Prevention and management of silica scaling in membrane distillation using pH adjustment

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Abstract

Membrane scaling by silica is a major challenge in desalination, particularly for inland desalination of brackish groundwater or geothermal resources, which often contain high concentrations of silica and dissolved solids. Adjustment of feed pH may reduce silica scaling risk, which is important for inland facilities that operate at high water recoveries to reduce brine disposal costs. However, water recovery of reverse osmosis is also limited due to increased osmotic pressure with feed water concentration. Membrane distillation (MD) is a thermally driven membrane desalination technique that is not limited by increased osmotic pressure of the feed. In this investigation, pH adjustment was tested as a strategy to reduce silica scaling risk in the MD process. With feed water pH less than 5 or higher than 10, scaling impacts were negligible at silica concentrations up to 600 mg/L. Scaling rates were highest at neutral pH between 6 and 8. Cleaning strategies were also explored to remove silica scale from membranes. Cleaning using NaOH solutions at pH higher than 11 to induce dissolution of silica scale was effective at temporarily restoring performance; however, some silica remained on membrane surfaces and scaling upon re-exposure to supersaturated silica concentrations occurred faster than with new membranes.

Keywords

membrane distillation; membrane scaling; membrane fouling; membrane cleaning; silica

1. Introduction

Control and mitigation of silica scaling on membranes is a challenging problem in the treatment of impaired waters requiring desalination. Silica is present in most natural water resources, it has low solubility, and when concentrated beyond its solubility limit of approximately 120 mg/L [1], precipitation may occur and form a hard scale that is extremely difficult to remove. Silica scaling on heat exchanger surfaces in thermal desalination processes increases thermal resistance, which reduces process efficiency and requires costly chemical and mechanical cleaning. In membrane processes such as reverse osmosis (RO) or nanofiltration (NF), silica scaling reduces water flux [2-5], and is resistant to simple cleaning methods used to manage other types of mineral scaling such as acid washing. The effectiveness of commercial cleaners to remove silica scale are limited and risk damaging the membranes [5]. Operating at low water recoveries that keep the concentrate below the solubility limit of silica can reduce the risk of silica scaling, but this may result in the production of large volumes of reject brine, which can be a substantial problem for desalination facilities, particularly in the case of inland desalination where brine disposal is difficult and expensive [6, 7]. Nevertheless, conventional inland water resources are becoming depleted in many parts of the world, and unconventional resources such as brackish groundwater and geothermal water are attracting more interest due to increased demand and technology advances that have reduced the cost of desalination [8]. However, these resources are often particularly high in silica and total dissolved solids (TDS) and must be demineralized before use [7, 9-12].

The chemistry of silica in water is complex and influenced by many factors, including temperature, pH, ionic strength, and interactions with other dissolved ions [1]. Silica scaling in desalination processes is typically the result of silica polymerization and the formation of amorphous colloidal silica. At low concentrations and neutral or acidic pH, soluble silica exists mostly in non-ionic form in as monosilicic acid, $Si(OH)_4$. As concentration increases, the monomeric form undergoes polymerization through a dehydration reaction to form polysilicic acids, which are connected by silica-oxygen bonds [6]. Soluble silica can be removed by pretreatment with sodium aluminate or lime-soda softening, which create precipitates that adsorb silica [13-15]; however, these strategies may not be practical for desalination due to incomplete removal of silica and the production of large volumes of sludge, disposal of which is costly and labor intensive. Antiscalants may reduce scaling risk at silica concentrations exceeding saturation by inhibiting polymer formation or preventing colloidal silica from attaching to surfaces [16], but may be expensive and are of limited effectiveness at very high silica concentrations [4]. Antiscalants can also contribute to fouling themselves and may increase the risk of organic fouling [17, 18].

Because both silica solubility and the kinetics of polymerization are highly influenced by pH, acidification or alkalization of feed water is a simple and potentially inexpensive technique to prevent silica scaling. Silica solubility increases dramatically above pH of 9 due to the deprotonation of silicic acid and formation of silicate anions, with all forms of solid silica converting to soluble silicates above pH 10.7 [1]. Operating with feed water above this point may eliminate any risk of silica scaling, although it may increase scaling risk of carbonate or silicate minerals for water containing calcium or magnesium [19]. On the other hand, polymerization rates are reduced at both high and low pHs, with the highest polymerization rates occurring at pH 7.5 [20]. Despite the low solubility of silica in acidic conditions, feed water acidification may also be an effective means to prevent silica scaling if polymerization rates are sufficiently low that colloids are unable to form during the residence time in the desalination process. Feed water acidification has been demonstrated using brackish water to allow sustainable operation of RO processes with silica concentrations up to 1,000 mg/L or more [7, 21].

Although pressure-driven membrane desalination processes such as RO may benefit from pH modification to reduce or prevent silica scaling in the treatment of impaired waters, recovery is still thermodynamically limited due to the increased osmotic pressure with high concentrations of dissolved solids [7, 22]. Development of technologies that are not limited by osmotic pressure and compatible with silica management strategies are crucial to achieve high-recovery desalination of water resources with high TDS and silica content. Membrane distillation (MD) is an emerging desalination technology that utilizes a temperature difference across a hydrophobic, microporous membrane to drive mass transport. The hydrophobicity of the membrane prevents liquid transfer through the pores, and mass transport occurs in the vapor phase only. Because it is an evaporative process, MD achieves almost complete rejection of dissolved solids and is very tolerant of extreme salinity, even at concentrations approaching or exceeding the solubility limit of NaCl [23-25]. Although MD has a high thermal energy demand, MD can operate at any temperature difference and energy costs may be alleviated through the use of inexpensive and renewable heat sources such as solar thermal, geothermal, or waste heat from other industrial processes [26]. These unique characteristics make MD a promising strategy for high-recovery desalination and brine management, and several studies have explored the potential of MD for the desalination of natural hypersaline brines [27, 28] as well as concentrates from other membrane processes [29-33]. Investigation of scaling and fouling in MD has also been reported in the literature, mostly focusing on salt and mineral scaling caused by NaCl, carbonates, and sulfates [34, 35]. Comparatively few studies exist that specifically address the problem of silica; however, one study found that while silica scaling reduces performance in the MD process, it can be removed by dissolution using a high-pH solution of Na_2CO_3 [36].

The membranes used and operating conditions applied in MD are substantially different than those used in pressure-driven processes such as RO. MD membranes are hydrophobic, and thus are not receptive for deposition of monomeric silica [1], and fouling by colloidal silica is not subject to compaction because the pressure difference between the feed and distillate is very low. Also, the solubility of silica and the kinetics of silica polymerization are affected by temperature, and the influence of feed pH on scaling behavior in MD may be different than in isothermal processes due to the elevated temperatures and polarization phenomenon encountered in MD. The main objectives of this study were to investigate the influence of pH on silica polymerization and scaling behavior in the MD process at pH ranges from 4 to 11, and how feed water pH adjustment might be used as a strategy to prevent silica scaling in MD. Additionally, the influence of pH on dissolution behavior of silica scale on MD membranes was investigated using process modification with neutral and high pH solutions. The long-term effectiveness of an alkaline cleaning process for MD membranes scaled with silica and its viability as a practical tool for silica scale management was also explored.

2. Materials and methods

2.1 Membranes and modules

A hydrophobic, microporous polypropylene membrane manufactured by 3M (St. Paul, MN) was used in the study. The membrane is symmetric with a nominal pore size of 0.2 μm, a porosity of 85%, and a thickness of 110 μm. This membrane was chosen due to its high performance as an MD membrane, which has been characterized previously [37], and because its isotropic nature allows the MD process to be reversed by swapping the feed and distillate channels.

Custom flow cells were fabricated using transparent acrylic and featured ten 18 cm (7") long, by 6.35 mm (0.25") wide, by 3.2 mm (0.0125") deep parallel flow channels on both the feed and distillate sides, providing a total membrane surface area of 125 cm^2. Spacers were not installed in the flow channels to ensure consistent hydrodynamic conditions near the membrane surface and to allow direct observation of scaling and fouling behavior on the membrane surface during experiments.

2.2 System description

An automated, closed-loop, bench-scale system was utilized for all experiments (Fig. 1). Data collection and operating conditions were controlled using LabVIEW software (National Instruments) and a Labjack U6 (Labjack, Lakewood, CO) DAQ device. Both feed and distillate solutions were pumped continuously through the system using gear pumps (Micropump Integral Series, IDEX Corp. Vancouver, WA). Water flux across the membrane was calculated by measuring the change in height of the water column in a cylindrical distillate tank over time using a pressure transducer (Model PX309-001G5V, Omegadyne Inc., Sunbury, OH). The distillate tank was also fitted with an automated solenoid valve to allow collected distillate to drain by gravity back into the feed tank, allowing for extended operation within a specified feed concentration range. To reduce losses from evaporation, the distillate tank was covered and the feed tank was completely sealed except for a small opening on the top, which was fitted with a pressure-relief tube extending several feet above the tank to allow water vapor to condense and drain back into the tank.

