CLEMSON UNIVERSITY, DEPT. OF ENVIRONMENTAL ENGINEERING AND
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DISSOLVED CARBON DIOXIDE FOR SCALE REMOVAL IN REVERSE OSMOSIS

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Abstract

Membrane fouling is a major operational issue in reverse osmosis desalination plants. In particular, plants treating brackish groundwater can encounter troublesome inorganic scales. A novel cleaning method is proposed to remove inorganic scales from fouled RO membranes using dissolved CO_2. As CO_2 molecules encounter membrane foulants, the surfaces serve as nucleation sites for small bubbles to form and shear off foulants. Dissolved CO_2 solutions were prepared by bubbling CO_2 gas into water held in a pressure vessel. Gas dissolution was confirmed by enhanced exit velocities for water containing CO_2, due to the increase in volume from exsolution, when compared to water containing less soluble N_2.

A dissolved CO_2 solution was effective in removing scale from RO membranes through bubble nucleation. Membranes scaled with $CaCO_3$ were cleaned for 10 minutes with a once-through dissolved CO_2 solution, achieving an average 80% flux recovery. Controls were performed with other cleaning regimes to isolate effects from pH and air scouring present in CO_2 cleaning. An HCl solution at pH 3 provided an average flux recovery of 79% after circulating through the system for 30 minutes, while an HCl solution at pH 4 only gave an average 20% flux recovery. Trials using N_2 gas in place of CO_2 only produced a 6% flux recovery on average. Lowering the pH of the N_2 solution to pH 4 with HCl boosted cleaning slightly to an average 8% flux recovery. Thus, the low pH of the CO_2 solution at pH 4.5 and bulk phase air scouring are minor mechanisms in scale removal. In addition, membranes scaled with calcium silicates were not cleaned using dissolved CO_2 – only NaOH at pH 12 plus sodium dodecyl sulfate provided significant cleaning. Future work should be done with additional scale types to narrow in on the mechanism for cleaning by dissolved CO_2.

Acknowledgements

I would like to acknowledge the continued support of the staff in the Environmental Engineering and Earth Sciences department at Clemson, without whom this research would have been much more difficult. I would like to say thanks to my research group members Ying Sun and Pooja Mahajan for training me on the equipment and to all my other group members for providing assistance and feedback during the course of this project. I would also like to thank Meric Selbes for his assistance in adjusting lab equipment and willingness to answer questions.

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1. Background: Brackish Water Desalination using Reverse Osmosis

Reverse osmosis (RO) is commonly used for the production of drinking water. The process involves passing water over a selectively permeable membrane at high pressure; the smallest molecules pass through the fastest and others more slowly. RO membranes are the most selective – typically only monovalent ions are measurable in the product water (American Water Works Association 2007). Brackish water desalination makes larger use of RO than seawater desalination, for which multistage flash distillation is the most common. Considering all desalinated waters, RO makes up about 44% (Wangnick 2002). Compared to seawater, brackish groundwater tends to contain more calcium, carbonate, and sulfate ions, and less sodium and chloride. These molecules are prone to precipitation when concentrations exceed solubility limits and membrane fouling from these precipitates on the membrane surface can be a major problem (Brady et al. 2005; Greenlee et al. 2009).

Brackish water requires lower applied pressure than seawater and can be done with low pressure RO membranes or nanofiltration membranes, while seawater requires high pressure membranes (Crittenden et al. 2005). High pressure RO membranes are typically considered to be nonporous while low pressure RO membranes (pores less than 0.5 nm) and nanofiltration membranes (pores from 0.5 to 2 nm) are considered porous (Van Der Bruggen et al. 2004).

1.1 Issues with Inland Groundwater RO

Groundwater encounters different obstacles compared to seawater. Where fouling from organics and particulates is more common in seawater desalination, the majority of groundwater RO plants have problems with fouling from inorganic scales. For example, a survey of brackish water desalination plants in Texas found that about a third noted inorganic scaling as a major fouling issue, the most of any foulant (Shirazi and Arroyo 2011). In addition, inland desalination has the added difficulty of limited options for concentrate disposal. Some practices, such as discharging to municipal sewers or saline ditches, put strains on other systems. Others are costly and impose an economical hindrance on desalination. (Brady et al. 2005; Greenlee et al. 2009)

1.1.1 Scaling

Scaling refers to the precipitation of salts onto the membrane surface which results in reduced permeate flow. Polyvalent ions in the source water, though below solubility limits, can precipitate onto the membrane surface due to enhanced concentration of solutes very near the membrane surface, a phenomenon known as concentration polarization. Scales fall under the categories of alkaline, non-alkaline, and silica based, with non-alkaline scales more difficult to remove than alkaline scales. The most common non-alkaline scale is calcium sulfate, and is typically prevented by maintaining unsaturated conditions. Another common scalant, calcium phosphate, is most effectively treated by acidification of the feedwater. Silica scale can be prevented by either pre-treatment or acidification. Silica scaling can be a limiting factor for brackish water RO since, unlike calcium carbonate and sulfate scale, antiscalants are not effective at preventing silica scales (Antony et al. 2011; Brady et al. 2005; Fritzmann et al. 2007;

Greenlee et al. 2009). The review by Antony et al. (2011) on scaling in high pressure membrane systems is summarized in Table 1 below.

Table 1: Summary of common scales in high pressure membrane systems and their formation and treatment (Antony et al. 2011)

Name	Formula	Scale Type	Formation Notes	Prevention/Removal Techniques
Calcium carbonate	$CaCO_3$	Alkaline	Common, but predictable and controllable.	Flushing procedures during shutdown
Calcium sulfate	$CaSO_4 * xH_2O$	Non-alkaline	Common	Pretreatment to bring concentration below saturation
Calcium phosphate	Ca_3PO_4	Non-alkaline	Problematic in wastewater streams	pH adjustment to 6.4 (no suitable antiscalants), pretreatment to reduce PO_4/Ca/Al/Fe/Fl, or dispersants if present as nanoparticles
Barium sulfate	$BaSO_4$	Non-alkaline	Rarely seen in RO scaling	Antiscalants effective
Strontium sulfate	$SrSO_4$	Non-alkaline	Rarely seen in RO scaling	Antiscalants effective
Silicates	$x*(SiO_2^-)_n$	Silicate	Below neutral pH, scales as a colloid. Above neutral pH, forms silicates when metals are present.	Pretreatment to lower metal concentrations, pretreatment to remove colloidal silica, and acidification of feed water

1.1.2 Concentrate Disposal

When disposal to a very large body of water, such as the ocean, is unavailable, other means of concentrate disposal are necessary. Inland desalination plants have few options for treatment and disposal of their brine streams. One method that avoids loading of surface waters is deep well injection wherein the brine is pumped underground. This method was chosen by the EPA as the most environmentally friendly – the EPA has also set up regulations for all underground disposal wells (Clark, Bonura, Van Voorhees 2005; Environmental Protection Agency 2012). However, the costs of deep wells may be limiting. Zero Liquid Discharge (ZLD) and similar ideas intend to maximize recovery and reduce the volume of waste which reduces the costs and impacts of disposal (Brady et al. 2005; Fritzmann et al. 2007; Greenlee et al. 2009; Lawler and Texas Water Development Board 2010).

This study does not focus on concentrate management but it is an important component to keep in mind when considering the proposed CO_2 scaling treatment.

1.2 Scale Treatment Techniques

1.2.1 Scale Prevention

Prevention techniques typically include feed water pretreatment or addition of antiscalants to the feed water. Often, scale prevention is the preferred solution since a fouled membrane can be very difficult to clean, whether it has membrane scaling or viscous particulate fouling. However, the cost of treating the entire volume of source water can also be limiting. For brackish water sources, surface waters tend to foul more easily than groundwater and pretreatment is often performed. Additionally, if biofouling is known to be a problem, disinfection using non-chlorine oxidants can be used. One last aspect that can be evaluated is changes in operation; for example changes in flow rate have been shown to be effective in mitigating scale in some cases (Antony et al. 2011; Greenlee et al. 2009). There are additionally many novel designs for scaling prevention; air sparging is covered below as it relates best to the proposed research. Other designs include designs to promote flow vortices, such as rotating the membrane module or using helical flow spacers, and pressure pulsing, a method which has been shown to be effective in RO applications (Al-Bastaki and Abbas 2001).

1.2.1.1 Pre-treatment

Pre-treatment is a useful method when the problematic compounds can be removed and is conventionally performed with coagulation/flocculation followed by granular media filtration and/or cartridge filtration. Acid is added before coagulation to solubilize existing precipitates, which reduces the load on the pretreatment system. Feedwater acidification is only useful for some scales; calcium carbonate is easily controlled through pH adjustment but other scales, such as calcium sulfate and barium sulfate, have weaker pH dependence and therefore are not controlled as effectively with acid feeding (Rahardianto et al. 2006).

One issue with pretreatment, aside from costs, is that any additions, including chemical coagulants and antiscalants, have the potential to interact with other molecules in the source water and cause scaling problems. This is true in particular with silica since aluminosilicates can form from the alum added as a coagulant (Antony et al. 2011; Greenlee et al. 2009).

1.2.1.2 Antiscalants

Antiscalants are typically polyelectrolytes with various functional groups to target different scaling problems. They function to disrupt crystallization and may do so through several mechanisms: as a crystal modifier to produce a less adherent precipitate, attaching to precipitates to prevent crystal growth, increasing the effective solubility limit, or acting as a chelating agent to form soluble complexes. The choice and dosage of antiscalants is highly dependant on the source water characteristics. Additionally, there are some drawbacks to antiscalant use, especially with improper dosing or feed water characterization, since antiscalants can act as foulants or enhance fouling in a number of situations (Antony et al. 2011).

The summary in **Error! Reference source not found.** shows barium and sulfate and strontium sulfate as very responsive to antiscalants while the others have other preferred prevention methods (Antony et al. 2011). The three main categories of antiscalants include polyphonates and phosphonates – antiscalants for prevention of metal scales such as calcium – and the more broadly applied polyphosphates. Another example of an antiscalant is the addition of ferrous iron for calcite inhibition (MacAdam and Parsons 2004). Silica is a notable exception as a prevalent scalant without suitable antiscalants due to highly variable surface characteristics under different formation conditions (Koo, Lee, Sheikholeslami 2001).

1.2.1.3 Operational Control

There are several methods of preventing scaling by avoiding conditions that enhance scaling. Limiting product recovery is one method that reduces scaling by reducing the solute concentration at the membrane wall. Another method alternates the location of concentrated feed water by reversing the flow through the system from time to time. A third method is to perform demineralization in-between two stages of an RO plant with the first stage operating under limited recovery. A fourth method is to use centrifugal force to reduce concentration polarization by rotating the membrane module itself

(Antony et al. 2011). Silica is an example of a scale that is mitigated through operational control; plants with silica scaling issues aim to operate under a critical flux level (Lisitsin, Hasson, Semiat 2005).

1.2.1.4 Air Sparging

Air sparging is touted less as a fouling prevention method and rather as a flux enhancement procedure. There are several mechanisms behind this phenomenon: disruption of the mass boundary layer or concentration polarization layer, an increase in the effective system pressure or crossflow velocity, and alteration of the cake layer in microfiltration (Cui, Chang, Fane 2003). The effect of air sparging depends highly on the bubble characteristics – it was found that a bubble diameter of approximately 60% of the channel width was ideal (Willems et al. 2009). It should be noted that this is primarily done with micro- and ultrafiltration membranes where air sparging has been shown to have significant impacts. However, studies are being done to see if similar benefits are seen in nonporous nanofiltration and RO membranes. Ducom et al. (2002) performed several experiments using vertical, flat sheet, nanfiltration membrane and found mixed results for co-current air sparging based on the foulant to be prevented. Oil-in-water emulsions and solid clay suspensions, which foul by particle deposition, fouled less air sparging; however, air sparging was not effective at increasing flux for non-scaling salt solutions where osmotic pressure is the limiting factor. It is noted that since air sparging is expected to affect the concentration polarization layer, air sparging method may work in situations where this is the driving factor behind scale formation (Ducom, Puech, Cabassud 2002; Ducom, Matamoros, Cabassud 2002; Ducom and Cabassud 2003).

1.2.2 Scale Removal

Membrane plants often perform cleaning after a certain level of flux decline or pressure increase is reached. Different from other filtration systems that call for a cleaning or backwashing protocol after a set time, RO systems can go for months and years before the flux necessitates a cleaning (Shirazi and Arroyo 2011). Guidelines for operation call for cleaning if there is a 10% reduction in permeate flow, 15% increase in pressure drop, or salt rejection by 10% within 2 days of plant start-up (Fritzmann et al. 2007). Additionally, common flushing methods such as backwash and reverse flow are not possible due to the nonporous nature of RO membranes. For membranes fouled by inorganic scale cleaning typically consists of acidic or basic chemical solutions and sometimes both are used (Greenlee et al. 2009). Cleaning procedures depend on the specific needs for each plant and thus there is no universal protocol.

