High recovery of concentrated RO brines using forward osmosis and membrane distillation

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A B S T R A C T
Vacuum-enhanced direct contact membrane distillation (VEDCMD) and forward osmosis (FO) were investigated for water recovery enhancement in desalination of brackish water. Past studies have demonstrated that both VEDCMD and FO can be effectively utilized in the treatment of a wide range of highly concentrated feed solutions. In the current study, two reverse osmosis (RO) brine streams with total dissolved solids concentrations averaging 7500 and 17,500 mg/L were further desalinated by VEDCMD and by FO. In both processes, high water recoveries were achieved; however, recoveries were limited by precipitation of inorganic salts on the membrane surface. Various cleaning techniques were able to remove the scale layer from the membrane and restore water flux to almost initial levels. FO achieved water recoveries up to 90% from the brines and VEDCMD achieved water recoveries up to 81% from the brines. Addition of a scale inhibitor during both processes was effective at maintaining high water flux for extended time. When considering the total water recovery (the recovery from the RO processes combined with the batch recovery from the VEDCMD or FO process), greater than 96 and 98% total recoveries were achieved for the two different brine streams.

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1. Introduction

Brackish water desalination is increasingly being practiced by inland communities to augment their limited fresh water resources [1]. Brackish water salinities range from 1000 to 8000 mg/L total dissolved solids (TDS) compared to approximately 35,000 mg/L TDS for ocean water. Eastern Municipal Water District (EMWD) in Southern California has implemented the Perris Basin Desalination Program to reduce its dependence on a costly and potentially limited supply of imported water. In order to utilize high-TDS groundwater from its basins, EMWD is operating two reverse osmosis (RO) desalination facilities and designing a third. The groundwater is blended with RO product water from the facilities to achieve product water with less than 500 mg/L TDS in the distribution system. The RO brine stream is discharged into the 22-mile-long Temescal Valley Regional Interceptor, which is a non-reclaimable waste pipeline that connects EMWD to the Santa Ana Regional Interceptor (SARI). The brine is then transported by the SARI to Orange County Sanitation District (OCSD) for treatment and discharge. Operation of all three RO facilities will ultimately produce brine quantities in excess of EMWD’s capacity in the SARI system, and additional capacity is not available. Furthermore, the cost of treatment and disposal by OCSD is expected to increase. Therefore, like many other inland water utilities, EMWD must improve water recovery. Additional brine treatment to approach zero liquid discharge (ZLD) would not only enable EMWD to produce more water, but also to reduce their reliance on existing brine disposal methods. 

In 2005, the California Department of Water Resources and the United States Bureau of Reclamation sponsored a study at EMWD with the objectives of increasing water recovery and decreasing brine volume [2,3]. Two RO brines were generated during the investigation. The first brine was concentrate from the primary RO process. Water recovery in the primary RO system was limited to 70% to avoid precipitation of sparingly soluble salts on the membranes. As part of the effort to achieve higher recovery, the primary RO brine was softened and further treated in an electrodialysis reversal (EDR) system or a secondary RO system, thus generating the second brine. In further studies, the brines from the primary and secondary RO systems were used to evaluate potential ZLD systems as part of the Perris Basin Desalination Program; this includes the
current investigation of membrane distillation (MD) and forward osmosis (FO).

Current technologies for brine treatment comprise well-established processes such as pressure-driven membrane processes (e.g., RO and nanofiltration (NF)) and current-driven membrane processes (e.g., electrodialysis (ED) and EDR) [4]. Although well-established, these processes are limited in their ability to achieve high water recovery. Total water recovery in these processes is limited in order to prevent scale formation and fouling of the membranes and to prolong membrane life [5]. Energy costs of ED and EDR are directly proportional to the feed water salinity and the rate of salt removal, and therefore, desalination of high salinity solutions (e.g., RO brines) is not economical [6].

More recently, ZLD or near-ZLD systems are being considered for recovery of clean water and minimization of brine streams. ZLD or near-ZLD systems consist mainly of thermal methods such as brine concentrators, crystallizers, thermal evaporators, and spray driers that reduce concentrate to a slurry or solid product that can be disposed of in landfills. These processes are capable of recovering an ideal treatment method for highly saline feeds. In a previous study [9–12] and thus, they are not typically used.