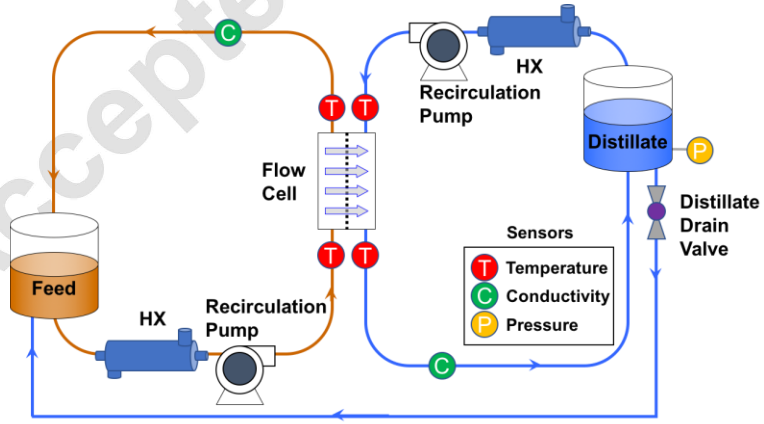

Fig. 1. Schematic of the MD system. Feed and distillate temperatures were monitored at the inlet and outlet of the flow cell and controlled by heat exchangers (HX). Conductivity was monitored in both the feed and distillate streams between the flow cell and tanks. The volume of the collected distillate was measured using a pressure transducer installed on the bottom of the distillate tank. Feed concentration was controlled by periodically returning the collected distillate to feed tank using an automated solenoid valve.

The temperature of the feed solution was maintained constant using water heated with a 1500 W electric heater (Model 1019, Hotwatt, Danvers, MA) on the opposite side of a heat exchanger, and the temperature of the distillate was maintained constant using a chilled glycol solution circulated on the opposite side of a second heat exchanger. Temperature was monitored at the inlets and outlets of both feed and distillate channels of the flow cell using silicon-type temperature sensors (Model EI1034, Electronic Innovations Corp., Lakewood, CO) to enable measurement of thermal efficiency during experiments. Thermal efficiency (η_{th}) of the MD process is defined as the ratio of latent heat transferred by vapor to the total heat transfer, which includes both latent heat transfer and conductive heat transfer through the membrane:

(1)

where Q_{vap} is the latent heat transferred by vapor through the membrane, and Q_{cond} is the conductive heat transfer through the membrane. The vapor heat transfer can be related to the vapor mass transfer, and the conductive heat transfer can be related to the thermal conductivity of the membrane using Fourier's equation:

(2)

where $\dot{m}_m$ is the mass flow rate of vapor through the membrane, ΔH_{vap} is the latent enthalpy of vaporization of water, k_m/δ is the thermal conductivity of the membrane, and ΔT_m is the temperature difference between the feed and distillate at the membrane surface. Thermal conductivity of the membrane is difficult to measure and not commonly provided by membrane manufacturers, and temperature difference at the membrane surface cannot be explicitly measured, but will always be lower than the temperature difference betwwn the bulk feed and distillate streams because of temperature polarization in the flow channels [38]. However, because the temperature of the distillate is close to the ambient temperature, the heat transfer to the environment on the distillate side is negligible. Therefore, the total heat transfer through the membrane is almost equal to the change in enthalpy of the distillate between the inlet and outlet of the flow cell. Thus, in the present study the thermal efficiency was calculated using Eq. 3:

(3)

where $\dot{m}_d$ is the mass flow rate of the distillate, $T_{d,in}$ and $T_{d,out}$ are the temperature of the distillate at the inlet and outlet of the flow cell, respectively, and $c_{p,in}$ and $c_{p,out}$ are the constant-pressure specific heat of pure water calculated at $T_{d,in}$ and $T_{d,out}$, respectively. Conductive heat transfer was calculated by subtracting the vapor heat transfer from the measured total heat transfer.

Conductivity was monitored continuously in both feed and distillate solutions using a toroidal type sensor (Model TCSMA, Sensorex, Garden Grove, CA) and a conductivity probe (Model T-35820-62, Cole-Parmer, Vernon Hills, IL), respectively. Salt rejection was calculated using Eq. 4:

$$(\quad) \quad \left(\quad \frac{}{(\qquad)} \right) \tag{4}$$

where σ_f and σ_d are the conductivities of the feed and distillate solutions, and V_{d1} and V_{d2} represent the total volume of the distillate system at times 1 and 2 across a time interval.

2.3 Analytical methods

Soluble silica concentration was determined using the Hach Silicomolybdate Method (Method 8185) and a Hach spectrophotometer (Model DR 5000, Hach Company, Loveland, CO) to measure absorbance at 452 nm. The silicomolybdate method is useful for molybdate-reactive silica in concentrations between 1 and 100 mg/L, which includes dissolved simple silicates, monomeric silica, silicic acid, and an undetermined amount of polymeric silica [39]. Colloidal polymeric silica is not measured by the method due to its unreactive nature, effectively allowing this approach to provide a measurement of polymerization as soluble silica is transformed into colloidal silica. Samples were diluted before analysis using ultrapure water to ensure that soluble silica concentrations did not exceed the range of the analysis method.

2.4 Experimental procedures

This study investigated feed water pH modification as a potential strategy to mitigate silica scaling in the MD process. Batch experiments were first performed using heated solutions supersaturated with respect to silica to investigate silica polymerization rates for different pH conditions at a temperature typical of those used in MD. The influence of pH on silica scaling behavior and its impacts were investigated using solutions with initial silica concentrations approximately equal to the solubility limit then concentrated with MD. A series of experiments were also performed to test the reversibility of silica scaling on MD membranes and to investigate dissolution behavior of silica scale at high pH.

2.4.1 Batch silica polymerization tests

Experiments were conducted in beakers to investigate the influence of pH on silica solubility and polymerization rates at concentrations and temperature similar to those that will be used in the MD experiments. Solutions were prepared by dissolving 2120 mg of sodium silicate pentahydrate, $Na_2SiO_3 \cdot 5H_2O$, into 1 L of deionized water to achieve an initial concentration of 600 mg/L SiO_2, which is approximately the maximum concentration that will be reached in the MD experiments. The solutions were then adjusted to a desired pH between 4 and 11 using HCl and NaOH, placed in a water bath to maintain temperature of 60 °C, and stirred periodically. Silica solubility and polymerization rates were determined by collecting 1 mL samples, diluting them with 9 mL of HCl solution at pH 1 to halt any further polymerization, and analyzed for soluble silica concentration using Hach Method 8185. Samples were collected every minute for the first 10 minutes, with the interval between sampling time gradually increasing within the first hour to 20 minutes. Sampling continued over the next 5–7 hours until measured soluble silica concentration stabilized and silica concentration reached equilibrium. To correct for evaporation in the test samples, the evaporation rate at the experimental conditions was measured using 1 L of deionized water maintained at 60 °C for a period of 8 hours.

2.4.2 MD performance and silica scaling tests at pH 4–11

Silica scaling behavior in the MD process was investigated using synthetic solutions prepared by dissolving 795 mg/L of $Na_2SiO_3 \cdot 5H_2O$ into deionized water to provide an initial concentration of 225 mg/L (3.74 mmol/L) as SiO_2, which is slightly less than twice the solubility limit of silica at neutral pH and 25 °C, and approximately equal to the solubility limit of silica at neutral pH and 60 °C, as calculated by OLI Stream Analyzer (OLI Systems, Inc., Cedar Knolls, NJ). Solutions were adjusted to a desired pH between 4–11 with concentrated HCl and NaOH.

For the silica scaling experiments, feed and distillate temperatures were maintained at 60 °C and 20 °C, respectively. Both feed and distillate were circulated through the system at a constant flow rate of 2.0 L/min in a countercurrent flow configuration, providing a flow velocity of 16.6 cm/s and Reynolds number of 1460 for the feed solution and 690 for the distillate. In each experiment, 4 L of feed solution was concentrated until a maximum of 2.5 L of distillate was collected. Then the solenoid valve on the distillate tank was opened momentarily, allowing 0.5 L of distillate to return to the feed tank while the MD process continues. After the initial concentration step the repeated collection of 0.5 L distillate and its return to the feed tank continued for the duration of the experiment, maintaining the concentration factor of the feed solution between 2 to 2.7, which corresponds to a SiO_2 concentration between 450 and 600 mg/L, based on the initial concentration of 225 mg/L.