1.2.2.1 Chemical Cleaning

In established RO systems with inorganic scaling problems, cleaning is typically carried out with prepared chemical solutions, often produced by adding chemical stocks to permeate water. Frtizmann et al. (2007) looks at the instructions provided by DOW FILMTEC for chemical cleaning. A separate path for flow is used so that the chemical solutions are cycled after draining any remaining feed water/concentrate. The solution is cycled at low pressure and high flow rate, thus flushing out any foulants, and often monitored for both pH and temperature. Membranes can also be soaked in the cleaning solution for up to 15 hours. Finally, all cleaning solution is flushed before plant operation begins again.

The type of chemical and pH used depends on the foulant and degree of fouling. Additionally, chemicals can be combined or used in series for better cleaning. Cleaners fall into several categories, including acids, bases, metal chelating agents, surfactants, enzymes, and disinfectants (Ang, Lee, Elimelech 2006; Mohammadi, Madaeni, Moghadam 2003). Some common cleaners include hydrochloric acid, phosphoric acid, sulfuric acid, sodium hydroxide, the chelator EDTA, and the surfactant sodium-lauryl-sulphate. DOW recommends acid cleaning for inorganic salts, but recommends caustic for silica scales (Fritzmann et al. 2007).

In general, acids are able to remove inorganic scales through either hydrolysis or solubilization, while alkalines and surfactants are required to remove organic foulants. EDTA is used in experiments as a control for maximum foulant removal. Several studies observed cleaning efficiencies on RO membranes for various membrane foulants:

- A membrane fouled by a natural water source had minimal cleaning with acids, moderate cleaning with caustics, and EDTA combined with caustic and surfactants were able to fully clean the membrane (Madaeni, Mohamamdi, Moghadam 2001).
- A membrane fouled with wastewater was best cleaned using a two-stage process beginning with surfactant and caustic followed by an acidic solution. This served to remove both organic and inorganic material from the membranes (Madaeni and Samieirad 2010).
- In cleaning a membrane fouled with sodium alginate and natural organic matter (NOM), an exploration of dosing and pH found that EDTA combined with SDS worked well and could be optimized through parameter control, but cleaning with NaOH was not effective and could not be optimized (Ang, Lee, Elimelech 2006).

- Commercial membrane cleaners were used to remove silica fouling. The generic cleaner for inorganic foulant gave moderate flux regeneration, while the cleaner specifically for silica and other inorganic foulants was successful at full regeneration given sufficient dosage. It should be noted that the latter cleaner has a pH of 4 (Koo, Lee, Sheikholeslami 2001).

1.2.2.2 Gas Sparging

A method known as air sparging or two-phase gas-liquid flow was mentioned above as a technique used for flux enhancement, primarily in micro- and ultrafiltration membranes. The same procedures can also be used in cleaning only scenarios. Some techniques are patented, such as Airflush, where two-phase feed side flushing is used intermittently, or gas blow back, where air is forced through the membrane from the permeate side. Gas sparging has also been shown as an effective add on to conventional backwashing technique (Cui, Chang, Fane 2003).

Nanofiltration and reverse osmosis membranes cannot be backwashed like micro- and ultrafiltration membranes due to their nonporous nature. However, feed side gas sparging is possible and has been found to be useful in removing biofilms. An examination of air/water cleaning effects on a vertically oriented nanofiltration flat sheet membrane found a daily cleaning routine of less than 5 minutes was sufficient to remove biofilms, with enhanced biofouling control when used with copper sulfate as a biocide (Cornelissen et al. 2007). In micro- and ultrafiltration applications, vertical membrane orientations produced the best results, whether for hollow fiber or flat sheet membranes (Cui, Chang, Fane 2003).

One very novel approach to membrane cleaning with a gas flow is the idea of forming gas bubbles at the membrane itself, thus providing shear stress at exactly the point of contact. To accomplish this, the gas must be fairly soluble in water, such as is the case for carbon dioxide. One study termed this cleaning method as CO_2 nucleation and successfully used it to remove biofilms from a low-pressure RO membrane and completely restoring the original flux (Ngene et al. 2010). This mechanism for cleaning is tested in this study to examine its use for the removal of inorganic foulants.

2. Proposal: Carbon Dioxide to Treat Scaling

Carbon dioxide is proposed as a green alternative to conventional antiscalants and chemical cleaning solutions. This study evaluates its effectiveness in removing certain inorganic scales from fouled RO membranes. With proven effectiveness, this can lead to further development of a non-toxic cleaning method and/or scale prevention method for RO membranes. If used in conjunction with underground well injection for brine disposal, adding CO_2 to the RO process could even have an added benefit of CO_2 sequestration. On goal in this study is to examine the feasibility of such a combined system – a hypothetical schematic is provided in Figure 2.

2.1 Compatibility with RO

CO_2 does not interact much with a membrane – it will not reduce solute rejection but neither will it be rejected by the membrane. As small, uncharged particles, dissolved gases can easily permeate the membrane. A feed with dissolved CO_2 will produce permeate and concentrate with the same concentration of CO_2 (Milstead, Riedinger, Lonsdale 1971). Charged carbonate ions, on the other hand, are easily rejected by the membrane, which leaves permeate with virtually no alkalinity (Crittenden et al. 2005). It is not clear how well carbonic acid permeates or is rejected by RO membranes since it is also an uncharged molecule, however, the formation of carbonic acid from CO_2 (Equation 1) is slow relative to its ionization to bicarbonate (Equation 2) thus it is present in relatively small concentrations – the concentration of carbonic acid at equilibrium is approximately 1/1000th the concentration of dissolved CO_2 (Butler 1991). Due to the high permeation of CO_2 and high rejection of HCO_3^- and CO_3^{2-} , equilibration of the permeate, which releases H^+ as H_2CO_3 dissociates to HCO_3^-, plays a large role in determining the final pH. A diagram of carbonate speciation is provided for reference (Figure 1).

Equation 1: Formation of carbonic acid from carbon dioxide in water.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Equation 2: Ionization of aqueous carbonic acid to bicarbonate and a proton.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

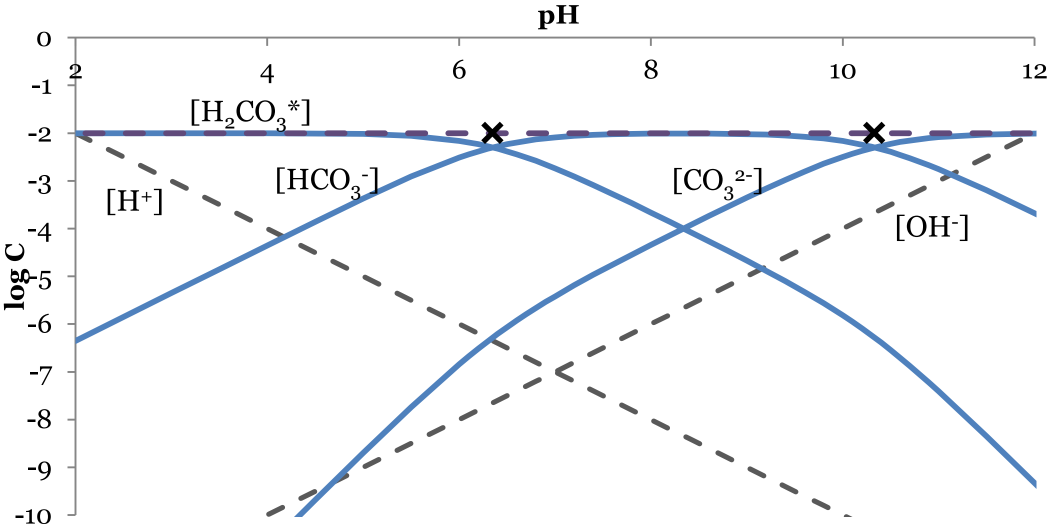


Figure 1: LogC-pH diagram of carbonate chemistry. In this example, the total carbonate concentration is 0.01 M. System points for pKa = 6.35 and pKa = 10.33 are shown as X's.

Many groundwaters have high concentrations of CO_2 – groundwater in Israel has reported concentrations up to 100 mg/L of CO_2 due to a high level of total carbonate species (Oren et al. 2012). The amount of gas in the feed water directly affects the permeate quality due to carbonate equlibration. Some plants may choose to degas or deaerate their feed during pre-treatment using an air-stripping tower. Plants can also degas during post-treatment, since dissolved gas does not affect membrane performance. Post-treatment is required to reintroduce minerals for taste and alkalinity for pH control; brackish feed can be added to the permeate for this purpose with caustic soda added to raise the pH (Greenlee et al. 2009). Post-treatment that involves degassing includes stripping of excess CO_2, which can cause corrosion, and raising the pH to drinking water standards (United States. Dept. of the Army 1986). Oppositely, some systems add CO_2 during post-treatment in order to achieve recarbonation and/or remineralization through added unit processes such as lime contactors (Withers 2005). In a novel approach, one study achieved post-treatment CO_2 dosing through feed acidification to drive carbonate species to become dissolved gas (Oren et al. 2012).

2.1.1 Saturated CO_2 Solution

In contrast to naturally present carbon dioxide, artificially introducing high concentrations of CO_2 will result in chemical changes to the solution, such as decreased pH. Part of the effectiveness of RO membranes comes from charged interactions that hinder the transport of ions while having no impact on uncharged molecules. Changes in pH alters the surface charge of the membrane which can affect the level of rejection achieved (Childress and Elimelech 1996). For composite polyamide membranes, the rejection stays constant through a broad pH range, however a pH above 8.5 or a pH near the membranes isoelectric point (often around 4-5) can cause a decline in rejection

(Cadotte et al. 1980). The pH of a solution can also affect RO performance by changing the chemical composition of the feedwater; a study on defluoridation using RO found a marked decrease in rejection below a pH of 6.5 attributed to the formation of hydrofluoric acid which has a higher solubility in the membrane (Arora et al. 2004).

2.2 Other Considerations

2.2.1 Carbon Sequestration through Deep Well Injection

Where surface water brine disposal is unavailable, deep well injection is an alternative given to options such as evaporation ponds, infiltration basins, and irrigation and it has the environmental benefit of not increasing the salt load of surface waters (Clark, Bonura, Van Voorhees 2005; Skehan and Kwiatkowski 2000). About 10% of RO plants in the U.S. use deep wells for disposal, primarily in the state of Florida (Crittenden et al. 2005).

Deep well injection is also used for a variety of other purposes, such as industrial and municipal waste streams and for wastes in the oil and gas industry, and is regulated by the EPA. A new well classification is emerging for long term geological storage of carbon, albeit typically for injection of CO_2 in its supercritical phase (Brady et al. 2005; Environmental Protection Agency 2012). It is conceivable that disposal of CO_2-saturated brine in underground geological formations could have the benefit of carbon sequestration. Experimental results indicate that CO_2 in water may be more stable than CO_2 injected in a supercritical form, though may also cause unintended issues such as rock dissolution or plugging of the rock formation (Canal et al. 2012; Saripalli, Sharma, Bryant 2000). A potential configuration for RO combined with CO_2 sequestration is sketched in Figure 2.

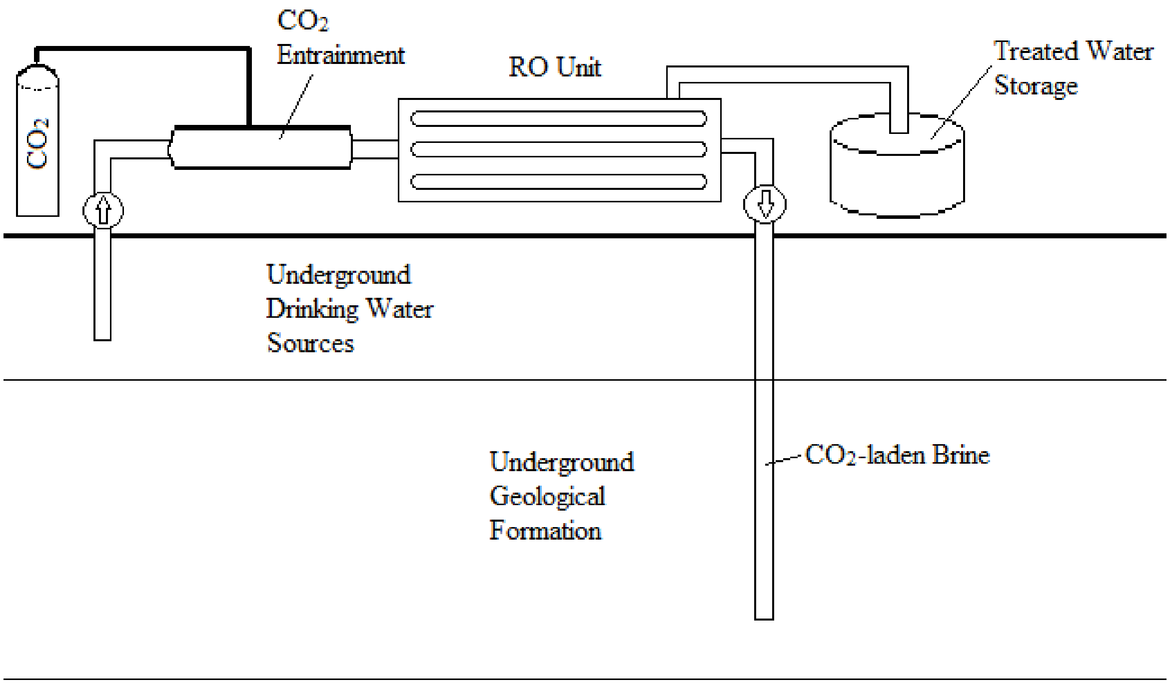


Figure 2: Sketch of a possible configuration for a brackish groundwater reverse osmosis unit with CO_2-entrained feedwater.