Advanced processes are sought that can enhance water recovery without the limitations associated with the current processes. Previous studies have demonstrated that membrane contactor processes such as MD and FO can potentially minimize brine volume at lower energy expenditure and with less complexity [13,14]. In the current study, direct contact MD (DCMD) and FO are investigated as potential processes to enhance water recovery in brackish water desalination—or more specifically, to enhance water recovery from brines generated during RO desalination of brackish water.

DCMD is a thermally driven separation process involving the evaporation of water through the pores of a hydrophobic, microporous membrane and direct condensation of that water vapor into a cold water stream flowing on the support side of the membrane [15]. In DCMD, warmer feed water is in contact with the active side of the membrane and a cooler water stream is in direct contact with the support side. The driving force for mass transfer in DCMD is the vapor pressure difference across the membrane induced by the temperature difference across the membrane. Because the partial vapor pressure of water is only minimally affected by increased concentrations of dissolved solids, DCMD has the potential to be an ideal process for highly saline feeds. In a previous study [14], it was shown that water flux in DCMD was nearly constant when feed concentrations of highly soluble NaCl or seawater salts were increased from 0.6 to 73 g/L.

The performance of DCMD can be improved in different ways. High-temperature DCMD (e.g., DCMD with the same temperature difference, but at higher temperatures) can achieve higher water fluxes than low-temperature DCMD [14]. This is because vapor pressure increases exponentially with increasing water temperature. In another configuration, vacuum-enhanced DCMD (VEDCMD), the cooler water stream flows under negative pressure (vacuum). Under specific operating conditions, VEDCMD has been shown to increase flux by up to 85% compared to the conventional DCMD configuration [14].

FO is an osmotically driven membrane separation process involving the diffusion of water through a semipermeable membrane. The driving force for mass transport is the difference in osmotic pressure between the feed solution and a draw solution; water diffuses from the feed solution of higher chemical potential (lower osmotic pressure) to a draw solution of lower chemical potential (higher osmotic pressure). As water diffuses through the membrane, the feed solution becomes concentrated and the draw solution is diluted; and thus, the draw solution must be reconcentrated in order to maintain the osmotic pressure driving force. FO has been shown to effectively concentrate a variety of feed streams, including municipal wastewater, landfill leachate, and grey water in life support systems [13,16–22].

This paper presents the findings of a bench-scale study evaluating VEDCMD and FO as potential processes for the concentration of brackish water RO brines. The importance of specific operating conditions, membrane cleaning, and chemical pretreatment on membrane performance was investigated for both processes. Two points specifically addressed in this study were (1) if the performance of the VEDCMD process would be substantially greater than that of the FO process considering that the flux in DCMD is only minimally affected by high concentrations of dissolved solids and (2) if the anticipated increase in flux for high-temperature VEDCMD would outweigh the environmental and economic benefits of low-temperature VEDCMD (which can operate off of waste heat sources).

2. Materials and methods

2.1. Feed solutions

The first feed solution (brine A) was the concentrate from the primary RO desalters at the EMWD groundwater desalting facilities; the average TDS concentration of brine A was approximately 7500 mg/L. The second feed solution was generated from brine A using three treatment steps. In the first step, brine A was chemically softened using sodium hydroxide and the precipitated solids were removed by clarification, conventional dual-media filtration, and 5-µm cartridge filtration. In the second step, the filtrate was treated with sulfuric acid and scale inhibitor (Vitec 3000, Avista Technologies, Inc., San Marcos, CA). And in the third step, the brine was further concentrated in a secondary RO desalter. The secondary RO concentrate (brine B) had an average TDS concentration of approximately 17,500 mg/L.

The ion compositions of the brines were analyzed using several methods. Calcium, magnesium, silica, and sodium were measured using inductively coupled plasma/atomic emission spectrometry (EPA Method 200.7) [23]; sulfate and chloride using ion chromatography (EPA Method 300.0) [24]; alkalinity, hydroxide, carbonate, and bicarbonate using an alkalinity titration (Standard Method 2320 B) [25]; and total solids and TDS using evaporation (Standard Method 2540 B and C) [25].

