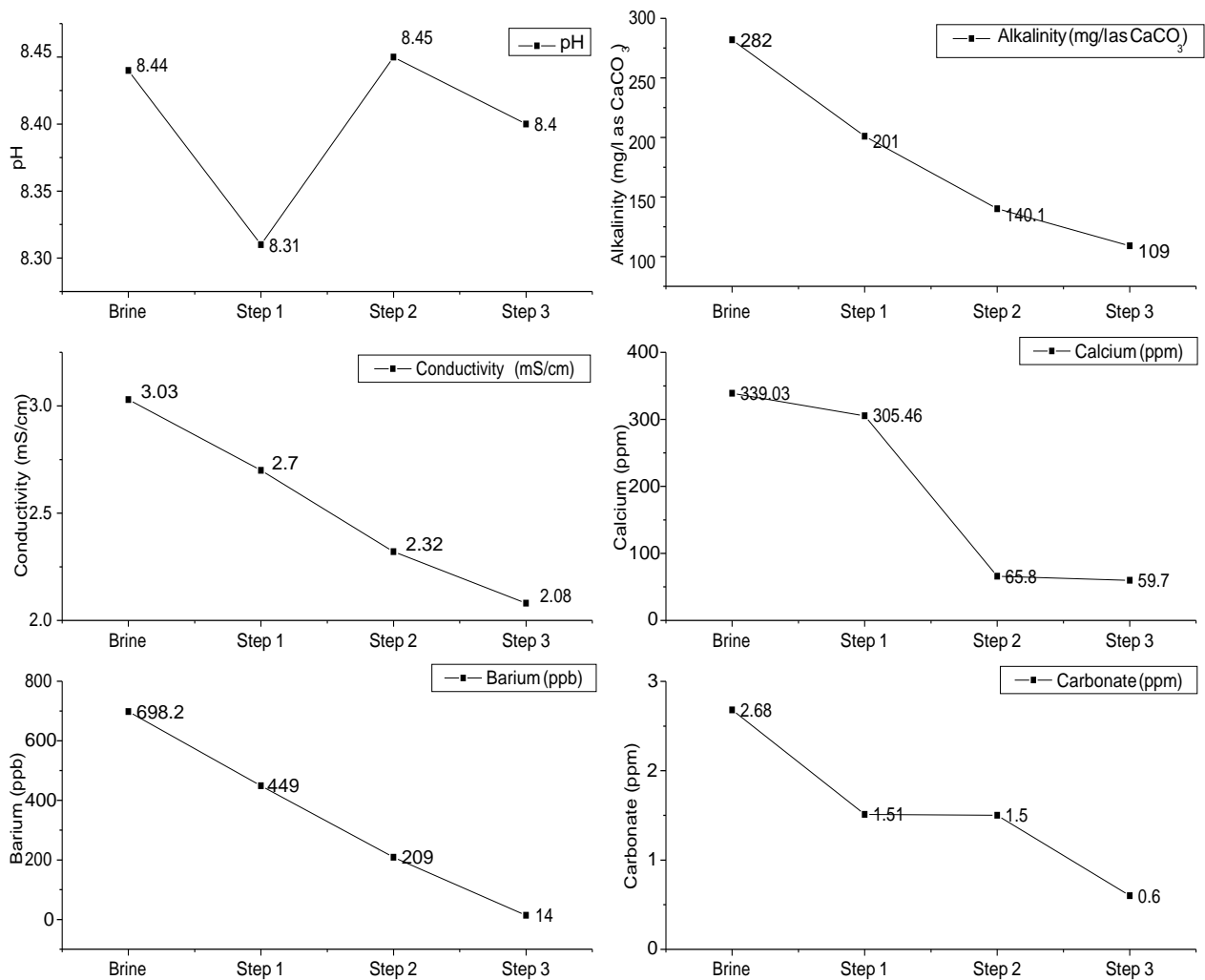


Figure S3. Changes to the composition of the brine after the three-step treatment process