2.4.3 Silica scale mitigation using MD reversal with deionized water

The membranes used in the study are isotropic and the performance of clean membranes is similar regardless of the direction of water flux. Temporarily reversing the MD process by circulating hot water through the distillate channel and chilled water through the feed channel has been demonstrated to be an effective method for mitigating the effects of scaling and fouling in the MD process [27, 28]. Although dissolution of polymeric silica proceeds slowly in solutions with low temperatures and ionic strength [40, 41], and because the scale layer is not subject to compaction in the MD process as in pressure-driven processes, the scale layer may not be strongly adhered to the hydrophobic membrane surface. Thus, temporarily reversing the direction of water flux may facilitate efficient membrane cleaning. To investigate the effectiveness of MD reversal as a cleaning strategy for silica scaling, a new set of experiments was conducted using the same procedure as described in Section 2.4.2 with a new membrane and 225 mg/L SiO_2 solution at neutral pH. Following concentration and scaling, the collected distillate was drained into the feed tank, returning the feed to its initial concentration, and stored. Deionized water was circulated through both feed and distillate channels for 10 minutes to flush any silica solution and the system was drained. The feed and distillate circuits were then swapped, and the system was operated for one hour using deionized water maintained at 50 °C on the distillate side of the membrane and deionized water maintained at 20 °C on the original feed side of the membrane. The system was then drained, and the feed and distillate were reconnected in the standard configuration and operation resumed with the original silica solution maintained at 60 °C as feed and deionized water maintained at 20 °C on the distillate side. To further investigate silica scaling and dissolution behavior during MD reversal, the feed and distillate circuits were then swapped again and operation continued with the silica solution circulated through the original distillate channel and deionized water circulated through the original feed channel.

2.4.4 Silica scale dissolution using MD reversal with NaOH solution

Silica is highly soluble in water above pH 10.7, and depolymerization rates of amorphous silica increase with pH [1]. To investigate the potential of silica scale removal from MD membranes using a high pH solution, an experiment was conducted combining MD reversal followed by a cleaning procedure with a solution of NaOH maintained at a pH of 11. In this experiment, a new membrane and new feed solution with initial concentration of 225 mg/L SiO_2 and neutral pH was concentrated using the same procedure as described in Section 2.4.2. After initial scaling, the feed and distillate channels were swapped to reverse the direction of water flux and the MD process was resumed for an additional 40 hours. The system was then drained, and several cleaning cycles were conducted using a solution of NaOH maintained at pH of 11. During the first cycle, the NaOH solution was maintained at 50 °C and circulated through the original distillate channel (where feed solution was most recently flowing) and deionized water maintained at 30 °C was circulate through the original feed channel for 6 hours. During the second cleaning cycle, the NaOH solution was circulated through the original feed channel and deionized water was circulated through the original distillate channel. The NaOH solution was maintained at 50 °C and the deionized water maintained at 30 °C for 3 hours, then the temperature of the NaOH solution was increased to 60 °C and the temperature of the deionized water reduced to 20 °C and circulated for an additional 3 hours. The pH of the NaOH solution was continuously monitored during the cleaning cycle, and additional NaOH was added as needed to maintain pH of 11. Membrane performance was then tested using a solution of 1 g/L NaCl maintained at 60 °C and deionized water maintained at 20 °C.

2.4.5 Alkaline cleaning as a silica scale management strategy in MD

The tenacity of silica scale has been noted in many investigations, and previous studies have reported remnant silica colloids on membrane surfaces and accelerated scaling rates following cleaning of membranes scaled with silica [12, 36]. To further investigate silica scale dissolution and the potential of an alkaline cleaning process as a silica scale management strategy for the membrane used in this investigation, a set of experiments was conducted with a more aggressive scaling and cleaning approach. Compared to pure water, the presence of up to 0.1 M NaCl has been shown to increase silica dissolution rates [40], and thus the addition of NaCl may be an inexpensive method to improve the effectiveness of membrane cleaning with NaOH. A solution was prepared with an initial concentration of 1000 mg/L SiO_2 and neutral pH and concentrated using a new membrane and similar operating conditions as described in

Section 2.4.2 Following initial scaling, the system was drained, flushed with deionized water, and the membrane was tested using a 1 g/L NaCl feed solution to test performance after scaling. A cleaning cycle was then implemented using a solution containing 0.1 M NaCl (5.85 g/L NaCl) with added NaOH to maintain pH of 11. During the cleaning cycle, the cleaning solution was maintained at 60 °C and distillate maintained at 20 °C and both were circulated through the system until water flux was restored. A second scaling experiment was then conducted with a new solution with an initial concentration of 1000 mg/L SiO_2 and neutral pH using similar operating conditions as described in Section 2.4.2.

2.4.6 Membrane characterization

Membranes were air-dried following scaling experiments. Scale layer morphology and composition were analyzed using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) (Quanta 600, FEI Corp., Hillsboro, OR). Membrane samples were prepared using an ethanol cryofracture technique to preserve the internal pore structure for analysis. The membrane samples were first submerged in ethanol until the pores were completely flooded, then submerged in liquid nitrogen and cut with a razor blade. The membranes were then air dried and gold sputtered before analysis.

3. Results and Discussion

3.1 Effect of pH on silica solubility and polymerization

Silica polymerization rates were determined at pH between 4 and 11 by measuring the change in soluble silica concentration over time using solutions with initial concentration of approximately 600 mg/L SiO_2. To correct for evaporation that occurred in the test samples, volume at each sampling time was determined using the measured evaporation rate of deionized water at similar conditions, which was found to be 0.4 mL/min. Total soluble silica for each solution is presented in Fig. 2. Soluble silica concentration stabilized between 290 and 330 mg/L for solutions of pH 5–8, which is consistent with the solubility of silica at 60 °C and similar pH reported in the literature [1, 42]. Polymerization rates varied considerably with pH, and were highest for solutions of pH 7 and 8, as indicated by the rapid initial decline in total soluble silica concentration for these solutions. The extent of polymerization for solutions at slightly acidic conditions were similar, but the rate of polymerization was lower compared to neutral and slightly alkaline solutions. Moreover, the induction time prior to the onset of silica concentration decline was longer for the solution of pH 6 and even longer for the solution of pH 5 compared to solutions of pH 7 and 8. These results are consistent with other observations that indicate similar silica solubility between pH 5–8, but reduced polymerization rates below pH 7 [7, 21, 43]. Polymerization rate for the solution of pH 9 was initially similar to that of the solutions of pH 7 and 8; however, the extent of polymerization was slightly lower due to the increase in silica solubility. Total soluble silica for solutions of pH 4, 10, and 11 were relatively constant and similar at the end of experiments to the initial concentration, indicating that negligible polymerization occurred at these pHs.

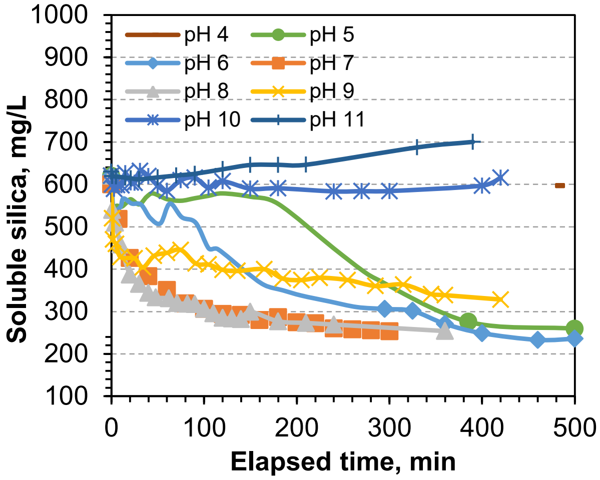

Fig. 2. Measured total soluble silica concentration for test solutions with initial concentration of 600 mg/L SiO_2, initial pH of 4–11, and maintained at 60 °C.

3.2 Effect of pH on silica scaling in MD

3.2.1 Scaling rates and impacts on performance

Baseline performance of the membrane for the experimental configuration used in the study was established by testing with a 1 g/L NaCl feed solution maintained at 60° and distillate maintained at 20 °C. Water flux and thermal efficiency for MD experiments conducted using solutions with initial concentration of 225 mg/L SiO_2 were similar to the measured baseline performance, although generally slightly higher than the water flux of 26.8 L/m^2/hr and thermal efficiency of 0.53 for the 1 g/L NaCl feed solution at similar operating conditions (Fig. 3a–b). Both water flux and thermal efficiency were unaffected in the initial few hours of operation despite an increase of concentration above the solubility limit of silica. After sufficient induction time at supersaturated concentrations, a decline in water flux and thermal efficiency was observed for solutions with pH of 5–9 due to silica polymerization and subsequent scaling of the membrane surface (Fig 3c–d).