2.2. VEDCMD experiments

Two flat-sheet membranes were tested in the VEDCMD experiments. The first was a laminated membrane made with a polytetrafluoroethylene (PTFE) active layer over a polypropylene (PP) support mesh and the second was asymmetric PP membrane. Both membranes have a nominal pore size of 0.22 µm and both were acquired from GE Osmonics (Minnetonka, MN). The membranes were tested in a modified SEPA-CF cell (Osmonics, Minnetonka, MN), which has symmetric channels on both sides of the membrane to allow for tangential flow on both the active and support sides of the membrane. The active membrane surface area was 139 cm².

The performance of the VEDCMD process was evaluated under various operating conditions using a bench-scale membrane test unit (Fig. 1). 4 L of feed solution were added to the feed reservoir and heated to either 40 or 60 °C and 2 L of deionized water were added to the permeate reservoir and cooled to 20 °C. Feed and permeate temperatures were monitored using dual channel digital thermometers (DigISense DualLogR, Cole-Parmer, Vernon Hills, IL).
2.3. FO experiments

A flat-sheet cellulose triacetate (CTA) FO membrane was utilized in the FO experiments. The CTA membrane was specifically developed for FO applications and was acquired from Hydration Technologies Inc. (Albany, OR). In previous investigations [21,22], this membrane outperformed other semipermeable membranes (i.e., RO membranes) tested in FO mode.

The performance of the FO process was evaluated using a bench-scale membrane test unit (similar to the VEDCMD apparatus) coupled with a pilot-scale RO system (Fig. 2). The pilot-scale RO system supplied the FO system with a constant-concentration draw solution (50 ± 2 g/L NaCl). ACS grade NaCl (Fisher Scientific, Pittsburgh, PA) was used to prepare the draw solution. The draw solution was recirculated on the support side of the FO membrane.

The feed solution and the deionized water were recirculated countercurrently on their respective sides of the membrane at 1.5 L/min. For each feed temperature, two different permeate pressures (vacuums) were tested: 660 mmHg (abs) and 360 mmHg (abs) (deeper vacuum). Permeate pressure was controlled using a needle valve at the water inlet to the permeate side of the membrane. As water evaporated through the membrane, the concentration of the feed stream slowly increased and excess water from the permeate reservoir was allowed to overflow; the overflow rate was used in calculating water flux and batch recovery. Conductivity meters (Jenway 4320, Jenway Ltd., UK) were used in the feed and permeate reservoirs to calculate salt rejection.

2.4. Cleaning experiments

Membrane cleaning procedures were developed to remove scale deposits from the membrane surface and the system (e.g., the tubing and the membrane cell). Membrane performance parameters (water flux and solute rejection) were evaluated before and after each cleaning cycle through a series of scaling experiments. The scaling experiments were conducted with brine A as the feed solution. For VEDCMD, the higher feed temperature (60 °C) was used to expedite scaling and for FO, a saturated NaCl draw solution (approximately 350 g/L) was used to expedite scaling.

The first cleaning method, a chemical method, was tested on both the VEDCMD and FO membranes. A chemical cleaning solution consisting of 0.029 M disodium ethylenediaminetetraacetic acid (Na₂EDTA) and 0.058 M sodium hydroxide (NaOH) was used. First, 4 L of deionized water were flushed through the feed side of the system to remove loose deposits. Second, 2 L of the cleaning solution were recirculated on the feed side for 30 min. Then, for VEDCMD, the flow was stopped and the membrane and system were soaked for 1 h in the cleaning solution; and for FO, the flow was reduced to 0.2 L/min for 1 h. Last, 8 L of deionized water were flushed across the active side of each membrane.

The second cleaning method, osmotic backwashing [26], was investigated for the FO process only. In this method, which is increasingly being used in full-scale RO desalination operations [27–29], the draw solution was replaced with deionized water and the feed solution was replaced with a draw solution of 100 g/L NaCl; both streams were recirculated on either side of the membrane for 20 min, thereby reversing the flow of water through the membrane and removing solids reversibly deposited on the membrane surface. Subsequently, each side of the membrane was thoroughly rinsed with deionized water and the feed solution and draw solution were re-introduced and recirculated on their respective sides of the membrane.