2.3 Bench-scale Work

Fundamental examination of dissolved CO_2 in an RO system provides information regarding the feasibility and/or practicality of this application. To determine efficacy, a solution of CO_2 dissolved in water is characterized and used to clean RO membranes scaled with various inorganic foulants. Comparison of flux recovery with other cleaning methods allows for an evaluation of dissolved CO_2 as well as a determination of the cleaning mechanism. The work is divided into two objectives.

Objective 1. Develop methods for bench-scale carbonation and testing of dissolved CO_2 solutions. Characterize differences between concentrate and permeate flows including visual differences and impacts on flux and rejection.

Objective 2. Develop method for bench-scale membrane scaling. Determine flux recovery after cleaning scaled membranes with dissolved CO_2. Compare with flux recoveries achieved through other cleaning methods.

Hypothesis. If flux is recovered after cleaning with dissolved CO_2, this method is an effective cleaning regime. Differing levels of scale removal for various scale types indicate mechanistic differences in cleaning. Comparison of dissolved CO_2 cleaning to other cleaning methods narrows in on the cleaning mechanism.

3. Materials and Methods

3.1 Bench-Scale Apparatus

The bench-scale test setup (Figure 3) was adapted from a system used previously (Ladner et al. 2010). A plunger pump cycled water through a GE Osmonics SEPA II membrane cell which held the RO membrane coupon. The concentrate flow from the membrane cell was diverted either to the feed tank during for recycle or to waste. Permeate flow passed through a holding tank for a conductivity reading and then dispensed to a beaker on top of a balance for continuous mass readings. A LabView program was used to monitor data continuously and convert mass readings into flux readings. A data acquisition unit (DAQ) was used to input data into LabView from the balance, pressure gauge before the needle valve, and two conductivity probes, one to measure feed concentration and one for permeate concentration. Measurement of permeate mass every 100 seconds, along with a known membrane area, was used for calculation of permeate flux. The difference in conductivity between the feed and permeate was used to calculate rejection.

Equation 3: Flux calculation from change in permeate mass, m_w, over change in time, t. Converted to units of lmh using density of water, ρ_w, and known membrane area, A_m.

$$J = \frac{\frac{\Delta m_w}{\rho_w}}{A_m \Delta t}$$

Equation 4: Calculation of rejection, R, from the conductivity of the permeate, K_p, relative to the conductivity of the feed, K_f.

$$R = \left(1 - \frac{K_p}{K_f}\right) \cdot 100\%$$

A vertically installed cylindrical pressure vessel was outfitted with ball valves for optional flow patterns: bypassing the vessel, only into the vessel, only out of the vessel, or through the vessel. The total height of the pressure vessel was 7 feet with a total volume of 9.7 liters. The port for flow out of the vessel was located in the bottom endcap; the port for flow into the vessel was located four inches above the bottom. Above the water flows was a port at 12 inches above the bottom for gas flows into the pressure vessel from a gas cylinder.

The LabView program also provided an interface for both manual and automated control of the pump speed and valve actuator. The needle valve opening on the membrane concentrate line was controlled by a voltage instruction sent to an attached actuator.

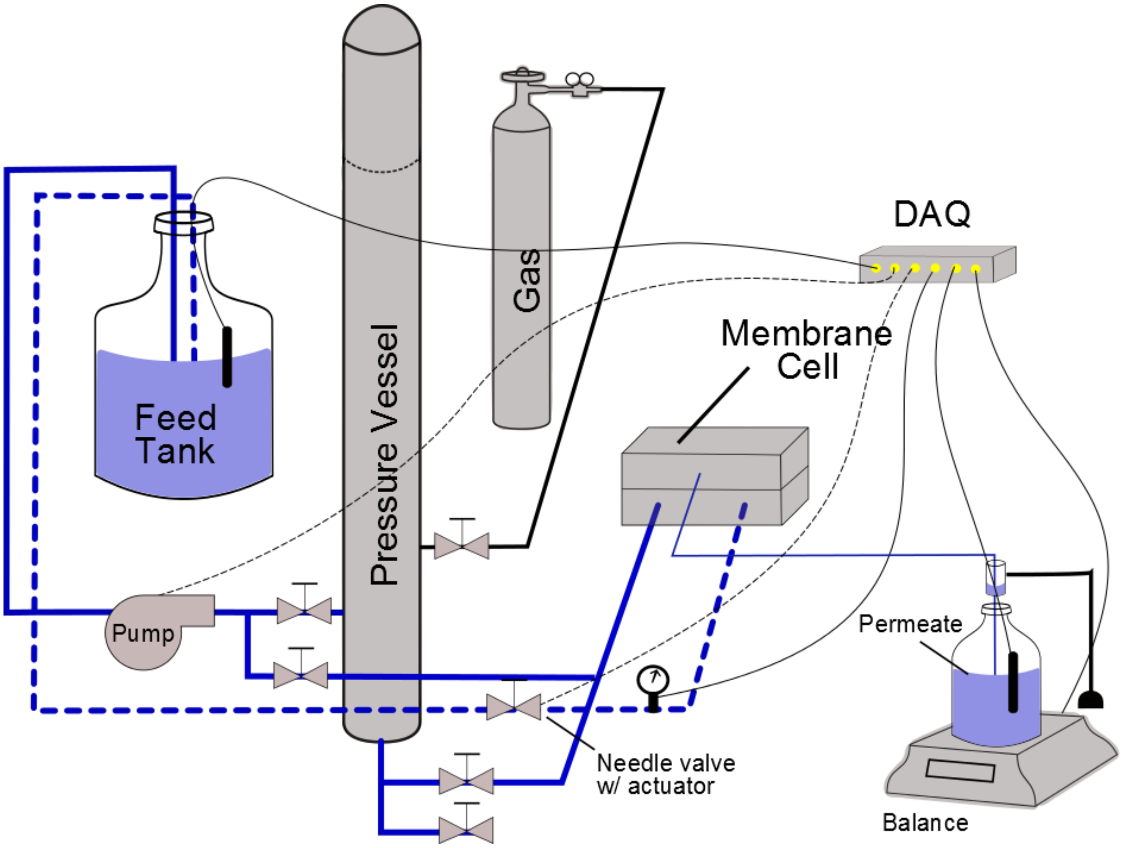


Figure 3: Left-to-right fluid flow in bench-scale apparatus. A series of valves allows for flow either through the pressure vessel or directly to the membrane. From the membrane, flows split into permeate (thin blue line) and concentrate (dotted blue line). The concentrate is returned to the feed tank for continuous operation. In total recycle mode, the permeate is manually returned to the feed tank to maintain feed concentration. Dashed lines from DAQ represent computer control of pump speed and needle valve opening; solid lines represent data input to DAQ from conductivity probes and balance.

3.1.1 RO Membrane

For this work, a CPA2 Hydranautics brackish water membrane was used. The CPA2 membrane has the following characteristics: composite polyamide membrane material, pH range 2-10, 45 °C max. temperature, and 600 psig max. pressure. Membrane coupons were cut from a larger membrane sample and maintained in an aqueous solution of sodium azide. Baseline tests performed on this membrane produced the results in Figure 4. The cross-flow velocity was kept a constant 800 mL/min and the pressure was controlled by the actuator-driven needle valve.

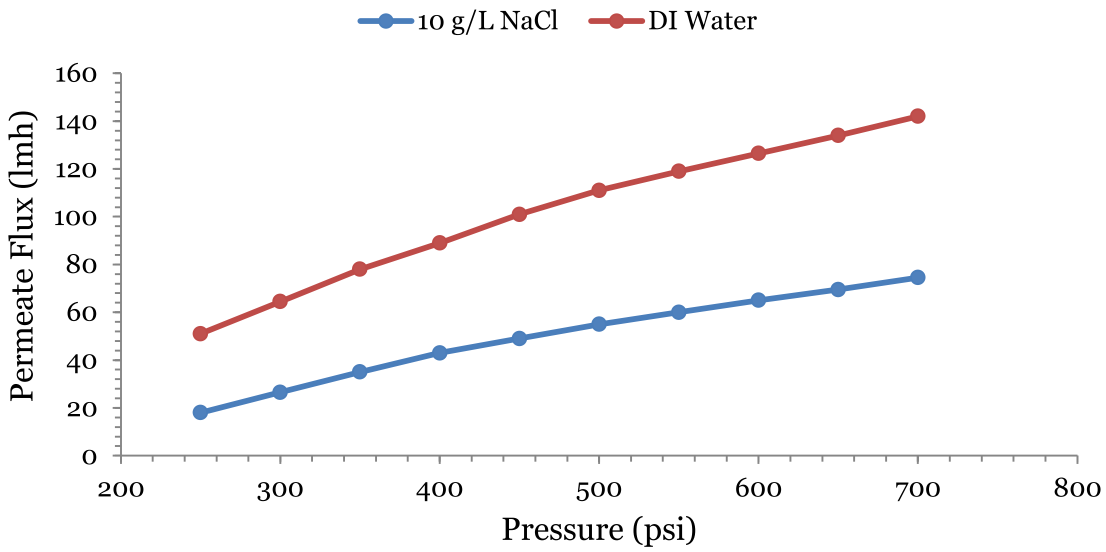


Figure 4: Flux measurements as a function of pressure for DI water and 10 g/L NaCl through the CPA2 membrane. A constant cross-flow velocity of 800 mL/min was used.

3.2 Analytical Methods

Permeate flux, the main parameter of concern, was continuously monitored through the LabView interface. Rejection was also continuously monitored to ensure proper membrane function. To obtain accurate rejection readings, a background ionic content of 10 g/L NaCl was used in all runs since the conductivity from the scaling molecules alone was not significant.

Alkalinity was measured by titration with 0.02 N H_2SO_4 using the indicator bromocreosol for total alkalinity measurement, and pH was measured using an Orion pH meter. During scaling runs, pH was monitored every few hours. For cleaning runs, pH was measured every few minutes and adjustments made if necessary to reach the target pH. The method for measuring carbonation is detailed below.

3.2.1 Carbon Dioxide Quantification

In the carbonated soft drink industry, filled cans are tested for carbonation by capturing escaped gases upon piercing. First, the container is pierced without agitation to release excess gas in the headspace. Then, the container is connected to a gas regulator and shaken to release all dissolved gas. The volume of captured gas is compared to the volume of the sample to determine the degree of entrainment (Steen and Ashurst 2006).

A measurement method following similar principles was used here. During operation of the bench-scale apparatus, all lines exiting the membrane are returned to atmospheric pressure. Thus CO_2 will tend to leave solution. This is particularly true in the concentrate line due to its higher flow rate and more turbulent depressurization. Real time monitoring of gas concentration is done by taking a gas flux to liquid flux ratio of the concentrate flow. This measures any exsolved gas at this point and is a good representation of changes in concentration. For a measurement of total CO_2 over atmospheric concentrations, samples are taken in syringes which are then capped and left to equilibrate overnight. Then, the total volume and the volume of water are recorded to obtain a ratio of gas to liquid. This ratio is added to the previously measured ratio for a total concentration. In the permeate line where there is little gas exsolution, only the syringe measurements are taken.

3.3 Objective 1 – CO_2 Entrainment

The goal of this objective is to develop a method for achieving a high degree of CO_2 entrainment within the context of a reverse osmosis system.

3.3.1 Method 1 – Gas Phase Entrainment

The pressure vessel in the RO setup served as a holding tank for water under a CO_2 headspace. When water is passed through the vessel, it entered at a side port and exited through the bottom port. A third port, above the water entry, was connected to a gas cylinder and used for pressurization.

Solubility and Diffusivity

Transport of CO_2 from a headspace into a liquid is determined by its solubility and diffusivity within that liquid. At the interface, the concentration of CO_2 is governed by the solubility and can be calculated using Henry's Law, shown below for dissolved CO_2 expressed in molar units and CO_2 gas expressed in atmospheres.

Equation 5: Henry's Law for CO_2 in water.

$$[CO_2] = k_H P_{CO2} = \left(0.033 \frac{mol}{L \cdot atm}\right) P_{CO2}$$

The Henry's Law coefficient, k_H, is equal to 0.033 for standard conditions, but the coefficient will vary with pressure, temperature, and pH. Additionally, this coefficient is only valid for dilute solutions. To check whether the brackish solutions used significantly change CO_2 solubility, an empirical correlation is used to calculate solubility based on the amount of dissolved ions. The correlation uses total dissolved solids (TDS) on a weight basis as the correlating measurement. (Enick and Klara 1990)

Equation 6: Correlation between the Henry's Law coefficient in pure water and in briny water as a function of total dissolved solids (TDS) concentration.

$$w_{brine} = w_{pure}(1.0 - 4.89 * 10^{-2}(TDS) + 0.13 * 10^{-2}(TDS)^2 - 0.19 * 10^{-4}(TDS)^3)$$

In Table 2, CO_2 solubility coefficients are calculated using this correlation for three solutions of interest – DI water, typical brackish water concentration of 10 g/L, and typical seawater concentration of 35 g/L. A temperature of 25 °C was used. As evident in Table 2, at the pressures and concentrations of interest, deviation from the standard coefficient is negligible.