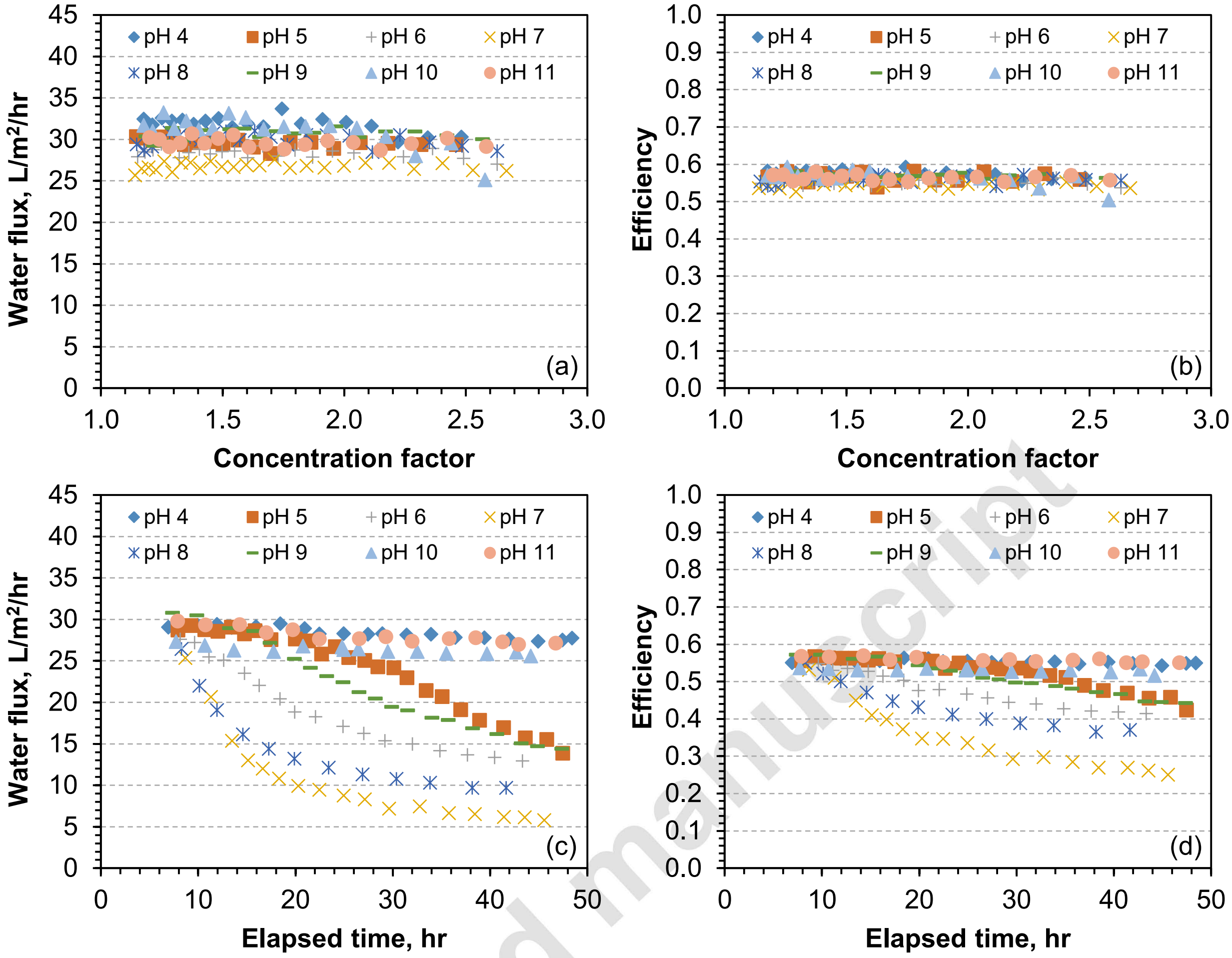

Fig. 3. Measured water flux (a) and thermal efficiency (b) for MD experiments during the initial concentration of 225 mg/L SiO_2 solutions with pH 4–11, plotted by concentration factor. Measured water flux (c) and thermal efficiency (d) for MD experiments using solutions with initial concentration of 225 mg/L SiO_2 and pH 4–11 during distillate cycling phase with concentration factor maintained between 2 and 2.67. All solutions were tested with feed temperature of 60 °C, distillate temperature of 20 °C, and countercurrent flow with velocity of 16.6 cm/s for both feed and distillate.

Impacts of silica scaling on thermal efficiency were less severe than water flux. For example, in the case of pH 7, water flux declined by 78% while the decline in thermal efficiency was only 55%. Also, the calculated conductive heat transfer over the course of the experiment performed at pH 7 declined from approximately 200 W to approximately 150 W. Decline in calculated conductive heat transfer occurred for other solutions with pH 5–9 and followed similar trends as water flux and thermal efficiency. This suggests that the silica scale layer increases overall thermal resistance; however, the thermal conductivity of hydrated solid silica gel is in the range of 0.9–1.2 W/m/K [45, 46]. Taking into consideration the fact that the scale layer may be porous and the thermal conductivity of water between 20° C and 60° C is in the range of 0.6–0.65 W/m/K [47], it can be estimated that the effective thermal conductivity of the scale layer including water-filled pores is between 0.6–1.2 W/m/K. Using an average thickness of 10 μm (based on SEM cross section images) the estimated heat transfer coefficient of the silica scale layer is between

60000 and 120000 W/m^2/K, which is orders of magnitude higher than the total heat transfer coefficient of the membrane [37]. Thus, the reduced conductive heat transfer is more likely related to the adsorbent properties of silica gel, which will be discussed further in Section 3.3.1.

Based on initial concentration of 225 mg/L SiO_2 and the maximum concentration factor of 2.67, silica concentration reached as high as 600 mg/L before scaling substantially impacted performance. The highest rates of flux decline were observed for solutions of pH 6–8 between 10 and 15 hours of experimental time (Fig. 4). After 15 hours, rates of flux decline decreased for pH 6–8 and stabilized near 40 hours. In contrast, rates of flux decline were highest between 25 and 40 hours of experimental time for pH 5, and 15 and 30 hours for pH 9. Rates of decline were generally lower for both pH 5 and 9 and did not begin to stabilize until approximately 60 hours of experimental time. Negligible flux decline was observed for pH of 4, 10, and 11. These observations regarding the influence of pH on performance decline due to silica scaling in MD are consistent with the behavior observed during the batch polymerization tests with solutions containing 600 mg/L SiO_2 at 60 °C, indicating that the timing of polymerization and rate of polymerization are closely tied to silica scaling behavior in the MD process. Distillate conductivity was not affected in any of the experiments despite feed conductivities in a range of 1500–3000 μS/cm, indicating no loss of rejection or wetting of the membrane pores due to scaling or pH effects.

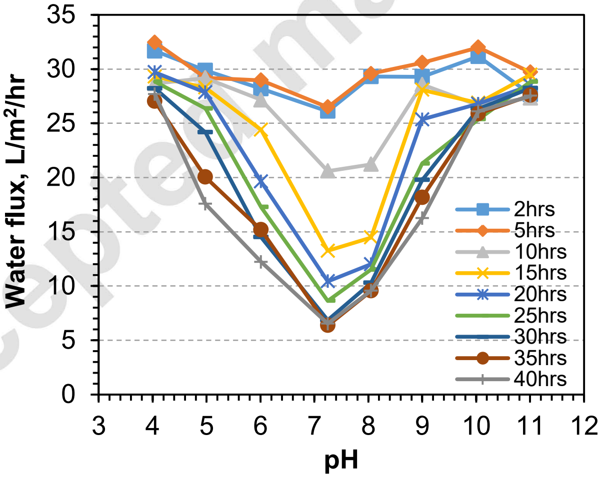

Fig. 4. Water flux for MD experiments with initial concentration of 225 mg/L SiO_2 and maximum concentration of 600 mg/L SiO_2 and pH 4–11. All solutions were tested with feed temperature of 60 °C, distillate temperature of 20 °C, and countercurrent flow with velocity of 16.6 cm/s for both feed and distillate.

3.2.2 Scale morphology

At the end of the experiments the membranes were covered with an opaque scale layer that was beige to light-brown in color. The scale layer was highly hydrophilic—the contact angle of the scaled membranes was impossible to measure and practically zero. SEM analysis of membrane scaling at neutral pH indicated the presence of an amorphous scale layer that completely covered the membrane surface, obscuring the membrane structure and pores (Fig. 5b). EDS analysis detected only silicon and oxygen in the scale layer, confirming its composition to be polymerized silica. Some gaps were observed in the scale layer; however, the gaps were typically only a few microns in thickness and may have resulted from the cracking of the scale layer as it dried (Fig. 5c and 5d). Scale morphology appeared as aggregates of spherical and cylindrical particles approximately 1 micron in size, suggesting that scale layer growth occurred at least in part by deposition of colloidal silica that polymerized in the bulk solution. Cross-section analysis indicated a more uniform scale layer beneath the surface structures except for scattered circular gaps; however, it is not clear whether this is due to more uniform scale growth early in the experiment or because of later polymerization that filled in the gaps between deposited colloidal silica (Fig. 5f). The scale layer did not appear to penetrate the membrane pores and was confined to the membrane surface.

