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Treatment of Highly Saline Brines by Supercritical Precipitation Followed by Supercritical Membrane Separation

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ABSTRACT: A two-stage supercritical (SC) desalination system is proposed to treat highly saline brines to high-purity steam that could be used in power generation. Highly saline brines with up to ~20% salt content are pressurized and heated to SC conditions of 500 °C and 3,500 psi to rapidly precipitate the dissolved salts and generate SC steam containing ~100 ppm salts. Two highly saline brines, collected from an oil field and a deep saline formation, and two concentrated NaCl solutions were treated in the SC desalination system. A SC membrane separation system with carbon filters is developed and used to purify the SC steam to a high purity level. Promising carbon filters or membranes prepared and tested for purifying SC steam included a porous graphite disk, a flexible graphite sheet, and a carbon nanotube-based membrane. The best performing membranes exhibited a very high water flux of ~200–800 kg/m^2·h, with a salt rejection of >90%.

1. INTRODUCTION

Management of highly saline brines produced as by-products from oil fields, desalination plants, wastewater treatment plants, or future CO_2 sequestration operations in deep saline reservoirs is one of the most challenging issues for the water and energy sectors. The total dissolved salts (TDS) of these brines are usually much higher than the maximum ~50,000–60,000 ppm limit that can be handled by the conventional reverse osmosis technology. Similarly, other commercially available technologies for brackish and seawater desalination, such as multiple-effect distillation or multistage flash distillation, cannot be used to produce freshwater from high-salinity brines. The only commercially available technology for large-scale treatment of highly saline water is the evaporation and crystallization technology, which could be utilized at a high cost.[1] Emerging technologies, such as forward osmosis and low-temperature membrane distillation, for treating high-salinity water need to be significantly improved to resolve issues such as low-permeate water flux and weak membrane performance.[1] Concentrated brines could be also discharged back to the sea (for coastal desalination plants), released to evaporation ponds (for inland desalination plants), or injected into deep wells (for oilfield brines). However, these options suffer from various environmental issues, high costs, or unavailability of the proper geology in some locations.

In a recent project supported by the U.S. Department of Energy, we investigated the feasibility of an integrated supercritical (SC) water desalination and power generation system for treating different types of highly saline brines while cogenerating electricity (Figure 1).[2] This system may offer a transformative approach to generating power and purifying water from high-TDS saline or produced water in a zero-liquid discharge plant. The closed-loop steam cycle of conventional power plants is replaced with an open-loop steam cycle that heats the pretreated brine above the SC point of water (374 °C and 221 bar) to precipitate and separate the dissolved salts. The solubility of salts in water under SC conditions is reduced to ~100 ppm;[3] therefore, the majority of dissolved salts precipitate rapidly under SC conditions. The SC steam generated from SC precipitation requires further treatment to reduce its salt content from ~100 to <1 ppm, to make it suitable for use in steam turbines for power generation. At present, no technology exists for high-temperature steam polishing without condensation and energy loss. We propose using an SC membrane separation system with carbon membranes as a polishing unit to prepare purified SC steam for the power generation system. In the proposed process, polished SC steam is sent through a series of turbines for power generation, and the steam exiting the low-pressure turbine is condensed to produce high-purity water that can be used for industrial (e.g., power plant) or municipal water uses.

Other researchers[4–6] have also treated brines by SC precipitation; however, the unique aspect of our approach is that the SC steam is further purified by using membrane separation under SC conditions. This approach enables us to recover the energy invested in the SC steam as electrical power while generating high-purity water for beneficial uses. The work presented here demonstrates the treatment of two NaCl brines and two highly saline brines (collected from an oil field and a deep saline formation) to a high level of purity. The SC steam is polished by membrane separation under SC conditions by using different types of carbon membranes or filters.