Table 2: Solubility of CO_2 in three solutions calculated as a function of TDS at 25 °C using a correlation by Enick and Klara (1990). Calculations made from 0-900 psi since these are in the range relevant to reverse osmosis operation.

Pressure (psig)	C_{eq} (mol/L) 0 g/L	10 g/L	35 g/L
0	0.033	0.033	0.033
100	0.258	0.257	0.257
200	0.482	0.482	0.481
300	0.707	0.706	0.705
400	0.931	0.931	0.930
500	1.156	1.155	1.154
600	1.380	1.380	1.378
700	1.605	1.604	1.602
800	1.830	1.829	1.826
900	2.054	2.053	2.051

Another consideration is the role of CO_2 in the carbonate system. Due to the formation and ionization of H_2CO_3, the standard form of Henry's law is not always applicable. Carroll and Mather have developed models to account for non-linear relationships at high temperatures and pressures. Fortunately, at typical RO operating temperatures, the relationship between pressure and solubility is sufficiently linear (Carroll and Mather 1992).

Beyond the gas-liquid interface, movement of CO_2 is dictated by its diffusivity in the solution. CO_2 has a diffusivity of 1600 $\mu m^2/s$. Figure 5 was generated using unsteady state penetration theory to model the penetration depth of CO_2 in pure water over time (Equation 7). The model shows that diffusion alone is a very slow process since transport of CO_2 has only reached 4 cm past the gas-water interface after 24 hours. The penetration depth depends only on time and not on the interface concentration – with a different interface concentration the amplitude of the curve changes but not its shape. Therefore, regardless of the pressure of CO_2 in the pressure vessel headspace, completely non-agitated diffusion will not produce a significant level of entrainment.

Equation 7: Equation of change for unsteady diffusion in one dimension (Bird, Stewart, Lightfoot 2007). The concentration C at depth x and time t is predicted by the Gaussian error function of the depth over the diffusion length, where *D*ₐ is the diffusivity.

$$C(x,t) = C_{int} \cdot erfc\left(\frac{x}{2\sqrt{\mathcal{D}_a t}}\right)$$

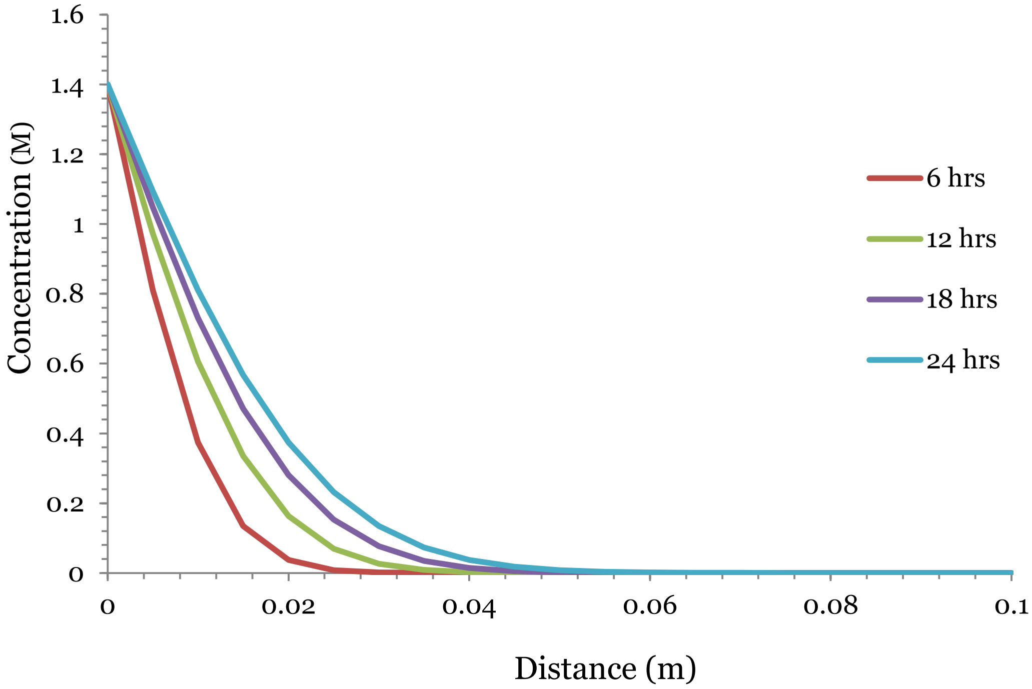


Figure 5: Diffusion distance into pure water with a pure CO_2-filled headspace at a pressure of 600 psi. With 24 hours to equilibrate, the carbon dioxide has only diffused 4 cm below the surface.

Agitated Entrainment

Typical agitated entrainment methods at an industrial level include spraying water into the headspace or mixing with paddles or similar mixers (Wheeler 1973). One bench scale study dissolved CO_2 by first micronizing the CO_2 at a pressure of 0.5 MPa before pressurizing the headspace to 4 MPa (~580 psi), but one week was still required to ensure saturation (Canal et al. 2012).

A common method used in soda production is inline carbonation. This process applies pressurized CO_2, often around 100 psi to produce around 40 psi in the finished product, to a flowing fluid line, often through a diffusing stone or membrane (Steen and Ashurst 2006). This method of entrainment is likely to be very effective, but was discarded due to the high price of inline carbonators. A similar method used in laboratories for introduction of gasses is through a sparge. To mimic a gas sparge, gas is bubbled into the pressure vessel by cracking the valve to the pressurized gas line, which is below the water surface.

3.3.2 Method 2 – Artificial Generation

Carbon dioxide can be generated through chemical reactions as well. One study succeeded in saturating the feedwater by first adding a carbonate species and then adjusting the pH through the addition of acid to shift the dominant species to H_2CO_3 (Oren et al. 2012). While this method is effective for increasing the concentration of CO_2 in the feedwater, it undermines the benefits of this coupling – acidification without toxic chemicals and utilization of waste CO_2 gas for possible sequestration. However, it may be a sufficient method of CO_2 entrainment for experimental purposes in lieu of an apparatus for pressurized carbonation.

3.3.3 Method Development

Both carbonation methods were tested for application to the pressure vessel system and in both continuous and batch modes. First, non-agitated dissolution was tested in a continuous mode. This was done by circulating water through the pressure vessel to the membrane while the pressure vessel on average contained 4 liters of water so that flow through the vessel caused minimal agitation in the water column. Samples taken from the permeate line showed a volumetric gas to liquid ratio, or volumes of CO_2, of approximately 0.07. Samples from the concentrate line had even less measured gas, though it is expected that not all of the gas left solution at that point. Next, a test was performed with agitated dissolution using only 1 liter of water in the pressure vessel so that flowing water would cause a high level of mixing at the gas-water interface. Samples taken from the permeate line in this experiment had a final measurement of 0.14 volumes of CO_2 after almost 8 hours of operation. Figure 6 presents data collected from the continuous entrainment experiments. The initial concentrations measured in the non-agitated experiment are higher than the agitated experiment as expected since gas passed through the water column when filling the pressure vessel during the non-agitated experiment. In the agitated case, the water line is below the gas port and did not receive any effects from bubbling.

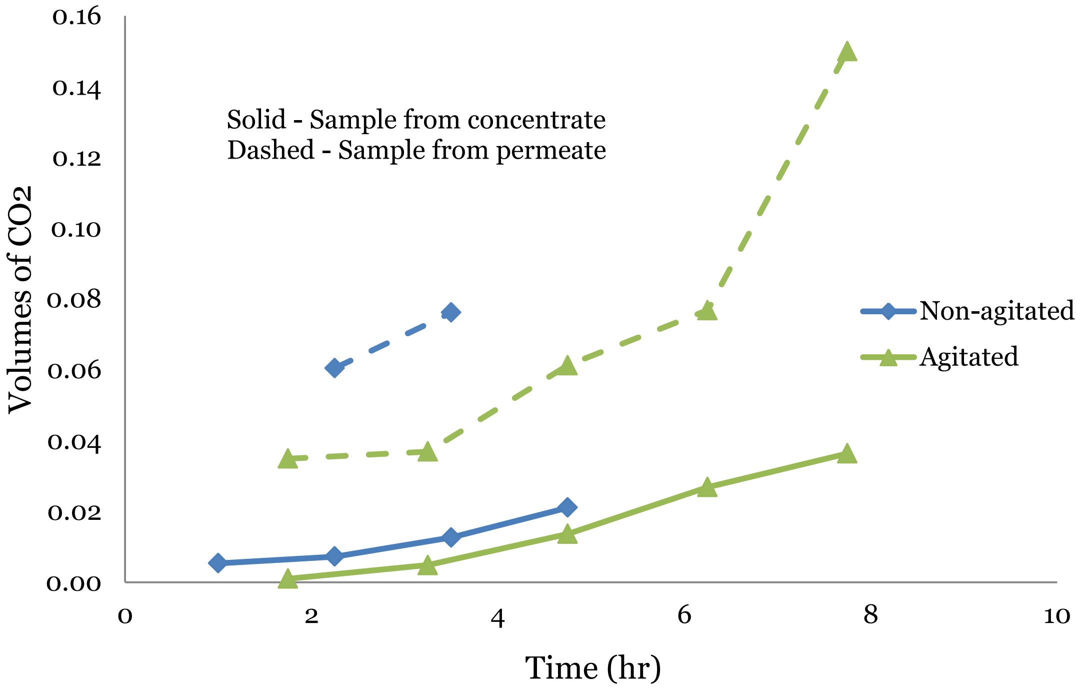


Figure 6: Continuous CO_2 entrainment using pure CO_2 headspace in the pressure vessel. Non-agitated entrainment started with 4 liters in the pressure vessel; agitated entrainment started with 1 liter. Concentration increases with continued flow but overall entrainment is low.

However, both of these experiments demonstrated a flaw. Despite the low levels of dissolution observed, the continuous operation meant that water with excess CO_2 was passing through the pump which caused gas to be released from solution. Over time, the gas accumulated to the point where the entire feed line was filled with gas. Additionally, the gas released caused the pump to perform poorly and required some amount of effort for the gas to be removed. This phenomenon was confirmed with a third test in which commercially available seltzer water was used as feed to examine the effect of the system on the retention of CO_2 in solution. In a matter of minutes after beginning pump operation, the feed line filled with gas and the pump displayed erratic behavior. A similar result occurred with artificial generation of CO_2 using a pH-adjusted sodium bicarbonate solution to release CO_2, thus negating the feasibility of Method 2. The system was not able to handle continuous flow with excess dissolved gas due to depressurization to atmospheric pressure in the feed tank and turbulence within the pump. It is possible that by using a pump that can withstand high pressures, the system can be unbroken in terms of pressurization and continuous operation would be possible. However, for the purpose of this study, only batch operations, and thus cleaning of scale instead of scale prevention, could be examined.

Further testing was conducted to determine the extent of dissolution possible in batch operation. Based on the theoretical rate of diffusion through the water column (see Figure 5), it was concluded that relying on the headspace for entrainment was not an option. A batch test was performed using only the pressure vessel. After filling the pressure vessel with 4.5 liters of water, CO_2 was leaked in slowly to fill the vessel to 500 psi. Gas was collected upon release of water from the pressure vessel. An estimated 12 volumes of CO_2 were dissolved in the batch experiment. Thus, bubbling is effective at initial entrainment, but its effects cannot be observed in continuous operation.

3.3.4 Selected Method

The method of entrainment to be used in this study is bubbling CO_2 into a pressure vessel pre-filled with water. Bubbling is achieved by slowly leaking CO_2 into the pressure vessel until the headspace reaches the target pressure. This is similar to the use of air sparges for increasing dissolved oxygen. A water volume between half to three-quarters of the total capacity will be optimal to avoid rapid pressurization – a volume of 7.5 liters is chosen.

3.4 Objective 2 – CO_2 for Scale Removal

CO_2 permeation through pressure-driven membranes is little studied. According to the results of Milstead (1971), it is expected that CO_2 will pass easily through the membrane and thus the concentrations will not be affected by membrane filtration. The goal is to determine whether passing CO_2-laden water through the system is effective at removing various types of inorganic scale and if so, whether the effect is in some way different from conventional cleaning regimes.

3.4.1 Scaling Solutions

The feed water is designed to mimic brackish groundwater as this source of drinking water commonly encounters scaling issues. Brackish water is that with a total dissolved solids content between 1000 and 10,000 mg/L. For this study, a background concentration of 10 g/L NaCl is used to generate brackish TDS since sodium and chloride will not react with other components to form sparingly soluble salts that could contribute to membrane fouling.