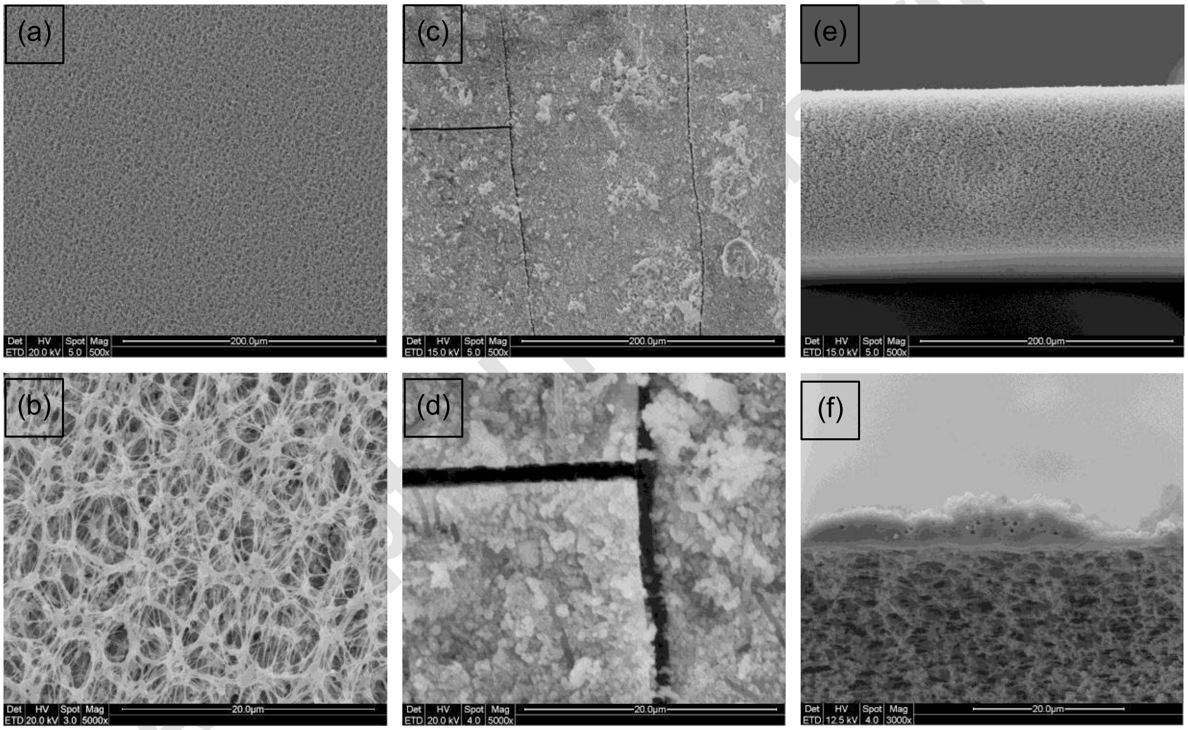

Fig. 5. SEM micrographs of (a, b) new MD membrane surface, (c, d) scaled MD membrane surface, (e) new membrane cross-section, and (f) scaled MD membrane cross-section after >40 hours of MD operation with maximum concentration of 600 mg/L SiO_2 and neutral pH.

3.3 Dissolution of silica scale from MD membranes at high pH

3.3.1 MD reversal with deionized water

The silica scale layer was observed to form as an amorphous deposit on only the surface of the membranes. An experiment using a new membrane and silica solution was conducted using the MD reversal process described in Section 2.4.3 to determine if reversing the direction of vapor flux would promote separation and removal of the scale layer from the membrane surface at neutral pH. Water flux was slightly improved following one hour of MD reversal operation, with an increase from ~7 L/m^2/hr at the end of the first scaling cycle to ~11 L/m^2/hr at the beginning of normal operation with the silica solution maintained at 60 °C and distillate maintained at 20 °C (Fig. 6).

No noticeable changes in the appearance of the scale layer on the membrane surface were observed, and water flux declined to ~9 L/m^2/hr over the next 15 hours (phase ii). Surprisingly, the reverse water flux during MD reversal using deionized water (not shown) was ~18 L/m^2/hr—much higher than the observed water flux in standard configuration before or after the MD reversal process. Also, despite the low flux observed in normal operation and silica scaling still present on the membrane surface, water flux was completely restored when MD reversal was applied to the original silica solution (phase iii). Additional scaling subsequently occurred on the original distillate side of the membrane (now feed side), resulting in a pattern of flux decline similar to that of a new membrane, albeit slightly less severe.

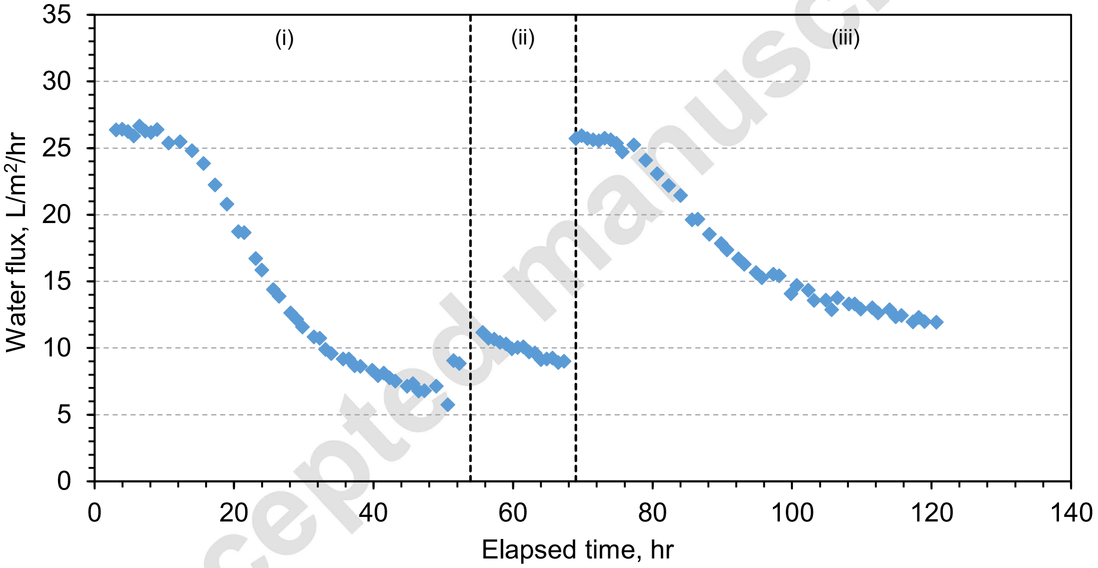

Fig. 6. Water flux and as a function of time for MD tested with maximum concentration of 600 mg/L SiO_2 and neutral pH. (i) Initial scaling cycle with new solution and new membrane and standard MD configuration. (ii) Operation with original concentration silica solution in standard MD configuration after one hour of MD reversal cycle using deionized water in both feed and distillate channels. (iii) Operation with original concentrated silica solution in reverse MD configuration.

At the conclusion of the experiment, SEM analysis confirmed the presence of silica scale completely covering both the feed and distillate sides of the membrane (Fig. 7). The scale layer on the original feed side was similar in thickness to the scale layer formed without MD reversal, indicating that the MD reversal process using deionized water was ineffective at removing the scale. Thus, the restored water flux observed during MD reversal indicates that the silica layer is porous and does not impact MD performance by reducing permeability or blocking the membrane pores, otherwise lower flux would be observed regardless of the direction of mass transfer. This phenomenon can be explained by considering the driving force in MD and possible mechanisms by which silica impacts the MD process. Evaporation from porous media occurs more slowly than evaporation from free surfaces due to the effects of confined spaces, and stronger intermolecular forces between the molecules of a liquid and the surfaces of the pore walls lead to lower evaporation rates [48]. Silica gel is hydrophilic, its adsorbent characteristics with respect to water have been extensively investigated for use in applications such as air dehumidification [49], adsorbent refrigeration [50-54], and adsorbent desalination [55]. Evaporation rates of water from narrow pores of silica gel can be orders of magnitude lower than evaporation rates from a free water surface [48]. Thus, while the silica scale layer does not substantially impede water flow to and from the membrane surface, reduced water flux is observed when the scale layer is present on the feed side because a substantial amount of evaporation is confined to the silica pores.