2.5. Scale inhibition experiments

Two scale-inhibitors, Pretreat Plus 0400 and Pretreat Plus Y2K (King Lee Technologies, San Diego, CA), were used in this study. Pretreat Plus 0400 was selected specifically to inhibit the formation of calcium sulfate and calcium carbonate and Pretreat Plus Y2K was selected to inhibit the formation of a broad spectrum of minerals (e.g., silica, calcium carbonate, barium/strontium sulfate, iron, aluminum, and calcium phosphate) [30]. Brine A was dosed with scale inhibitor during specific VEDCMD and FO experiments. For the VEDCMD experiments, Pretreat Plus 0400 doses ranged from 2 to 8 mg/L. For the FO experiments, the Pretreat Plus Y2K recommended dose of 10 mg/L [5] was used.

3. Results and discussion

3.1. Brine chemical analysis

The compositions of brines A and B are summarized in Table 1. The TDS concentration of brine B is approximately 2.5 times greater than that of brine A. Considering individual ions, sodium and chloride ion concentrations in brine B are higher than in brine A, while calcium, sulfate, and silica concentrations in brine B are lower than in brine A. These differences are due to the softening treatment of brine A before it was fed to the secondary RO to generate brine B.
Table 1

<table>
<thead>
<tr>
<th>Brine composition</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brine A</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>Sodium, Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>991</td>
</tr>
<tr>
<td>Calcium, Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>1032</td>
</tr>
<tr>
<td>Magnesium, Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>318</td>
</tr>
<tr>
<td>Chloride, Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2823</td>
</tr>
<tr>
<td>Sulfate, SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>1553</td>
</tr>
<tr>
<td>Bicarbonate, HCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>576</td>
</tr>
<tr>
<td>Carbonate, CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>5.2</td>
</tr>
<tr>
<td>Alkalinity as CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>470</td>
</tr>
<tr>
<td>Silica, SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>116</td>
</tr>
<tr>
<td>Total phosphate, P&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.4</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>7500</td>
</tr>
<tr>
<td>Osmotic pressure, π (psi)</td>
<td>60</td>
</tr>
</tbody>
</table>

The softening treatment was used to reduce calcium, sulfate, and silica concentrations in brine A to prevent scale formation on the RO membranes during secondary RO. The reductions in calcium, sulfate, and silica concentrations and the concentration process in the secondary RO system resulted in the increase in relative concentrations of sodium and chloride in brine B.

Salts that exceed their saturation and precipitate out of solution do not affect osmotic pressure, but will cause scaling of the membrane. A chemical simulation program was used to determine the saturation level of the potentially scaling minerals. In brine A, SiO<sub>2</sub> and CaSO<sub>4</sub> were found to be at 99 and 89% saturation, respectively; in brine B, SiO<sub>2</sub> and CaSO<sub>4</sub> were found to be at 57 and 50% saturation, respectively. Thus, it was anticipated that membrane scaling would occur earlier during experiments with brine A. Furthermore, because the solubility of CaSO<sub>4</sub> is inversely proportional to temperature (decreasing solubility with increasing temperature); a higher percent saturation would be expected for higher brine temperatures. However, the decrease in solubility (approximately 200 mg/L from 40 to 60 °C) results in a 0% change in percent saturation [31]; thus, inverse temperature effects are essentially negligible for the feed temperatures (40 and 60 °C) in the current VEDCMD investigation [32].

3.2. Vacuum enhanced direct contact MD

3.2.1. Water flux and recovery

Water flux as a function of concentration factor (CF) is illustrated in Fig. 3a and b for VEDCMD of brines A and B, respectively: batch recovery is also shown on the top x-axes. CF is the ratio between the concentration of the feed solution at any time and the initial feed concentration. Batch recovery is the cumulative volume of permeate collected during an experiment until a point in time normalized to the initial feed volume. CF is related to batch recovery by CF = 1/(1 – R); thus, CF and R are not linearly related.

The PTFE membrane was the only membrane initially tested because it was known to have higher permeability, and therefore higher water flux than the PP membrane [14]. The experiments were terminated when water flux reached approximately 5 L/(m<sup>2</sup> h). During all experiments, salt rejection was greater than 99.9%.

It is apparent from the results in Fig. 3a and b that flux decline is substantial for almost all experimental conditions. When comparing the flux declines in these experiments with those from a previous investigation (black line in Fig. 3a) [14], it can be seen that water flux decreases much more rapidly in the current investigation. In the previous investigation, water flux decreased only slightly with increasing feed TDS concentration because the salts studied were NaCl and sea salt—neither of which contains ions that are likely to exceed their solubility and form scale on the membrane in the range of feed concentrations tested.