Experimental solutions were generated from laboratory grade reagents to create scaling conditions for select scales. The scales of interest are calcium and silica based scales – common scales formed in groundwater treatment. Particular attention is paid to silica scales since these are not effectively treated with known antiscalants but rather can be treated with acidification (Antony et al. 2011). Calcium scales are very common but typically manageable. For this study, calcium carbonate scale is chosen to represent common alkaline scale and calcium silicates are used for silica scales. Each solution contained only the components for a particular chosen scale, in addition to background sodium and chloride, and are not meant to represent real groundwaters. Recipes were generated by adding small quantities of each reagent stepwise into a salt solution to determine the point at which precipitation occurred. Trials of these recipes in the membrane system further served to refine the recipe to create solutions that would reliably cause scaling.

$CaCO_3$ scaling solution was comprised of $CaCl_2$ at 170 mg/L and Na_2CO_3 at 170 mg/L with no pH adjustment (final pH around 10). Silicate scaling solution is comprised of Na_2SiO_3 at 600 mg/L with $CaCl_2$ at 375 mg/L with addition of HCl to reduce pH from 12 to approximately 8. Reagents were calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$ (EMD Chemicals), anhydrous sodium carbonate, Na_2CO_3(VWR), sodium meta-silicate 9 hydrate, $Na_2SiO_3 \cdot 9H_2O$ (J. T. Baker), and sodium dodecyl sulfate, $C_{12}H_{25}NaO_4S$ (Sigma-Aldrich). Recipes for each trial performed are summarized in Table 3 below. For comparison, a study on silica scaling used a fouling recipe containing 250 mg/L SiO_2, 750 mg/L Ca^{2+} and 500 mg/L Mg^{2+} (Koo, Lee, Sheikholeslami 2001).

3.4.2 Cleaning Solutions

To understand the mechanism by which dissolved CO2 in water is able to clean scaled membranes, several other cleaning runs are also performed, including low pH cleaning solutions, dissolved nitrogen gas, and DI water. A pH 3 solution is used to approximate solutions used for membrane cleaning in industry. Preliminary trials of preparing a dissolved CO_2 solution show a resulting pH around 4.5. Thus, trials with a pH 4 cleaning solution will be used to examine pH contributions to CO_2 cleaning. The nitrogen gas trial will perform the opposite control, looking at gas effects with no pH changes. A third combination, lowering the pH of the dissolved N_2 solution will isolate effects due to carbonate chemistry. For silicate scale, there is no known cleaning procedure to remove most of the scale; both acidic and basic solutions have shown to be somewhat effective. In this study, CO_2 cleaning of silicates will be compared to low pH cleaning at pH 3 and high pH cleaning at pH 12 combined with sodium dodecyl sulfate as a surfactant.

Table 3: Matrix of feed solutions and cleaning regimes used for scaling experiments. Each solution has a background ion content of 10 g/L NaCl. CO_2 and N_2 cleanings use the gas cleaning procedure; all other cleanings use the chemical cleaning procedure.

Purpose	Feed Solution					Cleaning Procedures
	NaCl	Na_2CO_3	$CaCl_2$	Na_2SiO_3	HCl	
DI Control NaCl control	 10 g/L					none
CaCO3	10 g/L	2 mM	2 mM			CO_2, pH 3, pH 4, N_2, N_2/acid, DI
Silicates	10 g/L		3.5 mM	5 mM	10 mM	CO_2, pH 3, pH 12 + SDS, DI

3.4.3 Scaling Procedure

A pressure of 500 psi, applicable for CPA2 membrane, and a crossflow velocity of 800 mL/min was used for all flux experiments. A new membrane coupon was used for each scaling run for accurate data comparison. Before each membrane installation, the new coupon and membrane cell components were rinsed in distilled water. With the membrane cell connected, the system was flushed to remove all stagnant water and replaced with fresh DI water. Then, the system was pressurized to 500 psi and DI circulated for one hour to compact the membrane. The first 10-15 minutes typically had significant flux decline due to membrane compaction and slight decline over the remaining time period.

After membrane compaction, a salt only flux decline experiment was performed on a few membranes to determine a profile for flux decline due to a concentrating salt solution that did not cause membrane scale. As expected by membrane theory, this flux declined linearly with increased concentration. The transport of water through the membrane is governed by the difference between the applied transmembrane pressure and the transmembrane osmotic pressure (Equation 8). Osmotic pressure increases with an increased salt concentration, but no change was made in the applied pressure, thus the water flux driving force must decrease with increasing feed concentration.

Equation 8: Solvent flux, J_w, through the membrane is a function of the difference between the applied transmembrane pressure, ΔP, and the transmembrane osmotic pressure at the membrane wall, $\Delta\pi_m$.

$$J_w = A_w(\Delta P - \Delta\pi_m)$$

To scale the membranes, the feed was switched to a prepared solution. Measurements of pH, alkalinity, and conductivity on the scaling solution were taken before each scaling run. To expedite scaling, scaling runs were operated in recycle to allow concentration of the feed and increase the propensity of scale formation. Care was taken to avoid the formation of precipitates in the feed so that membrane fouling could not be attributed to cake formation of colloids. This design ensured that crystal formation only occurred within the highly concentrated salt region next to the membrane surface known as the concentration polarization layer. Any experiments where cloudiness in the feed was observed were discarded. Flux was monitored to confirm additional flux decline over the expected amount due to the concentrating background salt.

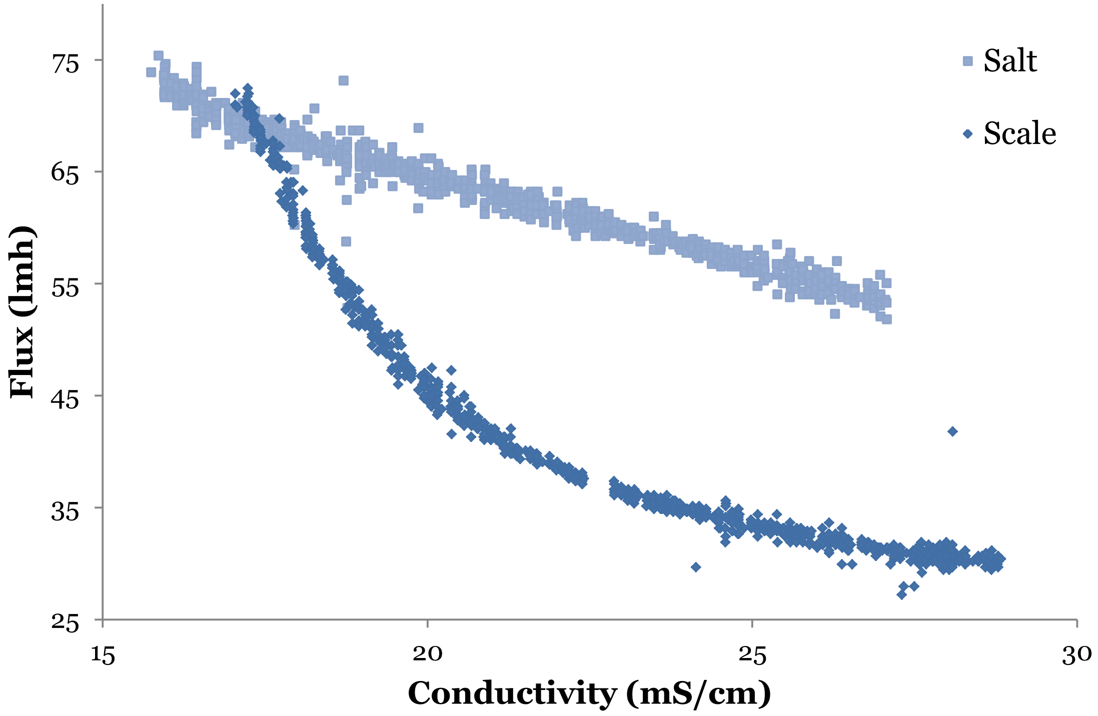


Figure 7: Examples of flux decline due to a salt solution, which is only a function of concentration, and due to a scaling solution, which is a result of particle build-up on the membrane. Both solutions had 10 g/L NaCl and were allowed to concentrate by recycling.

3.4.4 Cleaning Procedure

Dissolved Gas Cleaning

To generate a dissolved gas solution, the pressure vessel was filled mostly with water – 7.5 liters filled into the 9.7 L space – and gas sparged to fill the headspace to a pressure of 500 psi. The amount of gas dispensed, determined from the pressure reading of 180 psi after the pressure vessel was emptied of water, was approximately 0.5 moles. Cleaning was conducted by opening the valve between the pressure vessel and the membrane cell to allow water to flow through driven by headspace pressure. Identical procedures were followed for CO_2 cleanings and N_2 cleanings. For pH-adjusted N_2 cleaning, the pressure vessel was filled with water acidified with HCl instead of DI water.

Samples were taken from the concentrate and permeate and measured for pH and alkalinity. For CO_2 trials, three samples from the permeate were taken to measure the volumes of gas dissolved; samples were consistently taken at 400 psi, 300 psi, and 200 psi. No gas was observed in the permeate during N_2 trials.

After the pressure vessel was emptied of water, the remaining gas in the pressure vessel was vented through the bottom port and did not pass the membrane cell. A clean water flux was performed after cleaning to determine the extent of flux recovery.

Chemical Cleaning

Trials without dissolved gas did not utilize the pressure vessel. The procedure for chemical cleaning is based on industry convention for membrane cleaning, which circulates a cleaning solution through the RO system without added pressure (Fritzmann et al. 2007). For this study, a circulation time of 30 minutes was used. Cleaning was performed with all valves fully open – at a crossflow rate of 800 mL/min, the pressure in the system is approximately 140 psi. For the acid cleaning trials, the pH was monitored every few minutes to ensure a consistent pH throughout the cleaning cycle. Due to dissolution of membrane scale, the cleaning solution pH had a tendency to increase rapidly and frequent addition of acid was required to maintain the target pH. Acid addition was minimized by increasing the volume of cleaning feed used. It was found that for 5 L of a pH 3 solution, an average of 40 mL of an 0.1 M HCl solution needed to be added to maintain the pH over the course of the half hour cleaning run. After cleaning, the system was flushed and a clean water flux measurement was taken to evaluate the flux recovery.

4. Results and Discussion

4.1 Flux Recovery

Multiple trials were performed for each cleaning solution tested, each with a different membrane coupon. Flux values were compared from three different points: after membrane compaction for one hour, after scaling, and after cleaning. Flux readings were taken using DI water at 500 psi. To compare between runs, scaled and cleaned flux readings were normalized to the initial reading of the coupon. Even in the same membrane material, variability in initial flux is expected between coupons either due to the membrane itself or because of slight differences in membrane preparation and installation; observed initial flux ranged from 120-140 lmh after one hour of membrane compaction using DI at 500 psi. Additionally, each run varied in the extent of scaling. This was a result of any slight differences in the scaling solution and changes in the system over time, such as scale build-up within the pipes and tubes. Since the amount of scaling would affect the amount of flux that could be recovered, comparison between runs is accomplished by examining the percent of flux recovery, which is calculated as the difference between the clean water flux values after scaling and after cleaning divided by the difference between the initial clean water flux and the clean water flux after scaling. In other words, the flux recovery is the flux regained by cleaning relative to the flux lost due to scale and is presented as a percentage of the lost flux.

$$FR = \frac{J_c - J_s}{J_i - J_s}$$

The percent of flux recovery for each run is shown above each corresponding column in Figure 9 for calcium carbonate scale and Figure 14 for calcium silicate scale in the following sections. While the bars appear different for each trial, the flux recoveries reveal trends within and between trial sets. Statistical analysis was performed on flux recoveries from calcium carbonate scale tests since these were run in triplicate while calcium silicate tests were only run in duplicate. Results are summarized and discussed in the following section (Figure 10).

4.2 Calcium Carbonate Scale

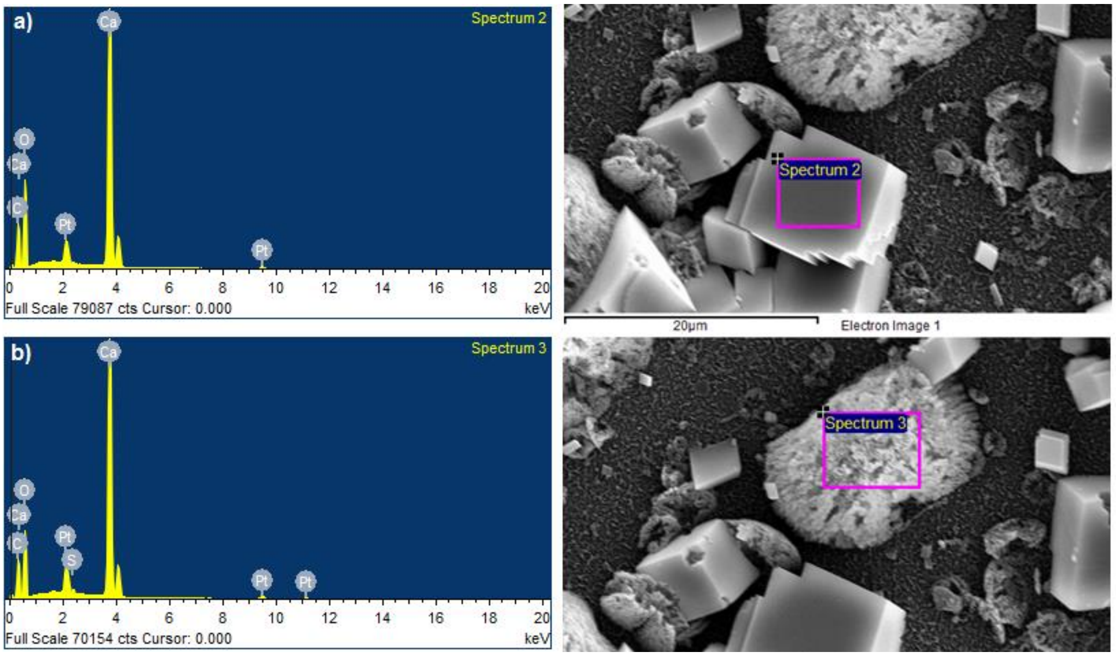


Figure 8: EDX analysis (left) and SEM imaging (right) of two $CaCO_3$ crystal structures on a pH 4 cleaned membrane. SEM reveals a) a rectangular crystal structure and b) a hexagonal crystal structure. Distribution of elements as analyzed by EDX is nearly identical.