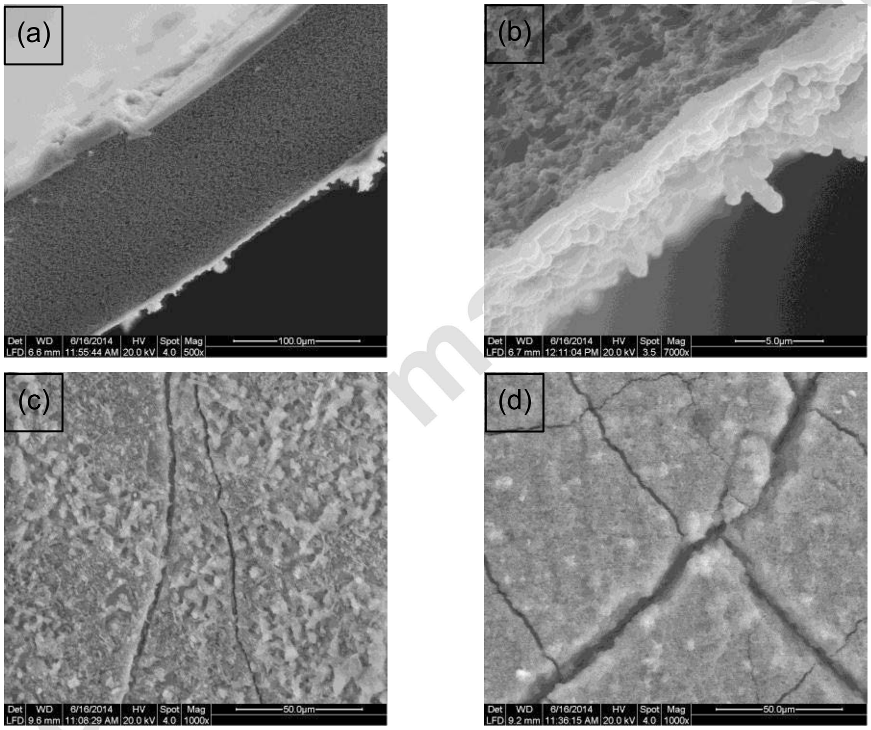

Fig. 7. SEM micrographs of (a) cross-section, (b) cross-section of distillate surface, (c) feed surface, and (d) distillate surface of MD membrane used in MD reversal mode with deionized water experiment. Maximum silica concentration was 600 mg/L SiO_2.

Additionally, adsorption is an exothermic process, and an important parameter of an adsorption pair is the latent heat of adsorption, which is the energy exchanged during adsorption or desorption of a unit mass of sorbate [56]. The latent heat of adsorption is generally higher than the heat of vaporization of the adsorbate and approximately 2800 kJ/kg for the silica gel/water pair, but values from 2500 to 3500 kJ/kg have been reported for commercially available silica gels [57-59]. Thus, the energy required to desorb water from silica gel is higher than the energy required to evaporate pure water. When the feed side of the membrane is covered in silica scale, this results in reduced temperatures at the membrane surface because some fraction of the total vapor transport is a result of desorption, which may explain why a decline in both water flux and conductive heat transfer are observed. In the opposite scenario, when the distillate side of the membrane is covered in silica scale, the adsorbent properties of the silica gel are negligible because it is already fully hydrated and porous enough that it does not impede condensation and transport of liquid water into the bulk distillate channel.

3.3.2 MD reversal with NaOH solution

During this experiment, both sides of a new membrane were exposed to concentrated silica solution and subject to scaling, followed by a cleaning cycle of both membrane surfaces using an NaOH solution maintained at a pH of 11 to promote dissolution of polymerized silica. Scaling and resulting decline in water flux followed a similar trend as in previous experiments at similar conditions (Fig 8a, phase i). Following initial scaling, performance was tested using deionized water as both feed and distillate in both standard and MD reversal configuration (phase ii). Water flux improved slightly to 12–13 L/m^2/hr using deionized water in the first test at the standard configuration, returned to ~26 L/m^2/hr in MD reversal, then improved slightly again in standard configuration to ~15 L/m^2/hr in the second test of standard configuration, confirming the results of the previous experiment that silica scaling only impacts water flux when present on the feed side of the membrane. In the MD reversal configuration using silica solution as feed (phase iii) (same operating conditions as phase i except with feed flowing on the original distillate side of the membrane), water flux was initially comparable to clean membrane performance, but slowly declined to 20 L/m^2/hr as scaling occurred on the original distillate side of the membrane. Performance was then tested again using deionized water as feed and distillate (phase iv). Compared to the end of phase i, water flux increased slightly to 10 L/m^2/hr when the silica solution was returned as feed and the system was operated in standard MD configuration (phase v), which is similar to the performance increase after one hour of MD reversal discussed in Section 3.3.1 (Fig. 6, phase i–ii). A similar phenomenon was also observed when the silica solution was used as feed in MD reversal configuration (phase vi, feed on the original distillate side of the membrane), and water flux increased slightly to about 23 L/m^2/hr compared to the 20 L/m^2/hr observed at the end of phase iii. Thus, while MD reversal does not remove the scale layer, it may cause some changes in structure or its interface with the membrane surface that slightly reduce its impact on performance.

Following the standard and MD reversal silica scaling cycles (phases i–vi), the system was drained and flushed with deionized water and the cleaning cycle using NaOH solution described in Section 2.4.4 was performed (phase vii). Membrane performance was then tested using a 1 g/L NaCl solution, both in standard MD (phase viii) and MD reversal (phase ix) configuration to test performance after cleaning. Water flux was fully restored to 25–27 L/m^2/hr for both configurations. Although distillate conductivity increased slightly during the cleaning cycle due to the swapping of the feed and distillate channels, calculated salt rejection during both performance tests with NaCl solution was very high, greater than 99.99%.

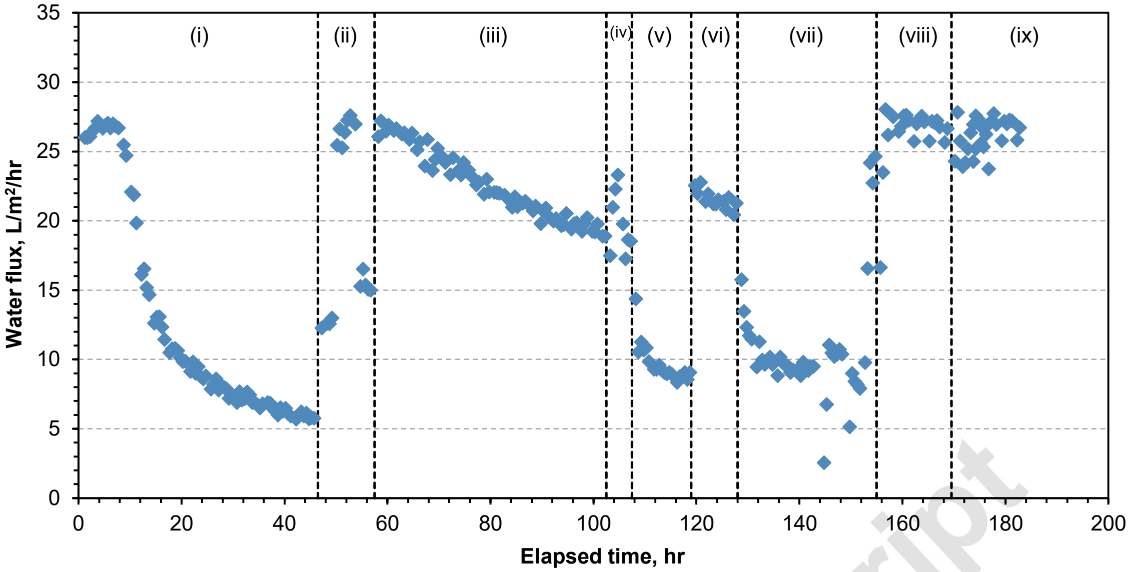

Fig. 8. Water flux and for MD tested with maximum feed concentration of 600 mg/L SiO_2 and neutral pH. (i) Initial scaling cycle with new solution and new membrane and standard MD configuration. (ii) Standard configuration and MD reversal test with deionized water. (iii) Operation with original concentration silica solution in MD reversal configuration after performance test using deionized water. (iv) Standard configuration and MD reversal test with deionized water. (v) Operation with original concentrated silica solution in standard MD configuration after performance test using deionized water. (vi) Operation with original concentrated silica solution in MD reversal configuration. (vii) Cleaning cycle using NaOH solution maintained at a pH of 11. (viii) Performance test in standard MD configuration using 1 g/L NaCl solution. (ix) Performance test in MD reversal configuration using 1 g/L NaCl solution.

Following the scaling testing and cleaning cycles, the membrane was removed from the flow cell, air dried, and analyzed using SEM. Scaling on the surface of the membrane was noticeably more fractured than the membrane tested using only MD reversal with deionized water, and the surface of the membrane was visible between scale plates (Fig. 9). Scaling on both sides of the membrane was also thinner and surface structures composed of spherical colloidal silica were absent. EDS analysis confirmed the scale layers as composed primarily of silicon and oxygen. The results suggest that the application of cleaning cycles using NaOH solution maintained at high pH may indeed promote dissolution of silica scaling on MD membranes, but complete removal of silica scale may require impractically long cleaning cycles due to the low rate of dissolution. Also, membrane performance using pure water or dilute salt solutions is not sufficient as an indicator that complete cleaning has occurred, and silica scale may remain on membrane surfaces despite restored performance.