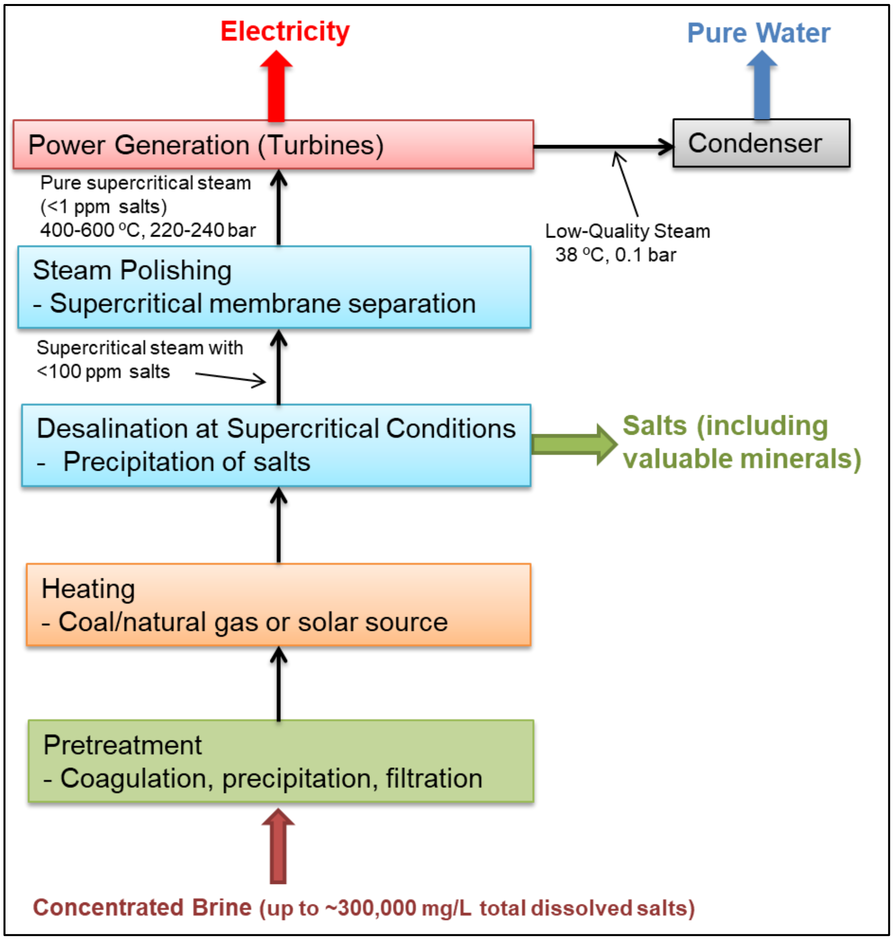

Figure 1. Conceptual diagram of the supercritical water desalination and energy generation system. A highly saline brine is treated to a high-quality water by first precipitating salts at supercritical conditions followed by steam polishing in a supercritical membrane separation system.

2. EXPERIMENTAL SECTION

2.1. Brine Sampling, Pretreatment, and Characterization

Brine samples were collected from a potential CO_2 sequestration site and an oil field in Decatur, Illinois, USA. Additionally, 10% and 20% NaCl brine solutions were prepared and tested as the baselines.

The CO_2 sequestration brine sample was collected from the Mt. Simon Sandstone Formation from a depth of ~2042 m (~6700 ft). The Mt. Simon brine had a TDS of 224,667 mg/L and a conductivity of 199.7 mS/cm. Details of the sampling and characterization of this brine sample can be found in a recent publication.[7] Mt. Simon brine was pretreated first by coagulation/sedimentation with alum (aluminum sulfate, $Al_2(SO_4)_3$) at a dose of 100 mg/L and then with lime (calcium oxide, CaO) at a dose of 150 mg/L, followed by filtration through a 0.45 µm glass fiber filter.

The oilfield brine was collected from an oil-producing formation at a depth of ~610 m (~2000 ft). The oilfield brine had a TDS value of 120,913 mg/L and a conductivity of 153.4 mS/cm. The oilfield brine was first separated from the residual oil by settling, then pretreated with alum at a dose of 100 mg/L, and finally filtered through a 0.45 µm glass fiber filter.

2.2. Carbon Filters and Membranes

The carbon filters and membranes used with the SC membrane separation system for purifying the SC steam were CNTH-750, AF5, FGS, and membrane C. AF5 (obtained from Poco Graphite, Decatur, TX) is a porous graphite disc with a 21.5 mm diameter and 3 mm thickness. CNTH-750 is a carbon nanotube membrane coated on a Hastelloy substrate that was recently developed and tested for conventional membrane distillation.[8] FGS is a flexible graphite sheet with a thickness of 100 µm that was purchased from Panasonic (Newark, NJ). The flexible graphite sheet was cut to a size of 21.5 mm in diameter for testing. Membrane C was prepared by modifying the CNTH-750 membrane with a proprietary method. At the time the membranes with graphite gaskets were sealed in the SC membrane separation module, each membrane had an effective area of 0.8 cm^2. The bubble point pressures of AF5, FGS, and membrane C, when measured based on standard method ASTM-F316-03 using isopropyl alcohol, were 46, >60, and >60 psi, respectively.

2.3. Supercritical Precipitation

The SC precipitation system is designed to pressurize and heat the pretreated brines beyond the critical point of water, precipitate the salt, and cool the SC steam to a near-ambient temperature.

This system includes a high-pressure pump, an SC salt precipitation vessel, a heater, temperature controllers, pressure regulators, and other components (Figure 2). The pressure of the system is controlled by a back-pressure regulator set at the desired pressure level (e.g., 3500 psi). The system also includes a cooling coil to cool the steam before it reaches the back-pressure regulator. The SC precipitation vessel and tubing are manufactured from Hastelloy-C276 to minimize corrosion.