Membranes scaled with a solution containing $CaCl_2$ and Na_2CO_3 produced two crystal morphologies as revealed by SEM imaging at 1000x magnification. The membrane shown in Figure 8 is one cleaned with a pH 4 cleaning solution. The rectangular structure in (a) appears to be a calcite crystal; the hexagonal structure in (b) appears to be a vaterite crystal. These crystals are expected; in precipitation experiments, vaterite and calcite were formed at temperatures below 30 °C while aragonite, a third form of calcium carbonate present in aqueous systems, was only observed at temperatures above 40 °C (Ogino, Suzuki, Sawada 1987). Additionally, vaterite is metastable and, given enough time, will transform to calcite at low temperatures. In natural water systems, vaterite is not common as it does not form well in the presence of magnesium (Antony et al. 2011). Energy-dispersive X-ray spectroscopy (EDX) was performed as an area analysis of the two different morphologies and the results revealed no difference in the chemical composition of the two structures, confirming that they are both calcium carbonate crystals. Similar results were produced by (Mitrouli et al. 2012) on CPA2 membranes lightly scaled with calcium carbonate from a synthetic brackish feed solution very similar to the one applied in this study. SEM images from their study, also taken at 1000x magnification, showed distributed crystals of both calcite and vaterite forms.

Six cleaning regimes were applied to membranes scaled with calcium carbonate: CO_2 gas, N_2 gas, pH-adjusted N_2 gas, pH 3 solution, pH 4 solution, and DI water. The first three experiments used the gas cleaning procedure while the last three experiments used the chemical cleaning procedure. The normalized clean water flux measurements of the unscaled, scaled, and cleaned membranes are shown in Figure 9 as white, dark grey, and light grey, respectively, where the values are normalized to the clean water flux of each membrane coupon after one hour of compaction.

High variability in the degree of scaling between runs results in variability of flux recovered since each cleaning regime was performed identically. Differences between runs are visualized in the bar graphs of Figure 9 (showing individual trials) and Figure 10 (showing averages). Flux recoveries in Figure 9 are per trial while Figure 10 displays average flux recovery plus the standard deviation.

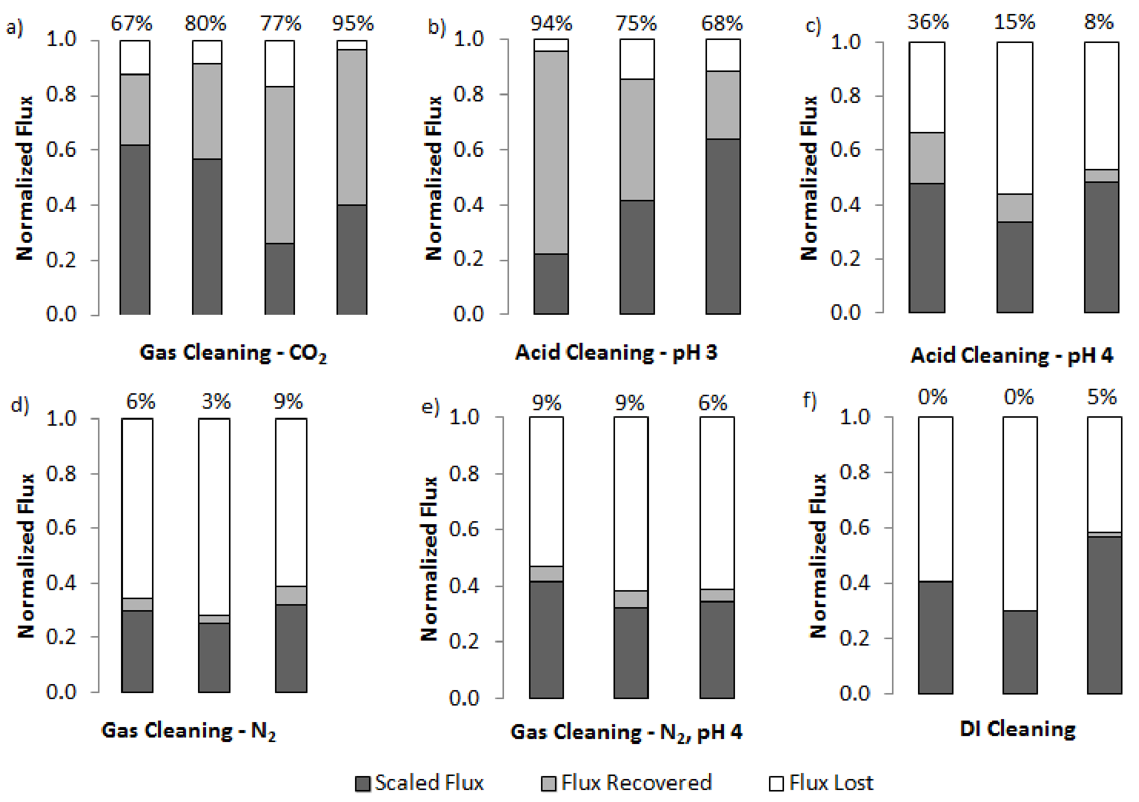


Figure 9: Cleaning results for membrane coupons scaled with calcium carbonate. Each bar represents one trial with the flux recovery shown above. Dissolved CO$_2$ gas (a) and pH 3 (b) cleaning had highest flux recovery. pH 4 (c) cleaning had moderate recovery; N$_2$ in DI (d) and N$_2$ in pH 4 water (e) had minimal recovery; DI cleaning (f) had virtually no recovery.

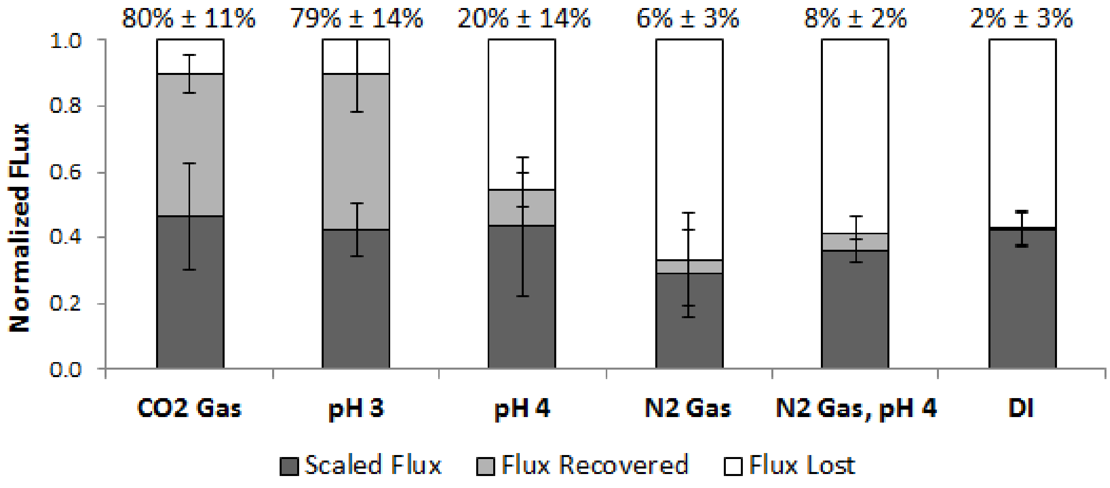


Figure 10: Averages of trials performed with calcium carbonate scale shown (individual runs shown in Figure 9). Error bars represent the high and low values within each set. Average flux recovery value and standard deviation for each set of trials is shown above each bar.

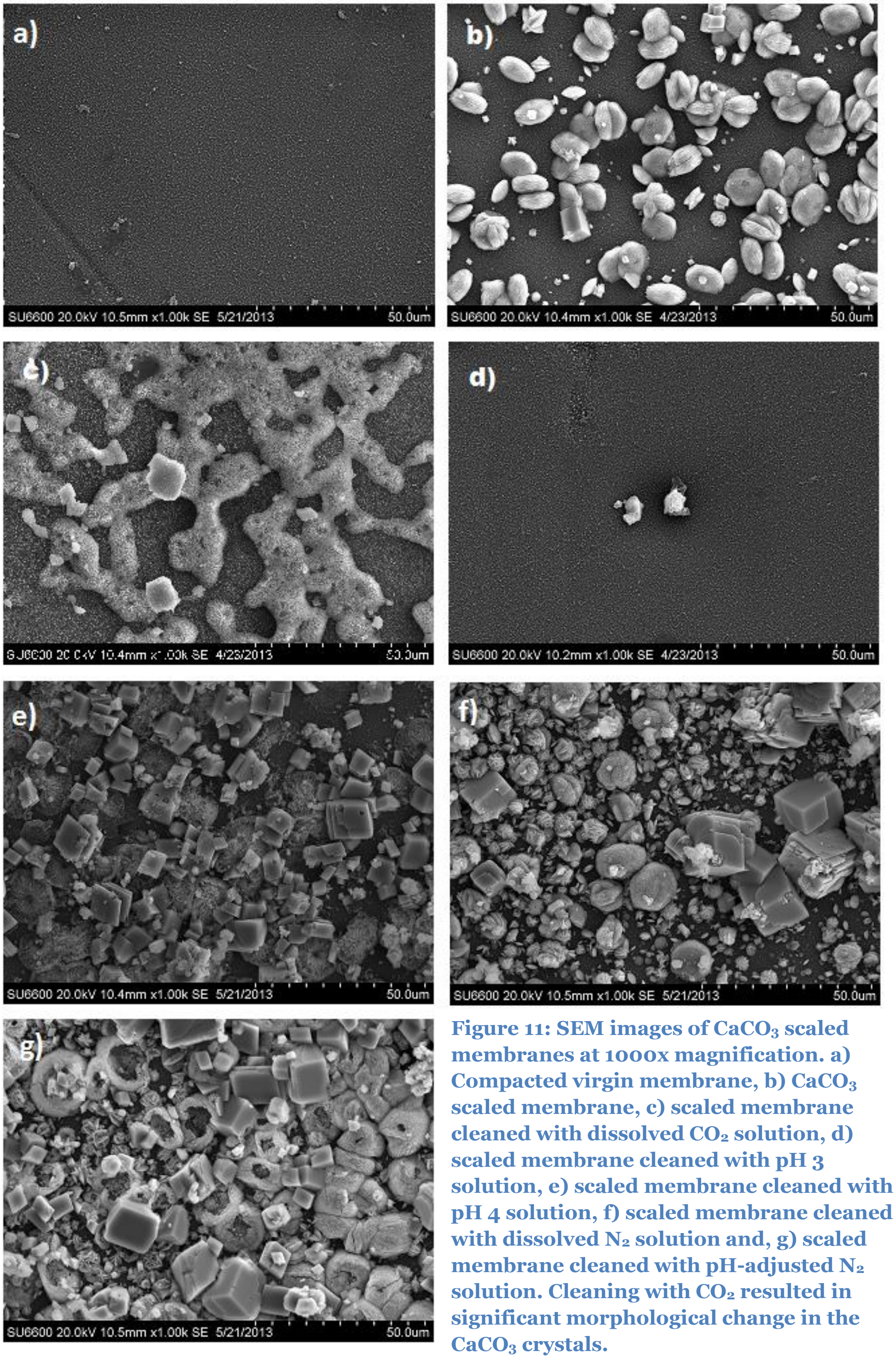


Figure 11: SEM images of $CaCO_3$ scaled membranes at 1000x magnification. a) Compacted virgin membrane, b) $CaCO_3$ scaled membrane, c) scaled membrane cleaned with dissolved CO_2 solution, d) scaled membrane cleaned with pH 3 solution, e) scaled membrane cleaned with pH 4 solution, f) scaled membrane cleaned with dissolved N_2 solution and, g) scaled membrane cleaned with pH-adjusted N_2 solution. Cleaning with CO_2 resulted in significant morphological change in the $CaCO_3$ crystals.