References

- Barthrope, R.T. (1994) Removal of scale-forming inorganic salts from a produced brine p. 5, Marathon Oil Co (MAOC), US.
- Baudequin, C., Couallier, E., Rakib, M., Deguerry, I., Severac, R. and Pabon, M. (2011) Purification of firefighting water containing a fluorinated surfactant by reverse osmosis coupled to electrocoagulation-filtration. *Separation and Purification Technology* 76(3), 275-282.
- Boels, L., Keesman, K.J. and Witkamp, G.J. (2012) Adsorption of Phosphonate Antiscalant from Reverse Osmosis Membrane Concentrate onto Granular Ferric Hydroxide. *Environmental Science & Technology* 46(17), 9638-9645.
- Bonny, S.M. and Jones, B. (2008) Controls on the precipitation of barite (BaSO₄) crystals in calcite travertine at Twitya Spring, a warm sulphur spring in Canada's Northwest Territories. *Sedimentary Geology* 203(1-2), 36-53.
- Bremere, I., Kennedy, M.D., Johnson, A., van Emmerik, R., Witkamp, G.J. and Schippers, J.C. (1998) Increasing conversion in membrane filtration systems using a desupersaturation unit to prevent scaling. *Desalination* 119(1-3), 199-204.
- Bremere, I., Kennedy, M., Michel, P., van Emmerik, R., Witkamp, G.J. and Schippers, J. (1999) Controlling scaling in membrane filtration systems using a desupersaturation unit. *Desalination* 124(1-3), 51-62.
- C. N. Alpers, J.L.J., and D. K. Nordstrom (2001) *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance*, Mineralogical Society of America.
- Caravelli, A.H., Contreras, E.M. and Zaritzky, N.E. (2010) Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges. *Journal of Hazardous materials* 177(1-3), 199-208.
- Davis, M. (2007) *Water and Wastewater Engineering*, McGraw Hill.
- Farrell, J. and Chaudhary, B.K. (2013) Understanding Arsenate Reaction Kinetics with Ferric Hydroxides. *Environmental Science & Technology* 47(15), 8342-8347.
- Gabelich, C.J., Chen, W.R., Yun, T.I., Coffey, B.M. and Suffet, I.H. (2005) The role of dissolved aluminum in silica chemistry for membrane processes. *Desalination* 180(1-3), 307-319.
- Gabelich, C.J., Ishida, K.P., Gerringer, F.W., Evangelista, R., Kalyan, M. and Suffet, I.H. (2006) Control of residual aluminum from conventional treatment to improve reverse osmosis performance. *Desalination* 190(1-3), 147-160.
- Gabelich, C.J., Williams, M.D., Rahardianto, A., Franklin, J.C. and Cohen, Y. (2007) High-recovery reverse osmosis desalination using intermediate chemical demineralization. *Journal of Membrane Science* 301(1-2), 131-141.
- Gabelich, C.J., Xu, P. and Cohen, Y. (2010) Concentrate Treatment for Inland Desalting. *Sustainable Water for the Future: Water Recycling Versus Desalination* 2, 295-326.
- Gerrity, D., Pecson, B., Trussell, R.S. and Trussell, R.R. (2013) Potable reuse treatment trains throughout the world. *Journal of Water Supply: Research and Technology—AQUA* 62(6), 321.
- Greinert, J., Bollwerk, S.M., Derkachev, A., Bohrmann, G. and Suess, E. (2002) Massive barite deposits and carbonate mineralization in the Derugin Basin, Sea of Okhotsk: precipitation processes at cold seep sites. *Earth and Planetary Science Letters* 203(1), 165-180.
- Griffith, E.M. and Paytan, A. (2012) Barite in the ocean - occurrence, geochemistry and palaeoceanographic applications. *Sedimentology* 59(6), 1817-1835.

Hein, J.R., Stamatakis, M.G. and Dowling, J.S. (2000) Trace metal-rich Quaternary hydrothermal manganese oxide and barite deposit, Milos Island, Greece. *Transactions of the Institution of Mining and Metallurgy Section B-Applied Earth Science* 109, B67-B76.

J. Garside, O.S. (1992) *Precipitation: Basic Principles and Industrial Applications*, Oxford, Oxford [England] ; Boston : Butterworth-Heinemann.

Jain, A., Raven, K.P. and Loeppert, R.H. (1999) Arsenite and Arsenate Adsorption on Ferrihydrite: Surface Charge Reduction and Net OH⁻ Release Stoichiometry. *Environmental Science & Technology* 33(8), 1179-1184.

Juby, G.J.G., Schutte, C.F. and vanLeeuwen, J. (1996) Desalination of calcium sulphate scaling mine water: Design and operation of the SPARRO process. *Water Sa* 22(2), 161-172.

Juby, G.J.G., Zacheis, A., Shih, W., Ravishanker, P., Mortazavi, B. and Nusser, M.D. (2008) Evaluation and Selection of Available Processes for a Zero-Liquid Discharge System for the Perris, California, Ground Water Basin, U.S. Bureau of Reclamation, Denver, Colorado.

Kim, M.M., Au, J., Rahardianto, A., Glater, J., Cohen, Y., Geringer, F.W. and Gabelich, C.J. (2009) Impact of Conventional Water Treatment Coagulants on Mineral Scaling in RO Desalting of Brackish Water. *Industrial & Engineering Chemistry Research* 48(6), 3126-3135.