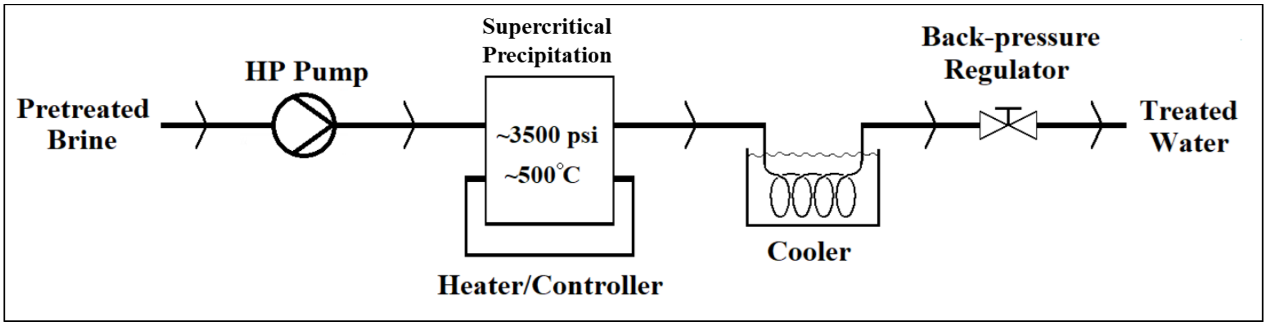

Figure 2. Schematic diagram of the supercritical precipitation system. Only the main components are shown. HP, high pressure.

To conduct the experiments, first deionized (DI) water was pumped in to pressurize the system to 3500 psi. The system was flushed with DI water for 60 min while checking for possible leaks and ensuring pressure stability. The SC precipitation vessel was then gradually heated to 500 °C while keeping the pressure at 3500 psi. Once the temperature and pressure of the SC precipitation vessel became stable, the feed DI water was switched and NaCl brine samples or pretreated Mt. Simon or oilfield brine samples were pumped in at a flow rate of 2 mL/min. During the experiments, the volumes of the feed water and treated water (effluent) and the conductivity of the treated water were monitored continuously. Selected feed and effluent samples were collected and sent to Activation Laboratories Ltd. (Ancaster, Ontario, Canada) for characterization by inductively coupled plasma-optical emission spectroscopy.

2.4. Supercritical Membrane Separation

The SC membrane separation system is designed to treat SC steam containing ~100 ppm of salt to high-purity steam. This system includes feed and permeate sides. The feed side includes a high-pressure pump, a high-pressure–high-temperature membrane module (the SC membrane separation unit), a heater, temperature controllers, pressure regulators, and other components (Figure 3). The components of the permeate side are similar to those of the feed side. An Equilibar diaphragm regulator (Fletcher, NC) is used to control the permeate-side pressure at a level close to that of the feed-side pressure. Pressure on the permeate side is kept at ~10 psi lower than that on the feed side. The feed-side pressure is controlled by a back-pressure regulator set at the desired level (e.g., 3520 psi). The system also includes heat exchangers on each side to cool the water at the end.

The SC membrane separation experiments were conducted with the SC membrane separation cell, which consisted of two compartments (i.e., feed and permeate sections) separated by a membrane (Figure 3). Feed and permeate streams were pumped at a fixed flow rate of 10 mL/min. The feed solution was pressurized to 3520 psi and heated to ~400 °C; thus, the feed matched the SC conditions of water at all times. A premeasured amount of DI water was used as a permeate fluid and was heated to a subcritical 350 °C at 3510 psi to test the FGS, CNTH-750, and AF5 filters, or to 250 °C and 3510 psi to test membrane C. The water flux was obtained by measuring the increase in weight of the permeate liquid with an electronic balance. Water flux J_w (kg/m^2·h) through the membrane was calculated by

$$J_w = \frac{\Delta M}{A \cdot \Delta t}, \tag{1}$$

where ΔM refers to the change in mass of the permeate stream during a specific time period (Δt) and A is the effective area of the membrane. The salt rejection fraction (R) was calculated by

$$R = 1 - \frac{\Delta C \cdot D_f}{C_t}, \tag{2}$$

where ΔC refers to the change in conductivity of the permeate stream (measured by an in-line conductivity meter at the end of the permeate side), D_f is the dilution factor on the permeate side, and C_t is the conductivity of the feed stream measured at the end on the feed side.

Control tests were performed with a solid Hastelloy disk instead of the membranes to check the mass balance and overall performance of the SC membrane separation system. The concentrations of dissolved salts in feed solutions used for testing different membranes varied in a range of ~200–300 mg/L. These solutions were prepared by diluting pretreated Mt. Simon and oilfield brines with DI water, instead of using treated effluents from the SC precipitation stage. This was due to the corrosion effect (as described later in Section 3.1.2) that resulted in leaching a considerable amount of Fe, Ni, Cu, and Co from the SC precipitation stage to the treated water. Additionally, baseline tests were performed with 90 or 250 ppm NaCl solutions.