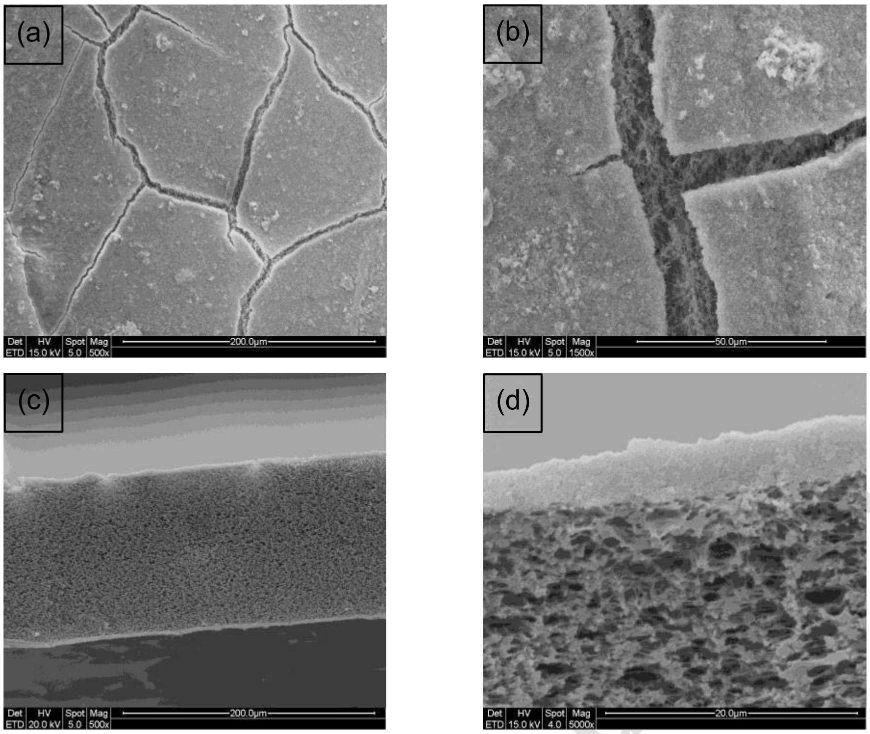

Fig. 9. SEM micrographs of (a, b) feed surface, (c) cross-section, and (d) cross-section of feed surface of MD membrane used in MD reversal with NaOH cleaning experiment. Maximum silica concentration was 600 mg/L SiO_2.

3.3.3 Silica scaling with NaOH and NaCl cleaning with repeated scaling cycles

A third experiment was conducted using a more aggressive scaling and cleaning approach using NaOH cleaning solution maintained at pH 11, which also contained 0.1 M NaCl. Not surprisingly, scaling began sooner and completed in less time than for solutions with initial concentration of 225 mg/L SiO_2. In the first scaling cycle using solution with initial concentration of 1000 mg/L SiO_2 and pH of 7.95, water flux and thermal efficiency were similar to the measured baseline performance in the first few hours of the experiment (Fig. 10). Impacts of scaling were first observed after 5 hours of experimental time, when the concentration was 1.68 times the initial concentration, or about 1,680 mg/L SiO_2 based on initial concentration. Water flux and thermal efficiency both declined rapidly for the next 7 hours, then stabilized somewhat. This pattern of decline is similar to what was observed in experiments with initial concentration of 225 mg/L, but occurred much faster. Water flux declined to ~5 L/m^2/hr after only 20 hours, and the scaling cycle was stopped shortly afterwards. After the initial scaling cycle, water flux and thermal efficiency were slightly higher at 9–11 L/m^2/hr and 0.36–0.4, respectively, when tested using a solution of 1 g/L NaCl. Similar performance was observed at the beginning of the cleaning cycle using a solution of 0.1 M NaCl and NaOH maintained at pH 11; however, both water flux and thermal efficiency increased rapidly and was almost completely restored to measured baseline performance after about 10 hours. To determine if the silica scale could be thoroughly removed, the cleaning cycle was continued for a total of 24 hours before beginning the second scaling cycle using a new solution of 1000 mg/L SiO_2 and pH 8.01.

Initial water flux of the second scaling cycle was slightly lower than that of the first scaling cycle, but still similar to baseline conditions. Water flux was stable for the first couple hours of the experiment, but induction time was less than during the first scaling cycle, and impacts of scaling began after only 2 hours of experimental time. Water flux then declined at a similar rate and followed a similar pattern of decline as the first scaling cycle. The early onset of scaling impacts on water flux indicates incomplete scale removal despite the long duration of the cleaning cycle, and residual silica on the membrane surface acting as seeds for silica polymerization.

Despite slightly lower water flux and total heat transfer, thermal efficiency at the beginning of the second scaling cycle was approximately equal to the efficiency of the new membrane and remained stable for slightly longer than water flux. This may be related to the residual silica scale leftover from the first scaling cycle and suggests that the scale layer may contribute to a slight increase in total thermal resistance. Trends in calculated conductive heat transfer were similar for both scaling cycles, declining from approximately 200 W to 140 W in the first cycle, then increasing to 200 W during the cleaning cycle, and declining again to 140 W by the end of the second scaling cycle.

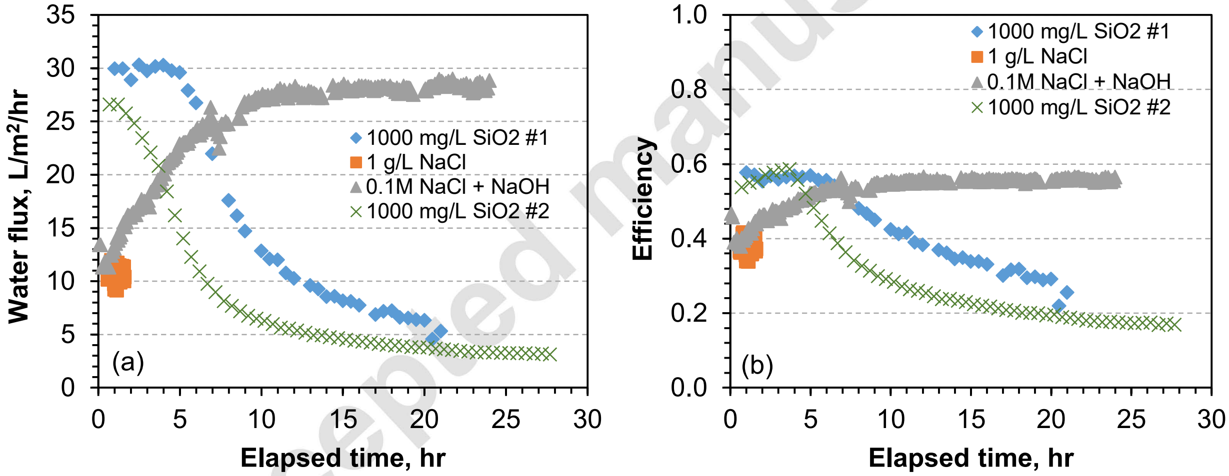

Fig. 10. (a) Water flux and (b) thermal efficiency for MD tested with maximum concentration of 2667 mg/L SiO_2 and neutral pH. First scaling cycle used new silica solution with initial concentration 1000 mg/L SiO_2 and pH 7.95. Performance test using 1 g/L NaCl followed first scaling cycle, followed by cleaning cycle using solution of 0.1 M NaCl and NaOH maintained at pH >11. Second scaling cycle used new silica solution with initial concentration of 1000 mg/L SiO_2 and pH 8.01.

3.4 Some aspects on the practical application of pH adjustment to natural water resources

Experimental results suggest that pretreatment of feed water by pH adjustment is more effective as a silica scale management strategy than scale removal with a high pH cleaning solution. Silica polymerization and scaling risk in MD was substantially reduced at pH of below 5 or above 10, but once scale formed, it was difficult to completely remove with deionized water or an NaOH solution of pH 11. However, pH adjustment of natural water resources may be costly and may lead to increased scaling risk of other minerals involving ions such as calcium and magnesium, which are commonly present in groundwater resources. Also, carbonate alkalinity acts as a buffer, and water with high alkalinity may require more acid or base to adjust pH. Thus, the total chemical composition of a natural water resource must be carefully considered to determine if acidification or alkalization is an appropriate strategy to reduce risk of silica scaling. Also, implications of pH adjustment on post-treatment requirements of the brines should be considered.

To address some of these concerns, the potential costs of pH adjustment and its impacts on mineral scaling tendencies were considered using data obtained from the cooling tower makeup water of a geothermal power plant. The original water resource was close to saturation with respect to silica, but relatively low in salinity, hardness, and alkalinity, and thus an ideal candidate for potential treatment using MD with pH adjustment. The major constituents in the synthetic solution are summarized in Table 1.