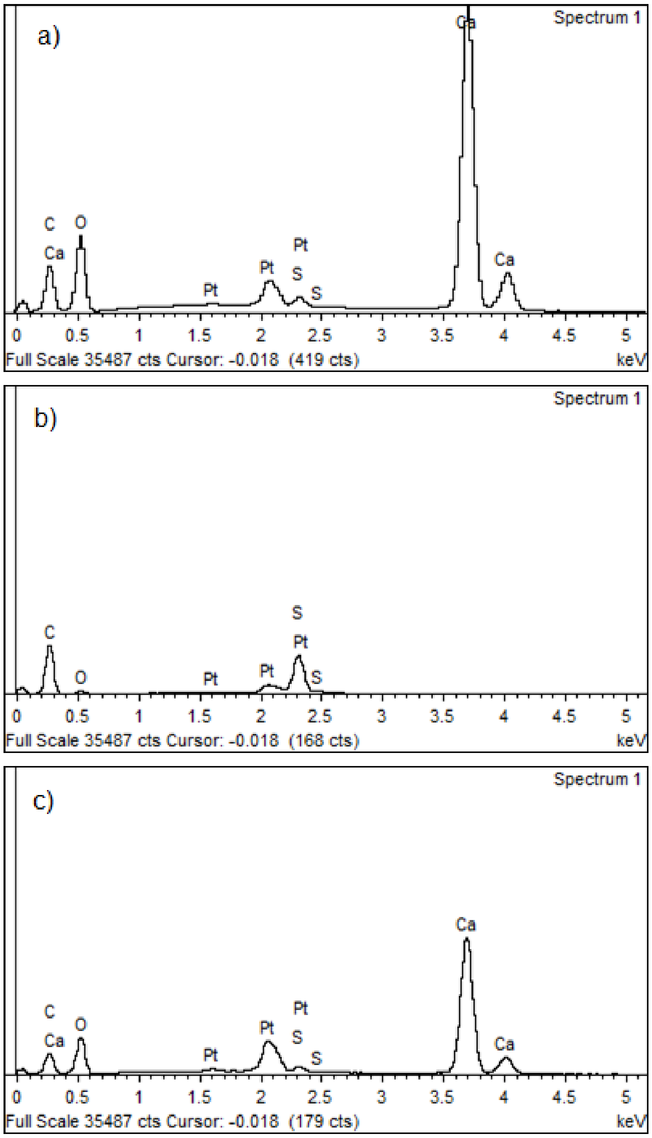


Figure 12: EDX analysis at one point of a) a membrane scaled with $CaCO_3$, b) a scaled membrane cleaned with a pH 3 solution and, c) a scaled membrane cleaned with a dissolved CO_2 solution. Platinum signals are due to the coating used in SEM imagine. Sulfur signals are due to the polysulfone membrane support layer.

4.2.1 Dissolved CO_2 Cleaning

Scaled membranes were effectively cleaned with a dissolved CO_2 solution. The average flux recovery among four trials was 81% with a standard deviation of 14%, showing a consistently high recovery among four trials (Figure 10). SEM imaging of the cleaned membrane at 1000x magnification showed dissolution of the crystal structure resulting in a more amorphous state. In Figure 11, the masses that appear closest in panel (c) were originally calcite crystals while the conglomerated mass nearest the membrane was originally distinct vaterite crystals as seen in panel (b), the SEM image of a membrane that was scaled and not cleaned. In looking at the membrane through SEM, the CO_2 cleaned membrane had large areas without scales, which is consistent with the level of flux recovery observed, dotted with stretches of the transformed crystals. EDX analysis of this membrane in panel (c) of Figure 12 also showed less calcium relative to the uncleaned membrane, though the nature of the point analysis does not allow for rigorous comparison.

During the CO_2 cleaning, water in the concentrate line from the membrane cell exited rapidly. Bubbles were observed in the permeate line after approximately 30 seconds, enough time for non-carbonated water to be flushed out of the system. Samples were taken of the gas to water ratio in the permeate line using the syringe method. An initial reading at 400 psi showed on average 20 volumes of CO_2 while readings at 300 psi and 200 psi showed on average 8 volumes of CO_2. The drop from 500 psi to 300 psi occurred within two minutes. The total run time from 500 psi to the final pressure of 180 psi in the pressure vessel was 7.5 minutes. The waste stream was tested for pH and alkalinity. In each case, the pH of the water after carbonation and passing through the system was approximately 4.5. The change in alkalinity after carbonation and cleaning was always positive though so small as to be negligible.

4.2.2 pH Effects

Most of the flux was regained when a pH 3 solution was used for cleaning. The average flux recovery was 79% with a standard deviation of 14%, nearly identical to the CO_2 cleaning results (Figure 10). SEM imaging confirms the absence of scale after cleaning –

only two particles are observed in the image, the rest of the image matched the image of the virgin membrane – and EDX analysis showed no calcium at the point of analysis (Figure 11, panel d, Figure 12, panel b). This is expected as low pH solutions are the conventional cleaning solution for inorganically scaled membranes.

Very little flux recovery was achieved using a pH 4 cleaning solution; the average flux recovery was 20% with a standard deviation of 14% (Figure 10). The low cleaning ability of the pH 4 solution demonstrates that the final pH of 4.5 observed with the dissolved CO_2 solution is not a major factor in the cleaning mechanism. While the pH 4 cleaning data set had the highest variability relative to the flux recovery, the highest recovery values were still far below those of the CO_2 cleaning and pH 3 cleaning values. Some morphological change in crystal structure was observed in the SEM image of the pH 4 cleaned membrane, which corroborates the mild cleaning effect observed in the flux results (Figure 11, panel e)

4.2.3 Dissolved Gas Effects

Trials were performed using N_2 gas in place of CO_2 gas to investigate non-carbonate bubbling effects. The dissolved N_2 was prepared using the same method as the dissolved CO_2 solution – by bubbling N_2 gas into the vertical pressure vessel. Trials were also run with the water adjusted to a pH of 4 before adding N_2 through bubbling. This trial served to isolate bubbling effects from the low pH observed in the final CO_2 solution. The average flux recovery from N_2 dissolved in DI was 6% with a standard deviation of 3%, while the average flux recovery of N_2 dissolved in solution adjusted to pH 4 was 8% with a standard deviation of 2% (Figure 10). The lower pH slightly enhances cleaning, though all the trials showed only limited cleaning of the calcium carbonate scale. SEM images of the membranes at 1000x magnification showed no difference between the N_2 cleaned membrane in panel (f) and the uncleaned membrane in panel (b). However, the membrane cleaned with N_2 in a pH 4 solution displayed an interesting result seen in panel (g); the vaterite crystals were not morphed as with the pH 4 chemical cleaning. Instead, the crystal spherulites appeared to be hollowed out, perhaps in some intermediate state between the original state and the morphed state (Figure 11). The calcite structures did not show much change from the uncleaned scales. Thus, it appears that the vaterite structure is more susceptible to removal than calcite.

Cleaning experiments with N_2 gas acted differently from experiments with CO_2 gas. Under the same pressure conditions and within the same timeframe, water with N2 bubbled through it exited very calmly from the concentrate line while water with CO2 bubbled through it exited very rapidly and in short bursts. This leads to the conclusion that there was an increase in volume with the CO_2 test, possibly from the production of gas as dissolved CO_2 molecules left the solution. Additionally, bubbles were not observed in the permeate line until the pressure reached 210 psi while bubbles were observed almost immediately in the CO_2 cleaning trials.

4.2.4 Mechanism of CO_2 Cleaning

To summarize the experimental results, the dissolved CO_2 solution cleaned the scaled membranes in under 10 minutes as well as the pH 3 solution cleaned the scaled membranes in half an hour while N_2 gas tests and pH 4 cleaning resulted in minimal flux recovery. Two conclusions can be drawn from these results. One, the pH of 4.5 of the carbonated solution plays a small role in membrane cleaning. Two, bulk phase bubbling as simulated with N_2 plays a very minor role in membrane cleaning.

One explanation for membrane cleaning with CO_2 is attributed to the higher solubility of CO_2 where scales are removed by shear force applied from CO_2 bubbles that form by nucleation at the membrane surface. This cleaning method, with similar procedures for preparation of the dissolved CO_2 solution, was previously employed successfully to remove biofims from NF and RO membranes (Ngene et al. 2010). Though the opaque membrane cell in this study prevents direct observation of bubble formation, as done in Ngene et al. (2010), the phenomenon of bubble nucleation can be observed through other behavior in the system. First, the rapidly exiting characteristic of the CO_2 solution was not seen with the N_2 solution, implying gas exsolution in the former and not the latter. Additionally, the N_2 solution appeared whitish, similar to aerated water, while the CO_2 solution did not have this appearance. This leads to the conclusion that the N_2 solution contained small, entrained bubbles as opposed to dissolved gas molecules. Secondly, bubbles were not observed in the permeate line during N_2 runs until the very end when the headspace pressure is around 210 psi. Conversely, bubbles are observed early in CO_2 runs and in high quantity. This further supports the theory that CO_2 exists as dissolved molecules which can easily pass through the membrane while N_2 exists as small bubbles which have difficulty permeating the membrane.

The other mechanism that may be employed is a reaction occurring between the CO_2 molecules and the calcium carbonate scale. This was not accounted for in any of the trials and should be considered in future experiments. For example, performing cleaning trials on calcium sulfate or calcium phosphate crystals may provide insight on any reaction-based scale removal present with the calcium carbonate crystals.

4.3 Calcium Silicate Scale

In silica experiments, membrane scaling was created with a solution containing Na_2SiO_3 and $CaCl_2$ to create calcium silicate complexes. This was confirmed through area EDX analysis of the scaled membranes which revealed the expected elements – platinum is from the sample coating and sulfur is from the membrane backing; all other elements were present in the feed (Figure 13). Amorphous silica may also contribute to some fouling but this was minimized by controlling the pH to be under 9. SEM imaging of the fouled membranes show an amorphous structure; the texture of the surface could only be discerned at a magnification of 10000x (Figure 13). This is consistent with descriptions of silica precipitates in the presence of a metal (Ning 2003). Similar images were seen with barium silicate scales at 10000x magnification. Also, the same surface cracking was observed in iron silicate scale as is seen in panel (b1) of Figure 13 (Sahachaiyunta, Koo, Sheikholeslami 2002).

Cleaning trials for membranes scaled with calcium silicates included CO_2 gas, pH 3, pH 12 with sodium dodecyl sulfate (SDS), and DI water. The CO_2 cleaning experiment followed the same gas cleaning procedure as used for the calcium carbonate scaled membranes, and the other three experiments used the chemical solution cleaning procedure of cycling the solution without pressure for 30 minutes. The normalized clean water flux measurements of the unscaled, scaled, and cleaned membranes are shown in Figure 14 as white, dark grey, and light grey, respectively. Normalization is used to negate membrane coupon differences that manifest as different initial fluxes. Each initial flux measurement was taken after a minimum of one hour of membrane compaction over which flux decline was often observed to be a difference of 5-10 lmh.

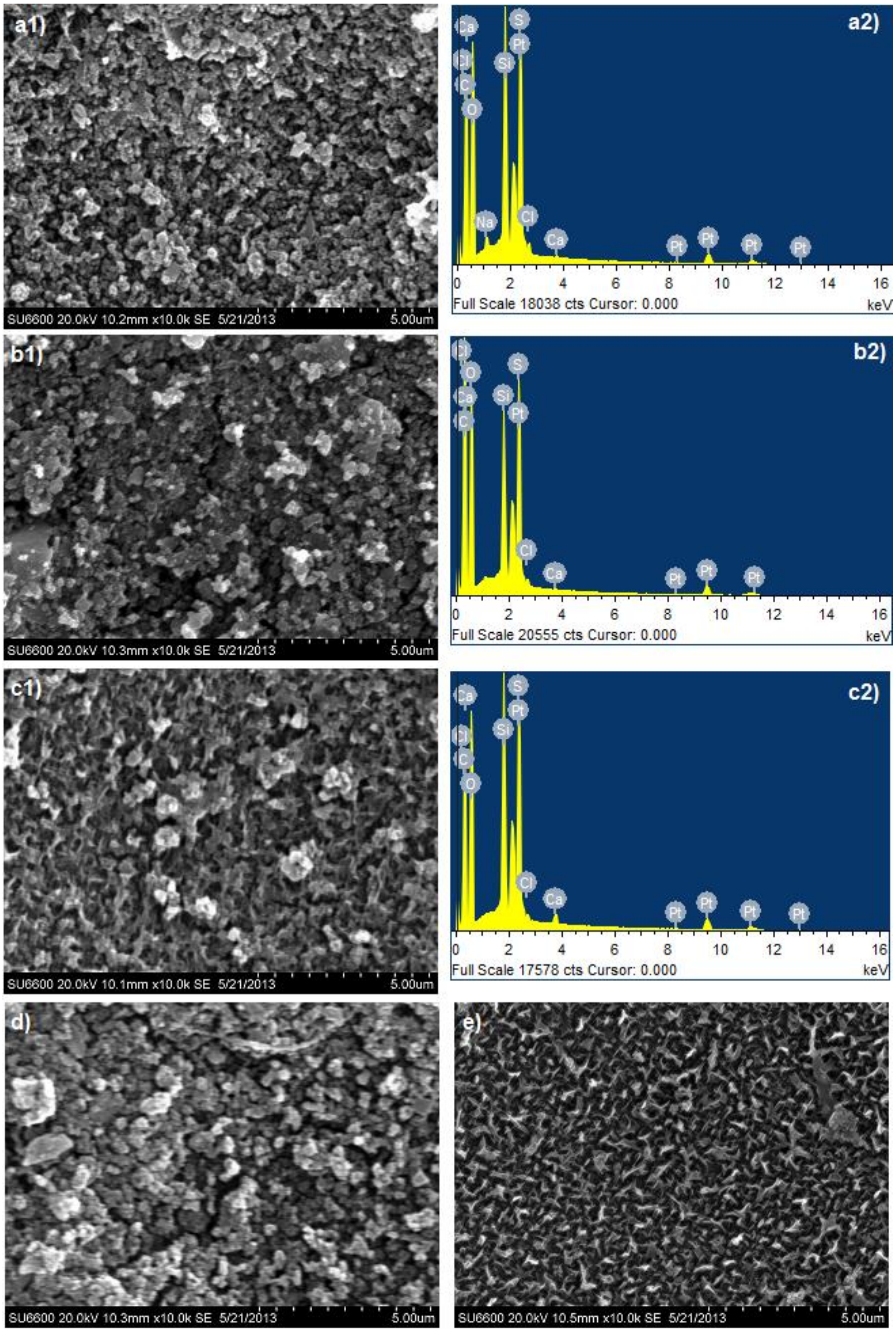


Figure 13: SEM images at 10000x magnification and EDX analysis of membranes scaled with calcium silicates. a) scaled membrane with no cleaning, b) scaled membrane cleaned with dissolved CO_2, c) scaled membrane cleaned with a pH 12 + SDS solution. Also shown d) scaled membrane with pH 3 cleaning and e) compacted virgin membrane at the same magnification.