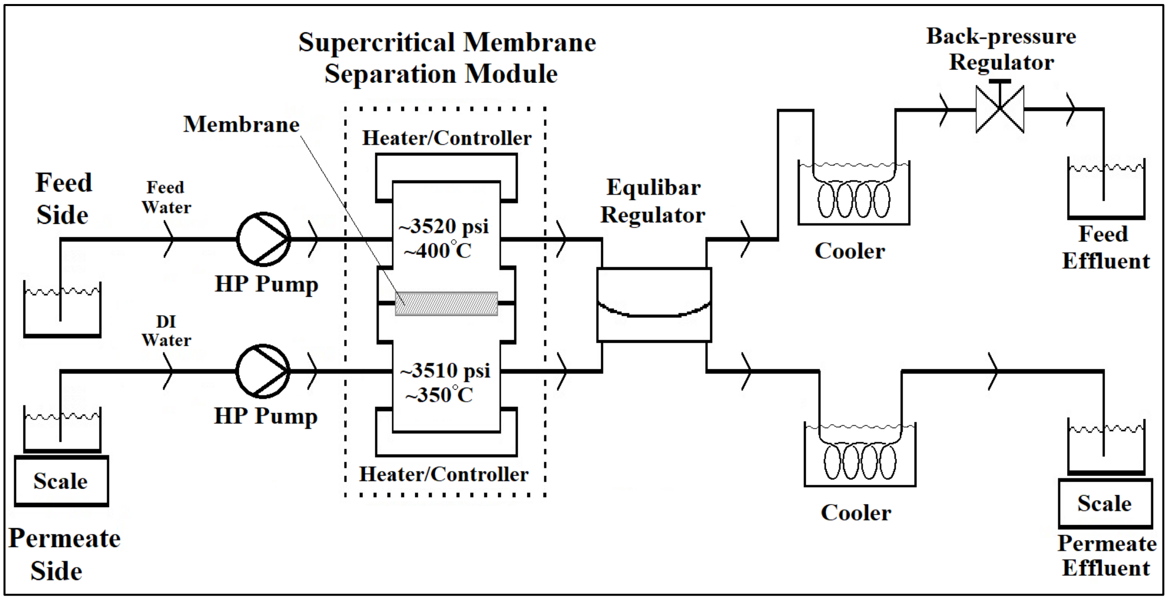

Figure 3. Schematic diagram of the supercritical membrane separation system. Only the main components are shown. HP, high pressure.

3. RESULTS AND DISCUSSION

3.1 Supercritical Precipitation

3.1.1. Treatment of the 10% and 20% NaCl Solutions

Baseline tests using 10% and 20% NaCl solutions were conducted (1) to confirm successful operation of the salt precipitation system within the desalination system and (2) to collect baseline data for comparison with the treatment results from the Mt. Simon and oilfield brine samples. Results of the NaCl precipitation experiments at SC conditions are shown in Figure 4. The initial conductivities of the 10% and 20% NaCl feed solutions were 127,000 and 208,000 µS/cm, respectively. The conductivities of permeate samples collected during the first ~50 min of the experiments were very low, but they increased sharply during a period of ~50–100 min to relatively stable values (Figure 4). The reason for this result was that the system was initially filled with DI water, so a lag time occurred before seeing a representative sample of treated feed.

According to the results shown in Figure 4, conductivity values of as low as ~320 µS/cm (equivalent to 130 ppm) were achieved by SC desalination at 500 °C for the NaCl feed concentrations, which is equivalent to a removal efficiency of >99.8%. The conductivity of treated water for the experiment with 20% NaCl increased after 270 min from 370 to 590 µS/cm as the SC salt precipitation vessel was filled with a large amount of the precipitated NaCl. Overall, we demonstrated the precipitation of salt from feed solutions with 100,000 and 200,000 ppm of NaCl at SC conditions. We were able to treat concentrated brine solutions to produce relatively pure water with a salt content of ~130 ppm by precipitating salt under SC conditions.

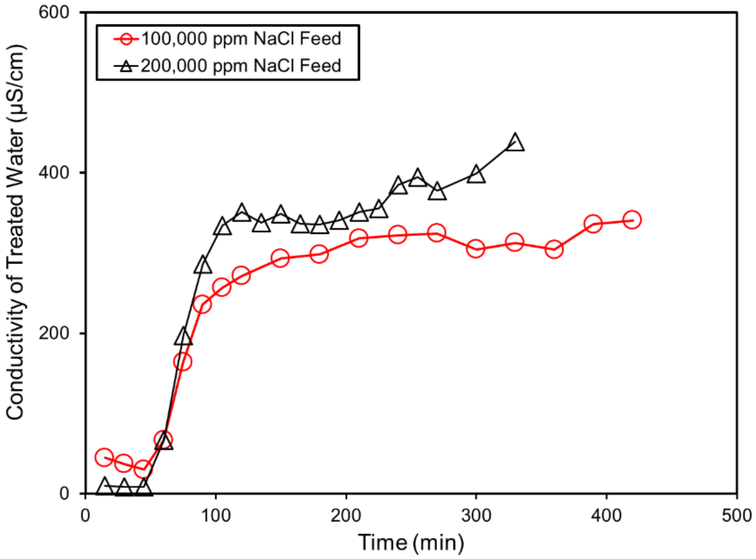

Figure 4. Desalination of NaCl feed solutions at supercritical conditions of 500 °C and 3500 psi. The conductivity of the treated water is plotted versus the operation time. The feed conductivity values of 10% and 20% NaCl brine samples injected into the precipitation vessel were approximately 127,000 and 208,000 µS/cm, respectively.