Also in Fig. 3a and b, initial water fluxes were substantially greater in experiments conducted with a temperature difference of 40 °C than those conducted with a temperature difference of 20 °C. A higher temperature difference results in a higher vapor pressure difference across the membrane and a stronger driving force for water evaporation. Initial water fluxes were even higher when the permeate pressure was lowered from 660 mmHg (abs) to 360 mmHg (abs). A lower permeate pressure results in a higher partial vapor pressure difference and an increased driving force [14].

In experiments conducted with brine A (Fig. 3a), a relatively constant water flux was observed up to a CF of approximately 1.75, at which point a rapid flux decline was observed for all experiments. These flux declines were preceded by observed changes in feed water clarity at CFs of approximately 1.5; this was likely evidence that silica and calcium sulfate had exceeded their saturation and were precipitating out of solution. Thus, the rapid flux declines were likely caused by precipitated solids (mineral scale) on the membrane surface that blocked the transport of water vapor through the pores. SEM micrographs of the membrane surfaces after experiments revealed thick scale layers on the membrane (Fig. 4). Calcium sulfate crystals and some silica aggregates are shown in the inset micrograph of Fig. 4.
The fact that the onset of flux decline in Fig. 3a and b is earliest and most rapid in the experiments that started with the highest initial flux (ΔT = 40 °C, \( P_o = 360 \text{mmHg (abs)} \)); and latest and most gradual in the experiments that started with the lowest initial flux (ΔT = 20 °C, \( P_o = 660 \text{mmHg (abs)} \)) can also be explained by the exponential relationship between water flux and concentration polarization (CP) at the feed–membrane interface. CP increases exponentially with increasing water flux according to the classical film model [33]:

\[
CP_{\text{modulus}} = \frac{C_m}{C_p} = (1 - R_0) + \frac{R_0 J}{k} e^{\Delta T/k}
\]

where \( C_m \) is concentration at the membrane, \( C_p \) is concentration in the bulk feed solution, \( R_0 \) is the observed salt rejection, \( J \) is the permeate flux, and \( k \) is the solute mass transfer coefficient on the feed side. Therefore, at higher water fluxes, the increased solute concentration near the membrane surface would cause SiO and CaSO to exceed their solubility and form scale on the membrane. Along the same lines, the highest batch recovery was achieved in the experiment with the lowest initial flux (ΔT = 20 °C and \( P_o = 660 \text{mmHg (abs)} \)).

When comparing results from experiments conducted with brine A (Fig. 3a) to those conducted with brine B (Fig. 3b), it is apparent that TDS concentration has minimal effect on initial water flux—a substantial advantage over pressure-driven membrane desalination processes. Also, when comparing results of brine A and brine B, similar trends in flux with time were observed. Much higher CFs (or batch recoveries) were achieved for brine B (Fig. 3b) than for brine A (Fig. 3a). Higher batch recoveries were anticipated for Brine B based on the water quality data (Table 1) and percent saturation values that were lower in brine B due to the softening process. Also, brine B contained residual scale inhibitor, which was used to inhibit the formation of CaSO and SiO during the secondary RO treatment [5].

3.2.2. VEDCMD membrane cleaning

One of the objectives of the study was to investigate the ease by which the scale layers could be removed from the membrane surface. The membranes were chemically cleaned with Na2EDTA solution after their water flux dropped below 5 L/(m² h). Brine A was used as the feed in these experiments because it scaled the membrane more rapidly than brine B (Fig. 3). Also, in order to expedite scale formation, experiments were conducted with a temperature difference of 40 °C instead of 20 °C.

Water flux and batch recovery before and after membrane cleaning are shown in Fig. 5a and b for the PTFE and PP membranes, respectively. The PP membrane was included in the cleaning experiments to compare its fouling tendency and chemical resistance with the PTFE membrane. The performance of the PTFE membrane (Fig. 5a) was different before and after cleaning. The initial water flux after cleaning was the same as the initial flux before cleaning, except that after cleaning there was an immediate onset of flux decline. This suggests that the majority of scale was removed from the membrane following cleaning, thus restoring water flux to its initial level [34]; however, the residual scale that did remain on the membrane most likely provided sites for crystallization, leading to more rapid scale formation and earlier onset of flux decline after cleaning. The performance of the PP membrane (Fig. 5b) was similar before and after cleaning. This implies that scale deposition on the PP membranes is less strongly adhered to the membrane and can be removed using a simple cleaning method.