Liao, M.Y. and Randtke, S.J. (1986) Predicting The Removal of Soluble Organic Contaminants by Lime Softening. *Water Research* 20(1), 27-35.

Mahvi, A.H., Shafiee, F. and Naddafi, K. (2005) Feasibility study of crystallization process for water softening in a pellet reactor. *International Journal of Environmental Science & Technology* 1(4), 301-304.

Malaeb, L. and Ayoub, G.M. (2011) Reverse osmosis technology for water treatment: State of the art review. *Desalination* 267(1), 1-8.

Malmrose, P., Lozier, J., Mickley, M., Reiss, R., Russell, J., Schaefer, J., Sethi, S., Manuszak, J., Bergman, R., Atasi, K.Z. and Management, A.M.R. (2004) Committee report: Current perspectives on residuals management for desalting membranes. *Journal American Water Works Association* 96(12), 73-87.

Naka, K., Huang, S.C. and Chujo, Y. (2006) Formation of stable vaterite with poly(acrylic acid) by the delayed addition method. *Langmuir* 22(18), 7760-7767.

Nicot, J.P. and Chowdhury, A.H. (2005) Disposal of brackish water concentrate into depleted oil and gas fields: a Texas study. *Desalination* 181(1-3), 61-74.

Oren, Y., Korngold, E., Daltrophe, N., Messalem, R., Volkman, Y., Aronov, L., Weismann, M., Bouriakov, N., Glueckstern, P. and Gilron, J. (2010) Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach. *Desalination* 261(3), 321-330.

Parkhurst, D.L., and Appelo, C.A.J. (2013) Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods.

Perez-Gonzalez, A., Urriaga, A.M., Ibanez, R. and Ortiz, I. (2012) State of the art and review on the treatment technologies of water reverse osmosis concentrates. *Water Research* 46(2), 267-283.

Rahardianto, A., Gao, J.B., Gabelich, C.J., Williams, M.D. and Cohen, Y. (2007) High recovery membrane desalting of low-salinity brackish water: Integration of accelerated precipitation softening with membrane RO. *Journal of Membrane Science* 289(1-2), 123-137.

Rahardianto, A., McCool, B.C. and Cohen, Y. (2010) Accelerated desupersaturation of reverse osmosis concentrate by chemically-enhanced seeded precipitation. *Desalination* 264(3), 256-267.

S. Sethi, A.Z., G. Juby (2005) State-of-science and emerging and promising technologies for brine disposal and minimization for reverse osmosis desalination.

- Service, R.F. (2006) Desalination freshens up. *Science* 313(5790), 1088-1090.
- Shen, D., Fu, G.M., Al-Saiari, H., Kan, A.T. and Tomson, M.B. (2009) Barite Dissolution/Precipitation Kinetics in Porous Media and in the Presence and Absence of a Common Scale Inhibitor. *Spe Journal* 14(3), 462-471.
- Sluys, J.T.M., Verdoes, D. and Hanemaaijer, J.H. (1996) Water treatment in a Membrane-Assisted Crystallizer (MAC). *Desalination* 104(1-2), 135-139.
- Subramani, A., Cryer, E., Liu, L., Lehman, S., Ning, R.Y. and Jacangelo, J.G. (2012) Impact of intermediate concentrate softening on feed water recovery of reverse osmosis process during treatment of mining contaminated groundwater. *Separation and Purification Technology* 88, 138-145.
- Subramani, A. and Jacangelo, J.G. (2014) Treatment technologies for reverse osmosis concentrate volume minimization: A review. *Separation and Purification Technology* 122, 472-489.
- W. Shih, B.Y., M. Marshall, D. DeMichelle (2013) Chino II desalter concentrate management via innovative byproduct resale and treatment, American Membrane Technology Association (AMTA)/American Water Works Association (AWWA), San Antonio, Texas.
- Yang, Q.F., Lisitsin, D., Liu, Y.Q., David, H. and Semiat, R. (2007) Desupersaturation of RO concentrates by addition of coagulant and surfactant. *Journal of Chemical Engineering of Japan* 40(9), 730-735.
- Yang, Q.F., Liu, Y.Q., David, H. and Semiat, R. (2008a) Scaling salt removal by addition of inorganic particles. *Journal of Chemical Engineering of Japan* 41(1), 6-12.
- Yang, Q.F., Liu, Y.Q., Hasson, D. and Semiat, R. (2008b) Removal of CaCO₃ scaling salt from RO concentrates by air-blow and inorganic inducers. *Journal of Chemical Engineering of Japan* 41(1), 13-20.