3.1.2. Treatment of the Mt. Simon and Oilfield Brines

Results from the SC precipitation desalination of oilfield and Mt. Simon brine samples are shown in Figure 5. Similar to the baseline NaCl brine experiments (Figure 4), the conductivity measurements of samples collected during the first 50 min of experiments were close to the conductivity of DI water because of the time delay needed to push the DI water out of the system.

For the Mt. Simon brine, the final effluent conductivity was ~5200 µS/cm, which is equal to a concentration of 3282 ppm of TDS. The TDS concentrations of permeate solutions were estimated based on the conductivity–concentration correlations of diluted brine samples. The final permeate effluent conductivity for the oilfield water was measured at ~3500 µS/cm (i.e., 1882 ppm).

The estimated TDS values of effluents from the SC precipitation vessel for the tested brine samples were in the range of ~1800–3300 ppm, significantly higher than the 130 ppm value observed for the NaCl baseline tests (Figure 4). Precipitated mixed salts from the oilfield and Mt. Simon brines were fine particles and appeared more porous than the precipitated NaCl crystals from the baseline experiments (Figure 6). We also observed some operation issues triggered by the transport of fine salt particles to the outlet port of the SC vessel, which caused the line to clog and some experiments to be terminated. We did not encounter the clogging issue when the NaCl solutions were desalinated at different concentrations. Kawasaki et al. also reported that different salts (e.g., KCl and $CaCl_2$) had different precipitation and agglomeration characteristics than NaCl when they were precipitated at SC conditions.[9] After NaCl, the predominant dissolved salts in the Mt. Simon and oilfield brine samples were $CaCl_2$ and KCl. We had also expected the Mt. Simon and oilfield brine samples to create more corrosive conditions (because of the more corrosive effect of $CaCl_2$ or other dissolved salts) than would a pure NaCl solution. The corrosion and leaching of metals from the precipitation vessel and tubing materials into water was further investigated as described below.

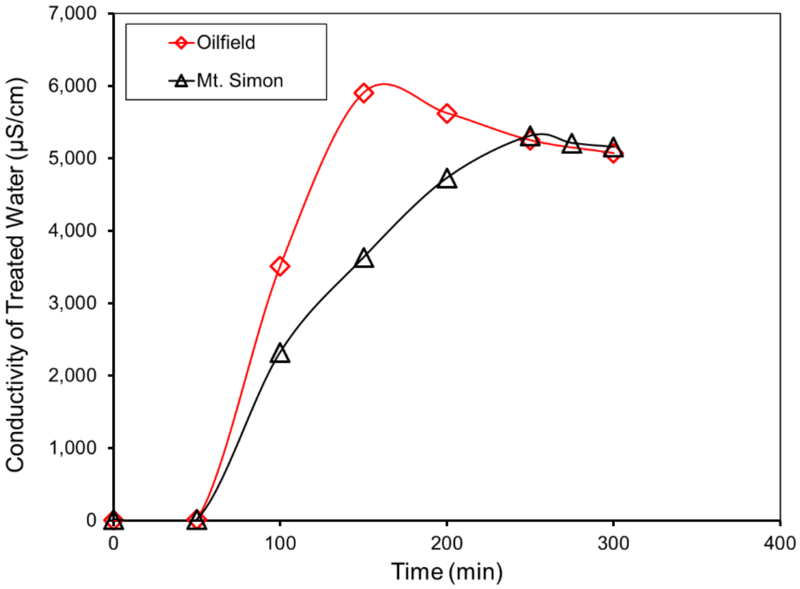

Figure 5. Permeate conductivity versus operation time, measured at the exit port of the system. The feed conductivity values of pretreated oilfield and Mt. Simon brine samples injected into the precipitation vessel were approximately 153,000 and 191,000 µS/cm, respectively.

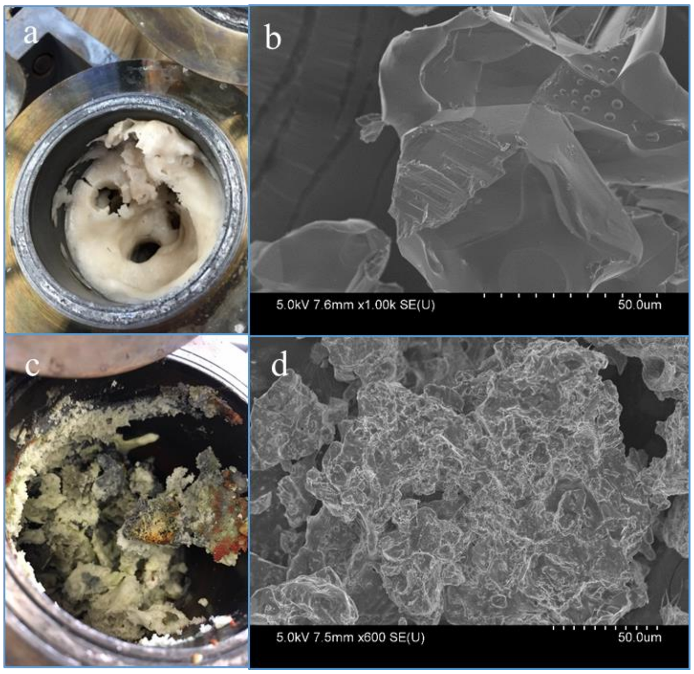

Figure 6. Photographs and scanning electron microscopy images of precipitated salts in the supercritical salt precipitation vessel (a, b) for the 20% NaCl brine feed and (c, d) for the oilfield brine feed.