Both the PTFE and PP membranes are characterized as having high chemical resistance [35,36]. To ensure that exposure to the EDTA cleaning solution did not damage the membranes, their rejection was monitored throughout the experiments; both membranes maintained greater than 99.9% salt rejection before and after cleaning. This suggests that the PTFE and PP membranes are indeed chemically resistant to the EDTA over short terms.

3.2.3. VEDCMD with scale inhibitor

The effect of dosing brine A with CaSO scale inhibitor (Pretreat Plus 0400) was investigated in a separate set of VEDCMD experiments. The experiments were conducted under low flux conditions (ΔT = 20 °C, 660 mmHg (abs)) using the PTFE membrane. Water flux...
as a function of CF and batch recovery is illustrated in Fig. 6. For reference, a VEDCMD experiment was performed without addition of scale inhibitor (solid black line).

A very rapid flux decline followed by partial recovery was observed during all of the experiments with the scale inhibitor. Although the flux recovery is not fully understood, the unusual flux behavior is likely due to the formation of amorphous silica. Amorphous silica and silicates precipitate in a series of steps generating soft and then hard gels [37]. In the current investigation, it is likely that the rapid flux decline was due to the formation of soft silica gels that form on the membrane surface. Further reaction of the silica resulted in hard gels that were scoured off of the membrane surface [37]; this resulted in the flux recoveries observed in Fig. 6. It can also be seen in Fig. 6 that the highest batch recovery occurred with a scale inhibitor dose of approximately 4 ppm, yet, further optimization and better understanding of the chemical and physical phenomena are needed.

### 3.2.4. VEDCMD water recovery

Approximately 62% batch recovery was achieved for VEDCMD of brine A using the PTFE membrane at the lowest flux conditions ($\Delta T = 20^\circ C, 660$ mmHg (abs)) (square symbols in Fig. 3a). The use of scale inhibitor brought the water recovery to approximately 78% (Fig. 6). In comparison, greater than 80% batch recovery was achieved for VEDCMD of brine B using the PTFE membrane at the lowest flux conditions ($\Delta T = 20^\circ C, 660$ mmHg (abs)) (square symbols in Fig. 3b).

In order to determine the total water recovery, the recovery from EMWD’s RO processes and the batch recovery from the VEDCMD process were both considered. The total recovery was calculated using:

$$R_{\text{tot}} = R_{\text{RO}} + (1 - R_{\text{RO}})R_{\text{VEDCMD}}$$  \hspace{1cm} (2)

where $R_{\text{tot}}$ is the total water recovery, $R_{\text{RO}}$ is the water recovered from EMWD’s RO processes, and $R_{\text{VEDCMD}}$ is the batch recovery from the current study. For brine A, $R_{\text{RO}}$ was 70% and $R_{\text{VEDCMD}}$ was 62%. For brine B, $R_{\text{RO}}$ was 89% and $R_{\text{VEDCMD}}$ was 80%. Thus, when combining the recoveries of the RO processes and the VEDCMD process, the total recovery was greater than 89% for brine A and greater than 98% for brine B.

### 3.3. Forward osmosis

#### 3.3.1. Water flux and recovery

During FO experiments, the draw solution was maintained at a constant concentration of 50 ± 2 g/L NaCl (i.e., constant osmotic pressure) using a pilot-scale RO system. The NaCl draw solution concentration was high enough to produce initial water fluxes comparable to those achieved using VEDCMD at a temperature difference of $20^\circ C$. As water crossed the FO membrane, the concentration of the feed solution, and thus its osmotic pressure, slowly increased. At the same time, the osmotic pressure difference, and thus, the driving force and the water flux across the FO membrane decreased. The experiments were terminated when water flux reached approximately 4 L/(m$^2$ h).