Table 1. Composition of real cooling tower makeup water from the Tuscarora geothermal power plant (Nevada, USA) and synthetic solution with similar chemistry

Composition	**Concentration (mg/L)**	
	Real Tuscarora makeup (T-MU) cooling water	Synthetic T-MU solution
Sodium, Na^+	23.5	74.8
Potassium, K^+	8.94	8.94
Magnesium, Mg^{+2}	2.54	2.54
Calcium, Ca^{+2}	9.59	9.59
Barium, Ba^{+2}	0.22	0.22
Aluminum, Al^{+3}	0.23	0.23
Iron, Fe^{+3}	0.24	0.24
Chloride, Cl^-	8.33	33.8
Sulfate, SO_4^{-2}	12.4	12.4
Silica, SiO_2	90	90
Alkalinity (as mg/L $CaCO_3$)	84	84
pH	7.0	7.0

Synthetic solutions were prepared with similar chemical composition as the real water sample. Two experiments were conducted using 100 mL of synthetic T-MU solution to determine how much HCl or NaOH is required to adjust pH to outside the range where silica polymerization and scaling is a substantial risk. Concentrated HCl (32% by volume) was added to one sample to lower the pH to 5. In the other sample, a 0.2 g/L NaOH solution was added until pH reached 11. NaOH required progressively higher dosing per cubic meter as pH increased (Fig. 11a). This is not surprising due to the buffering effect of silica with increased pH as silicic acids and monomeric silica are converted into soluble silicates. Assuming a cost of \$300 per metric ton for industrial-grade concentrated HCl, and \$400 per metric ton for 99% pure NaOH, the amount of HCl and NaOH required to reach the desired pH was used to calculate the approximate cost for pretreatment of the Tuscarora T-MU water. The cost of pH adjustment was relatively low at about \$0.025 per m^3 using HCl and just over \$0.04 per m^3 using NaOH (Fig. 11b).

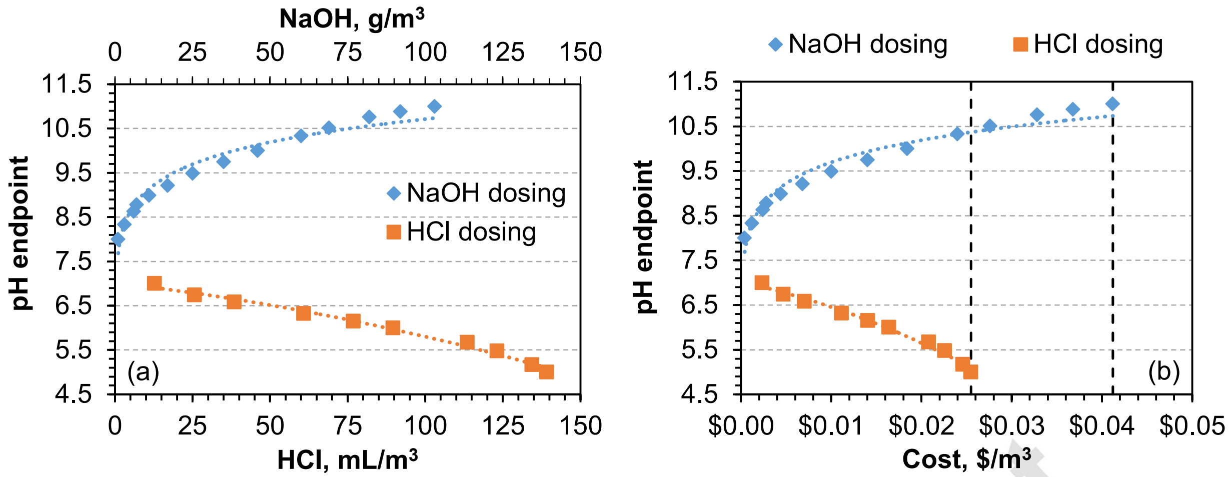

Fig. 11. (a) HCl and NaOH dosing required to adjust synthetic Tuscarora T-MU solution to pH 5 and 11, respectively. (b) Estimated cost of pH adjustment of Tuscarora T-MU water based on results of experimental results from adjustment of synthetic solution.

Scaling tendencies were calculated using OLI Stream Analyzer, and found that the original T-MU water exceeded saturation with respect to $CaCO_3$ above pH 9, which is not high enough to substantially reduce silica scaling risk. Considering the lower cost of pH adjustment with HCl, feed water acidification may be a viable pretreatment strategy in this particular case. This analysis did not consider the potential costs of neutralization of brine following treatment with MD. However, it should be noted that in some cases brine neutralization may not be required. For example, well injection is the most common method of brine disposal for inland desalination, and it may be preferable to inject brine at low pH to reduce mineral scaling during the injection process. Also, because it is not limited by the osmotic pressure difference between the feed and permeate, the successful application of scale prevention strategies with MD may allow sufficiently high water recoveries that a zero-liquid-discharge process could be considered.

4. Conclusions

This study investigated the application of pH adjustment as a pretreatment strategy for the prevention of silica scaling in the MD process applied to water supersaturated with respect to silica, and the effectiveness of various cleaning strategies for MD membranes scaled with silica. It was determined that both acidification and alkalization are effective pretreatment strategies to prevent silica scaling if pH can be adjusted outside the range where silica polymerization occurs, i.e. lower than 5 or higher than 10. Outside of this pH range, the MD process was capable of producing high quality distillate with silica concentrations as high as 600 mg/L for more than 40 hours and negligible decline in performance. For water resources containing high silica but relatively low in carbonate alkalinity or hardness, pretreatment using HCl or NaOH may be an inexpensive pretreatment strategy for water resources with no adverse effects on performance characteristics including water flux, thermal efficiency, or rejection.

Removing silica scale once it occurs proved to be much more difficult. Simply flushing the membrane using deionized water by reversing the temperature difference between the feed and distillate had no substantial effect on removing silica scale. Despite increased silica solubility and complete lack of polymerization at high pH, the application of a cleaning solution maintained at pH >11 was only partially effective at dissolving polymerized silica from membrane surfaces. Although cleaning cycles were successful at restoring water flux even after operation using silica concentrations exceeding 2500 mg/L, scaling occurred more rapidly on cleaned membranes when exposed to new silica solutions compared to new membranes. If complete cleaning of silica-scaled MD membranes is possible at all, it would likely require very long and impractical cleaning cycles based on the results of this investigation. Therefore, pretreatment and careful monitoring of performance for indications of scaling is imperative for long-term implementation of MD as a treatment strategy for silica-laden water resources.

Silica scaling on MD membranes was found to adversely affect water flux and thermal efficiency, although the impacts on thermal efficiency were less severe due in part to the insulating effect of the scale layer. Surprisingly, silica scaling was found to adversely affect MD performance only when present on the feed side of the membrane. Even with silica scale completely covering the membrane surface, performance was almost identical to that of a new membrane when the direction of water flux was reversed, indicating that silica scaling does not impede mass transport in the MD process by reducing overall permeability of the scale layer and membrane. Rather, it is proposed that the pore structure and adsorption properties of silica gel lead to reduced evaporation rates at the interface between the scale layer and membrane surface.

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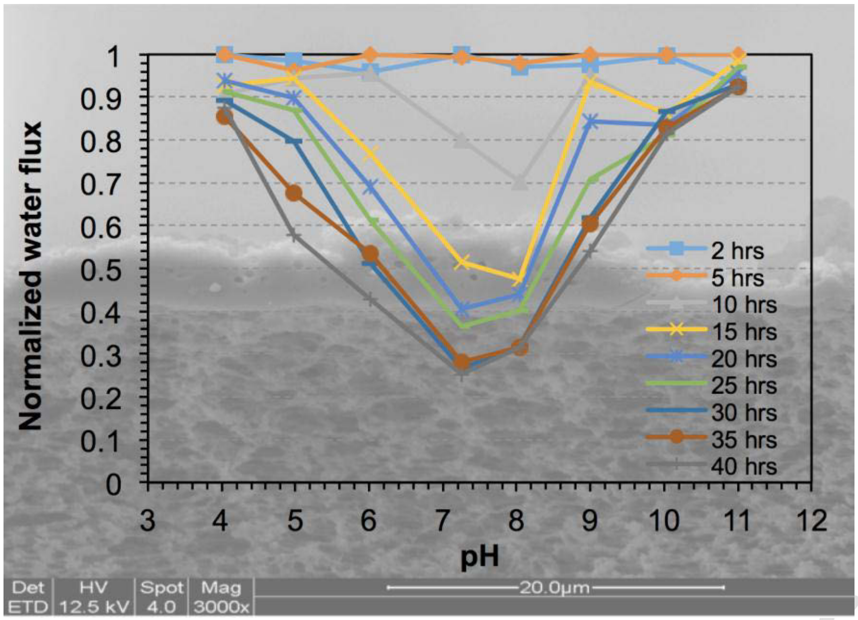
Highlights:

- Silica scaling in membrane distillation can be reduced with feed pH adjustment
- At similar pH and concentration, scaling rates correlate to polymerization rates
- Acidification is less costly than alkalization for comparable scale reduction
- Silica scale may be partially removed by rinsing with NaOH solution
- Silica scale has negligible impact on MD performance with temperatures reversed



Graphical abstract