Concentrations of various cations in the pretreated Mt. Simon and oilfield brine samples (feed streams) and in the effluent streams from the SC precipitation system are shown in Table S1. Other metals detected at concentrations of <0.1 ppm are not shown. The concentration of the dominant cation, Na, was reduced dramatically from 47,400 to 21 ppm for the Mt. Simon brine and from 38,400 to 29 ppm for the oilfield brine. Concentrations of other major cations (Ca, Mg, Sr, and K) also decreased significantly from initial values of ~1000–22,000 to ~1 ppm or less (Table S1). Contrary to the observed dramatic reduction in concentrations of Na, K, Li, Ca, Mg, Sr, Ba, and Mn (Group 1), we observed a significant increase in concentrations of Fe, Ni, Cu, and Co (Group 2). The cumulative concentrations of Group 1 cations in the effluent from the SC desalination system for Mt. Simon and oilfield samples were 27 and 36 mg/L, respectively. However, the cumulative concentrations of Group 2 cations were 432 mg/L for the Mt. Simon sample and 630 mg/L for the oilfield sample. The cumulative amount of Group 2 cations in both brine feed samples was only ~2 mg/L (Table S1). This observation suggests Group 2 elements leached from the system (precipitation vessel, filters, tubing), which is made of alloys containing Fe, Ni, Cu, and Co.

When the impact of the metals that leached from the reactor system was excluded, the SC desalination system was able to decrease the TDS of the Mt. Simon and oilfield brines from initial values of ~224,000 and ~120,000 mg/L, respectively, to <100 mg/L, which is similar to the solubility values of salts in water at SC conditions.[10,11]

3.2. Supercritical Membrane Separation

The SC membrane separation system was first tested with an impermeable Hastelloy disk to completely separate the feed and permeate sections and obtain baseline data by monitoring both the conductivity and weight of the permeate stream. This testing was performed by pumping in 90 ppm of NaCl solution on the feed side and DI water on the permeate side. The feed side of the membrane was maintained at SC conditions of 3,520 psi and 400 °C, whereas the permeate side was controlled at subcritical conditions of 3,510 psi and 350 °C. Results of a 3-h test showed that the conductivity of the outlet stream on the permeate side stayed at a constant value of ~0.5 μS/cm, which is similar to the conductivity of the inlet DI water. Furthermore, no change in the weight of the permeate stream was observed. A near-zero flux and no significant change in the permeate conductivity for the Hastelloy block test confirmed that the system had no leaks in the feed and permeate sides or between the feed and permeate chambers of the membrane separation module.

Membrane separation of the SC steam generated from the 90 ppm NaCl solution was performed with the CNTH-750 carbon membrane. This membrane was recently developed and tested for water desalination by membrane distillation at a near-atmospheric pressure and at feed and permeate temperatures of 80 °C and 5 °C, respectively.[8] Testing results of CNTH-750 at SC conditions indicated that the SC water from the feed side could be transported almost freely through the membrane, with a very low salt rejection of ~10%. The CNTH-750 membrane, which had a hydrophobic surface with water contact angle of 163°, pore openings of ~50–500 nm, and a liquid entry pressure of ~5 psi, had performed well in previous conventional membrane distillation experiments.[8] However, its large pores and relatively low liquid entry pressure of 5 psi (less than the pressure difference between the feed and permeate membrane sides) were not suitable for SC membrane separation. Furthermore, the hydrophobicity of the membrane did not appear to be a critical factor for membrane separation at SC conditions. In conventional membrane distillation, the hydrophobic surface of the membrane prevents liquid water from entering but allows the transport of water vapor. However, at SC conditions, only one phase (i.e., SC fluid) exists. Additionally, it is likely that, because of dramatic changes in the dielectric and other properties of water at SC conditions,[12] the carbon membrane surface is totally wetted with the SC steam. The membrane separation at SC conditions appears to be mainly controlled by a combination of pressure, temperature, density, composition or activity difference between the feed and permeate sides and membrane characteristics. Overall, membrane CNTH-750 was not suitable for SC membrane separation, although it stayed intact during testing under harsh SC conditions, without any sign of membrane damage (i.e., carbon coating delamination, substrate corrosion, deformation, etc.). The CNTH-750 membrane was further modified, via a proprietary method, for the SC membrane separation application. This membrane is identified as membrane C and was tested for the purification of SC steam.