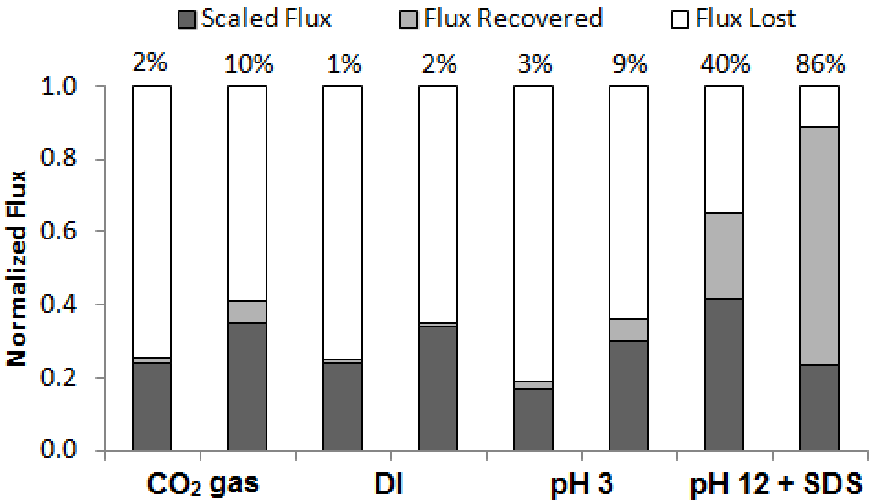


Figure 14: Cleaning results for membrane coupons scaled with calcium silicates. Flux recovery values are shown above each respective trial. CO_2 gas, DI water, and a pH 3 solution all resulted in minimal cleaning to none. The only cleaning regime with significant scale removal was the use of a pH 12 solution with sodium dodecyl sulfate (SDS).

4.3.1 Dissolved CO_2 Cleaning

Dissolved CO_2 cleaning had very little effect on the removal of silicate scale with removals of 2% and 10% over two trials (Figure 14). There were no observed differences in the cleaning operation, thus the mechanism that allows for calcium carbonate removal did not apply to calcium silicates. SEM imaging of the cleaned membrane showed no discernible difference when compared to the non-cleaned membrane. The EDX analysis is also nearly identical; there is no labeled peak for Na in the CO_2 cleaned membrane but it appears as if a slight peak is present at that location nevertheless (Figure 13). Thus, all analyses show no change as a result of the dissolved CO_2 cleaning solution.

4.3.2 Chemical Cleaning

Two chemical solutions were applied to clean membranes scaled with calcium silicates. The pH 3 solution performed equally poorly as the CO_2 cleaning with very little flux recovery – 3% and 9% over two trials. The only solution that resulted in significant flux recovery was a solution adjusted to pH 12 with SDS added which produced flux recoveries of 40% and 86% over two trials (Figure 14). This moderate flux recovery matches recommendations by DOW Filmtec for silicate scale cleaning regimes which call for high pH for silicate cleaning as opposed to low pH for other inorganic foulants (Fritzmann et al. 2007). The SEM image of the pH 12 cleaned membrane supports this cleaning – detail of the membrane surface can be seen in the background of panel (e) (Figure 13).

5. Conclusion

CO_2 gas, when dissolved in a pressure vessel, was effective at removing calcium carbonate scale from low-pressure RO membranes. The same cleaning regime was not effective at removing calcium silicate scale. More work should be conducted to determine if CO_2 cleaning applies to other common scalants.

Two possible mechanisms for CO_2 cleaning were deemed minor – a pH around 4.5 and bulk phase bubbling. One possibility is the nucleation of bubbles at the membrane surface that results in cleaning. Another possibility is a chemical reaction occurring between CO_2 and the calcium carbonate that results in cleaning. Future experiments should be designed to narrow in on the primary mechanism behind this cleaning.

On the bench-scale system, the dissolved CO_2 cleaning worked quickly and efficiently, removing heavy fouling with a ten minute once-through cleaning. Despite the failure to remove silicate scale, the cleaning ability of CO_2 for calcium carbonate scale is significant and leads to the possibility of future green and cost-effective applications where calcium carbonate scale is currently treated using antiscalants or acid cleaning regimes.

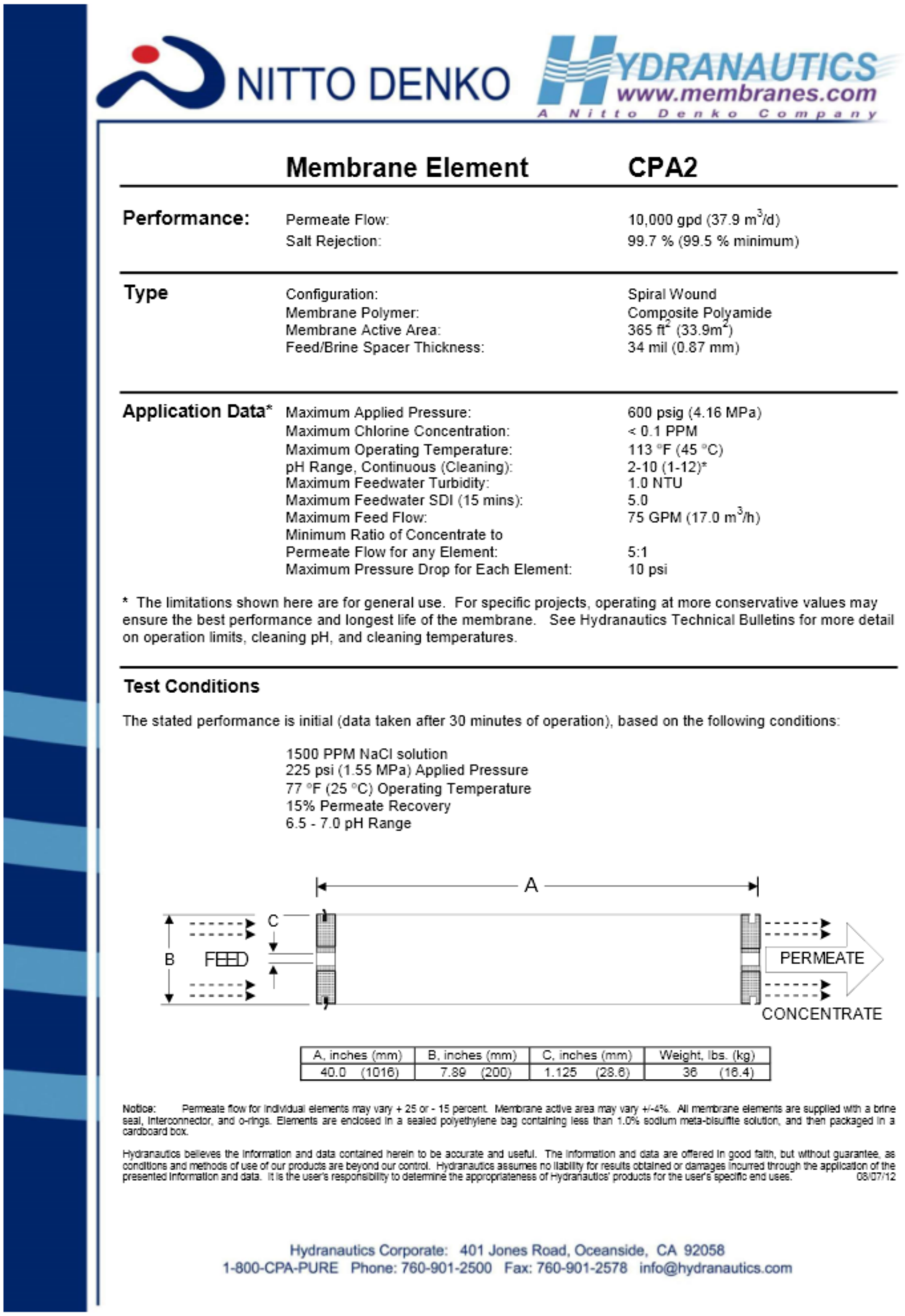
6. Future Work

Future work should be performed to continue to explore the effectiveness of dissolved CO_2 on different types and combinations of scale. In addition to measuring the cleaning effect on various scales, these experiments will also provide more information on the fundamental mechanism behind the cleaning ability of dissolved CO_2. One starting point would be to examine the ability to clean calcium sulfate scale from membranes. Calcium sulfate is a common and problematic scale that is neither a carbonate nor a silicate, thus it can provide a good comparison for the existing work. Other membrane foulants to consider include non-calcium scales, such as barium sulfate.

It will also be interesting to consider the possibility of an in-line application of dissolved CO_2 to examine any scale prevention benefits. In order to test this, it will be necessary to devise a system appropriate for continuous pressure without atmospheric breakpoints. Alternatively, this examination would be possible by comparing two membrane modules using the same feedwater, except for the addition of CO_2, to perform this experiment without system recycle under pressure.

Since this study has demonstrated the effectiveness of dissolved CO_2 in removing calcium carbonate scale, it is possible for this work to be applied to a reverse osmosis plant that is subject to high levels of calcium carbonate scale. A study could be performed to test the effectiveness of cleaning with a system using the particular feedwater as compared to cleaning with existing treatments, including pre-treatment and acid cleaning regimes. Data collected from such a study would give an indication as to the real advantages and disadvantages of using dissolved CO_2 for cleaning, including factors such as cost, ease of use, and sustainability.

Appendix: CPA2 Membrane Specifications



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	Membrane Element	CPA2
Performance:	Permeate Flow:	10,000 gpd (37.9 m^3/d)
	Salt Rejection:	99.7 % (99.5 % minimum)
Type	Configuration:	Spiral Wound
	Membrane Polymer:	Composite Polyamide
	Membrane Active Area:	365 ft^2 (33.9m^2)
	Feed/Brine Spacer Thickness:	34 mil (0.87 mm)
Application Data*	Maximum Applied Pressure:	600 psig (4.16 MPa)
	Maximum Chlorine Concentration:	< 0.1 PPM
	Maximum Operating Temperature:	113 °F (45 °C)
	pH Range, Continuous (Cleaning):	2-10 (1-12)*
	Maximum Feedwater Turbidity:	1.0 NTU
	Maximum Feedwater SDI (15 mins):	5.0
	Maximum Feed Flow:	75 GPM (17.0 m^3/h)
	Minimum Ratio of Concentrate to Permeate Flow for any Element:	5:1
	Maximum Pressure Drop for Each Element:	10 psi

* The limitations shown here are for general use. For specific projects, operating at more conservative values may ensure the best performance and longest life of the membrane. See Hydranautics Technical Bulletins for more detail on operation limits, cleaning pH, and cleaning temperatures.

Test Conditions

The stated performance is initial (data taken after 30 minutes of operation), based on the following conditions:

1500 PPM NaCl solution
225 psi (1.55 MPa) Applied Pressure
77 °F (25 °C) Operating Temperature
15% Permeate Recovery
6.5 - 7.0 pH Range

A, inches (mm)	B, inches (mm)	C, inches (mm)	Weight, lbs. (kg)
40.0 (1016)	7.89 (200)	1.125 (28.6)	36 (16.4)

Notice: Permeate flow for individual elements may vary + 25 or - 15 percent. Membrane active area may vary +/-4%. All membrane elements are supplied with a brine seal, interconnector, and o-rings. Elements are enclosed in a sealed polyethylene bag containing less than 1.0% sodium meta-bisulfite solution, and then packaged in a cardboard box.

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