Water fluxes as a function of CF and batch recovery for brines A and B are illustrated in Fig. 7a and water fluxes and specific fluxes as a function of feed concentration are illustrated in Fig. 7b. The flux during concentration of brine A was higher than the flux during concentration of brine B at the same CF or feed concentration. Brine B has a higher ion concentration and thus a higher osmotic pressure; therefore, the osmotic pressure difference between the feed and draw solution, and thus the water flux, are lower. It is important to note that the linear flux decline observed initially for brine A and continuously for B in Fig. 7b is due to decline in driving force described above and not due to membrane scaling. During experiments conducted with brine A (blue squares in Fig. 7b), water flux began declining more sharply upon approaching 30 g/L TDS; likely indicating that both driving force and permeability (decline due to scaling) are changing at the same time. This sharper decline was
Two membrane cleaning strategies were investigated. In the first method, the membrane was chemically cleaned with Na$_2$EDTA in the second method, the membrane was cleaned by osmotic backwashing [26]. Brine A was used as the feed solution in the experiments because the CaSO$_4$ is closer to saturation in brine A than in brine B. Also, in order to expedite scale formation, experiments were conducted using a highly concentrated draw solution (saturated NaCl solution at approximately 350 g/L) instead of the 50 ± 2 g/L NaCl. Each scaling cycle was terminated and cleaning was performed when batch recovery reached 80% so that performance before and after cleaning could be compared by water flux alone.

Water flux and batch recovery as a function of time are shown in Fig. 8. The Na$_2$EDTA cleanings (indicated by the solid gray arrow in Fig. 8) and osmotic backwashings (indicated by the dashed gray arrows in Fig. 8) were used following membrane scaling. Because the draw solution concentration was very high relative to the feed concentration, the osmotic pressure of the feed, $\pi_{\text{feed}}$, had little influence on the osmotic driving force and therefore, the observed decline in water flux was largely due to membrane scaling.

The initial water flux of the new membrane was approximately 31 L/(m$^2$.h). The initial water flux after the Na$_2$EDTA cleaning dropped to approximately 29 L/(m$^2$.h), which is approximately 93% of the initial water flux of the new membrane. Thus, the Na$_2$EDTA was effective in removing the majority of scale deposited on the membrane and throughout the system. Prior to the first cleaning, flux declined by approximately 57% due to scale depositing on the membrane surface. After the first cleaning, water flux declined by approximately 45% during the scaling experiment. Thus, after the Na$_2$EDTA cleaning, there was a lower rate of flux decline; this is likely due to the lower initial flux after cleaning that resulted in a lower CP modulus, and thus, less scale formation on the membrane surface.

After the first osmotic backwash at 15 h, the initial water flux was equal to the initial water flux after the Na$_2$EDTA cleaning. Thus, the osmotic backwashing appeared to be equally as effective in removing scale deposited on the membrane. However, faster flux decline was observed after the first osmotic backwash and some scale particles were observed to be flushed through the system in the experiment after the first osmotic backwash. Because osmotic backwashing is a physical membrane cleaning process, it is likely that scale remained deposited throughout the system; the osmotic backwashings physically removed the scale from the membrane surface but did not necessarily result in removal of the scale deposited in the system.

There was concern that the high pH (pH 11.8) of the Na$_2$EDTA solution might hydrolyze the CTA membrane and potentially degrade portions or even the entire membrane active layer, causing substantial decline in rejection. This was tested during the current investigation by exposing samples of the CTA membrane to Na$_2$EDTA solution (pH 11.8) for durations of 0, 1, 2, 4, 8, and 15 h and then measuring NaCl rejection in RO mode. (RO mode simplified the rejection analysis by eliminating the highly concentrated draw solution from the permeate stream.) The applied pressure in RO mode was adjusted to provide a water flux of 12–15 L/(m$^2$.h), which was the water flux during operation in FO mode. The NaCl rejection of the unexposed membrane was calculated to be approximately 96%. At exposure times of 1, 2, 4, 8, and 15 h, the rejections were calculated to be 92, 90, 88, 78, and 0%, respectively. Therefore, although EDTA is effective at removing calcium sulfate scale, the high pH solution did degrade the CTA membrane and is not recommended. Future investigations should focus on
osmotic backwashing or milder cleaning agents either alone or in combination.