The SC membrane separation results for membrane C and two other carbon filters (AF5 and FGS) at 3520 psi and 400 °C are shown in Figure 7. The salt rejection in Figure 7d is indicative of the overall salt rejection during the course of each experiment. A feed solution of 90 ppm of NaCl in DI water was used for generating SC steam to test the AF5 and FGS filters. Additionally, filters AF5 and FGS were tested with solutions prepared from diluting pretreated Mt. Simon and oilfield brines with DI water to a conductivity range of 524–534 µS/cm for the Mt. Simon solution and a range of 530–607 µS/cm for the oilfield solution, values which correspond to TDS of ~250–300 ppm. Membrane C was tested with a 250 ppm NaCl solution and with solutions with conductivities of 400–480 µS/cm (~200–240 ppm of TDS) prepared from pretreated Mt. Simon and oilfield brines. It should be noted that the concentrations of salts in different feed water solutions (~200–300 ppm), regardless of their initial concentrations, were expected to be reduced to ~100 ppm (i.e., the solubility limit of salts at SC conditions) in the SC steam generated in the feed chamber of the SC membrane separation module.

The AF5 porous graphite disk showed a high initial water flux of ~200 kg/m^2·h for the NaCl solution; however, the NaCl rejection was only 53%. In contrast, a much higher NaCl rejection of ~96% was obtained with the FGS membrane, which also had a reasonable water flux of ~20–50 kg/m^2·h during the 3-h test (Figure 7). Similar to the baseline testing results for NaCl solutions at SC conditions, water flux values for the AF5 membrane for purifying diluted Mt. Simon and oilfield brine solutions were significantly higher than those for the FGS membrane, mainly because of the larger pores of the AF5 disk (Figure 7a,b). The initial water flux of the AF5 was >100 kg/m^2·h, which was reduced to a relatively stable flux of ~50 kg/m^2·h for all the diluted brine solutions, whereas the water flux for the FGS membrane for diluted brine solutions approached a value of ~10–15 kg/m^2·h (Figure 7b). The FGS membrane had a high salt rejection of >96%, about twice the salt rejection of the AF5 disk (Figure 7d). The higher salt rejection of the FGS membrane was likely due to its smaller pore size. These results indicate that the FGS membrane was suitable for polishing SC steam. A one-stage SC membrane separation treatment with FGS was able to reduce the concentration of dissolved salts to <10 ppm, and this could be further reduced to <1 ppm with a second-stage treatment.

Duplicate testing results of membrane C with NaCl solutions at SC conditions showed a very high and relatively stable flux value of ~200 kg/m^2·h, which is one order of magnitude higher than the conventional membranes used for water purification. The developed membrane also exhibited a high salt rejection of ~93%. Additional testing of membrane C showed extremely high flux values of ~400 kg/m^2·h for the Mt. Simon sample and ~800 kg/m^2·h for the oilfield sample, which were higher than the baseline NaCl results (Figure 7c). The oilfield and Mt. Simon samples were tested with a membrane that was used for performing two baseline tests, and it is possible that during these tests, the membrane structure changed and pores became wider, resulting in a greater flux. The salt rejection of diluted brine samples treated with membrane C were 91% and 87% for the oilfield and Mt. Simon samples, respectively, which are slightly lower than the salt rejection of 93% for the baseline NaCl test (Figure 7d). These results demonstrate the promising performance of membrane C for the purification of SC steam. However, membrane C must be developed further to achieve more stable performance during multiple cycles of testing and longer operation times. A multistage polishing treatment by these membranes will be able to lower the salt content of the SC steam to levels below parts per million or at parts per billion, which may be the steam quality required for the power cycle.

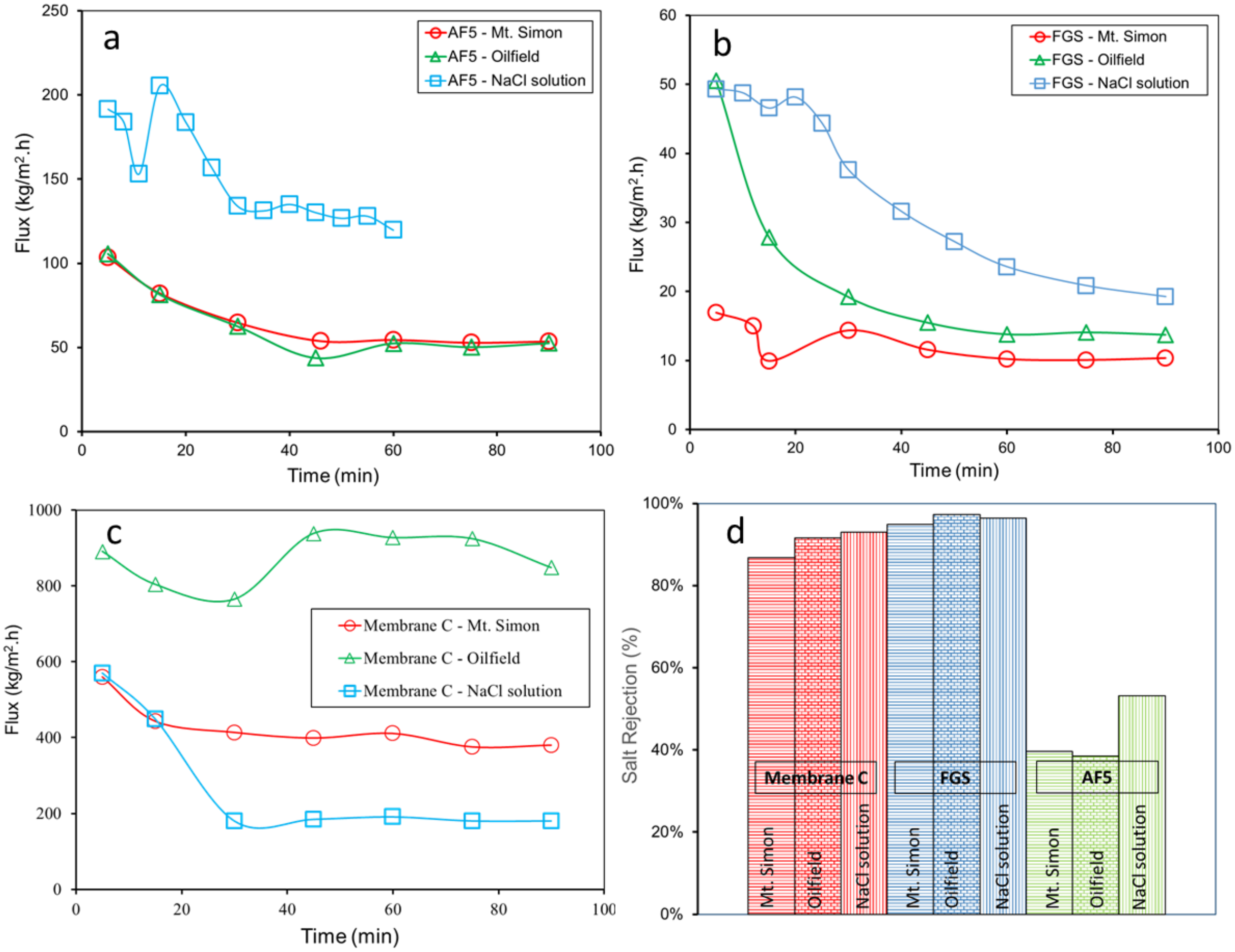

Figure 7. Treatment of supercritical steam by supercritical membrane separation. Water flux through the (a) AF5, (b) FGS, and (c) membrane C filters is plotted versus treatment time. (d) Overall salt rejection percentage for each case.

4. CONCLUSIONS

Highly saline brines with TDS concentrations of >100,000 ppm were treated to high-purity steam by using a two-stage SC desalination system. The proposed system includes precipitation of salts at SC conditions, followed by a polishing treatment with a membrane separation process that operates at SC conditions. The high-purity SC steam generated by SC membrane separation could be used for power generation by steam turbines.

Through the rapid precipitation of salts at SC conditions of 500 °C and 3,500 psi, it was possible to remove >99.8% of dissolved salts from several brine samples with initial TDS concentrations of >100,000 to <100 ppm. Mt. Simon and oilfield brine samples created more corrosive conditions than did NaCl brine when treated at SC conditions, which resulted in the metals Ni, Fe, Cu, and Co leaching from the precipitation vessel or tubing materials into the treated water.

A SC membrane separation system is developed and used to purify the SC steam to a higher purity level by using carbon filters. Initial testing with the carbon nanotube membrane CNTH-750 (previously developed for conventional membrane distillation) indicated that the typical pore openings of 50–500 nm of conventional membrane distillation membranes are too large for membrane separation at SC conditions because they allow almost unrestricted flow of SC steam through the membrane, with only very low salt rejection. The membrane separation at SC conditions appears to be mainly controlled by a combination of pressure, temperature, density, composition or activity difference between the feed and permeate sides and membrane characteristics.

Promising carbon filters or membranes with smaller pores that were prepared and tested for purifying SC steam included a porous graphite disk, a flexible graphite sheet, and a carbon nanotube-based membrane. The porous graphite membrane has a high water flux of ~50 to >100 $kg/m^2 \cdot h$ but a low salt rejection of ~40–50%. The flexible graphite sheet membrane has a high salt rejection of >95% but a water flux of ~10–20 $kg/m^2 \cdot h$. By developing membrane C, we were able to make a membrane that provides an extremely high flux of ~200–800 $kg/m^2 \cdot h$ with a salt rejection of 87–93%. These results demonstrate the promising performance of membrane C for the purification of SC steam. However, membrane C needs to be developed further to achieve more stable performance during multiple cycles of testing and longer operation times. After further development, the carbon filters developed here might also be promising materials for other gas or liquid separation applications under high-pressure–high-temperature or corrosive conditions.

5. ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Concentrations of various cations in pretreated brine feed samples and in effluent samples from the supercritical precipitation system.

6. AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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Graphical Abstract