3.3.3. FO with scale inhibitor

The effect of dosing brine A with silica scale inhibitor (Pre-treat Plus Y2K for silica inhibition) was investigated in a separate FO experiment. No scale inhibitor was used for CaSO₄. The draw solution concentration was maintained constant at 50 ± 2 g/L NaCl using the pilot-scale RO system. Water flux as a function of time is shown in Fig. 9 for experiments with and without scale inhibitor addition. In both cases, water flux declined gradually as the feed concentration increased. However, when scale inhibitor was not added to the brine, a rapid flux decline was observed after approximately 15 h. The addition of 10 mg/L scale inhibitor to the brine resulted in a more gradual flux decline after 15 h. Thus, FO treatment can likely be enhanced with careful selection of a scale inhibitor.

3.3.4. FO water recovery

Approximately 86% batch recovery was achieved during FO of brine A (Fig. 7a). In comparison, approximately 60% batch recovery was achieved from FO of brine B (also Fig. 7a). These results are interesting because it was expected that the batch recovery from brine B would be higher due to the additional treatment processes it received (i.e., softening and secondary RO). However, the effect of the higher NaCl concentration, and hence, higher osmotic pressure of brine B, was greater on the driving force than the effect of brine A scaling on flux decline. Thus, FO for brine A is a much more effective treatment scheme than for brine B considering that higher recoveries are achieved with the use of fewer treatment processes.

In order to determine the total water recovery, the recovery from EMWD’s RO processes and the batch recovery from the FO process were both considered. The total recovery was calculated using equation (2) with \( R_{\text{FO}} \) in place of \( R_{\text{EVDCMD}} \) (where \( R_{\text{FO}} \) is the batch recovery from FO treatment). For brine A, \( R_{\text{FO}} \) is 70% and \( R_{\text{FO}} \) is 86%. For brine B, \( R_{\text{FO}} \) is 89% and \( R_{\text{FO}} \) is 60%. Thus, when combining the recoveries of the RO processes and the FO process, the total recovery was greater than 96% for brine A and greater than 95% for brine B.

3.4. Comparing VEDCMD and FO for brine treatment

A comparison between VEDCMD and FO of brine A is shown in Fig. 10a. High temperature VEDCMD (40 °C) had a substantially higher initial flux than low temperature VEDCMD (20 °C) or FO. For both VEDCMD experiments, rapid flux decline is observed due to scale depositing on the membrane surface. Flux decline is more gradual during the FO experiment. This suggests that scaling was not as severe in FO as it was in VEDCMD. The highest water recovery was achieved using FO; with a batch recovery of 87%, it substantially outperformed the VEDCMD processes. A comparison between VEDCMD and FO of brine B is shown in Fig. 10b. Again, high temperature VEDCMD had a substantially higher initial flux than low temperature VEDCMD or FO. For high temperature VEDCMD, a steep flux decline was observed; for low temperature VEDCMD and FO, relatively gradual flux declines were observed. The water recovery from brine B was low using FO because the high ion concentration in the brine substantially increased the feed osmotic pressure, which in turn reduced the osmotic pressure difference, and thus the driving force across the FO membrane. The highest water recovery was achieved using low temperature VEDCMD; with a batch recovery of 79%, it substantially outperformed both high temperature VEDCMD and FO.

4. Conclusions

In this study, it was found that FO outperformed low- and high-temperature VEDCMD when treating a feed with high scaling propensity but low TDS concentration (i.e., brine A); and low-temperature VEDCMD outperformed high-temperature VEDCMD and FO when treating a feed with lower scaling propensity but high TDS concentration (i.e., brine B). High temperature VEDCMD results in higher initial water flux, but also greater flux decline. In FO, the high osmotic pressure of the feed solution coupled with the scaling environment may limit the utilization of the process for desalination of highly saline source waters; however, new draw solutions and methods of reconcentration could alleviate the low performance observed when treating feeds with high osmotic pressure. In all experiments, scale formed on the active surface of the membranes and adversely affected batch recovery, but cleaning methods were effective at removing scale from both the MD and FO membrane surfaces. It was also found that by dosing the feed water with an appropriate scale inhibitor, a substantial improvement in batch recovery for both VEDCMD and FO could be achieved. When considering the total water recovery (the recovery from the RO processes combined with the batch recovery from the VEDCMD or FO process), greater than 96 and 98% total recoveries were achieved for the two different brine streams.
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