Assessment of Traditional and Novel Membrane Processes for Recovery of Cooling Tower Water in Geothermal Power Plants

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Keywords

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ABSTRACT

Cooling towers in geothermal power plants use large quantities of water to ensure high-efficiency generation of power. However, low quality of make up water results in inefficient use of water and discharge of large volumes of blowdown water. Membrane processes can be utilized in conjunction with cooling towers to reclaim blowdown water and beneficially reuse the product water; thereby reducing operating cost and increasing water use efficiency. In the current study conventional pressure-driven membrane processes (i.e., nanofiltration and reverse osmosis) are tested for treatment of blowdown water alongside testing of novel, thermally-driven and osmotically-driven membrane processes. Results from bench- and pilot-scale investigations will be presented. Additionally, novel thermally-driven membrane processes have been tested for degasification of blowdown water before injection to the subsurface. Results demonstrated that savings can be achieved by reducing chemical use and degassing with membranes.

1. Introduction

Many power plants, including geothermal power plants, use impaired make-up water for their cooling towers. Some power plants use water from irrigation ditches (Figure 1), which is pumped, chemically conditioned, and treated through pressure filters before use in the cooling system. In power plants that use steam condensate in the cooling towers, cooling water can be recirculated many times in the system without damaging wet surfaces; in some cases more than 30 cycles are possible (Brady Hot Springs, NV). When using lower quality impaired make-up water, cooling towers are operated at less than 5 cycles, and therefore, water is not efficiently utilized and large volume of blowdown (BD) water must be wasted.

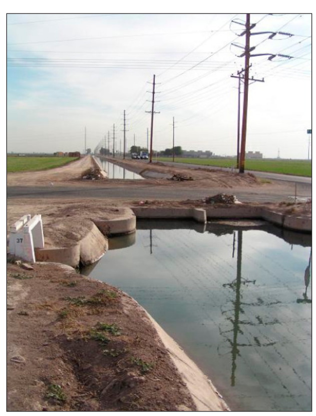

Figure 1. Irrigation canal in El Centro, CA. Heber II geothermal power plant can be seen in the background.

Table 1. Summary of membrane technologies used for treatment of BD water.

Membrane Technology	Pressure (psi)	Rejection Mechanism
Microfiltration (MF)	Low	Sieving
Ultrafiltration (UF)	Medium	Sieving
Nanofiltration (NF)	Medium-High	Solution-Diffusion
Reverse Osmosis (RO)	High	Solution-Diffusion
Membrane Distillation (MD)	Ambient	Volatility

Many processes have been used for treatment of cooling tower water. The majority of these treatment processes are applied to either the makeup water entering the cooling tower or, if water recycling is the focus, on the BD water before it is sent to waste; the product water in both case supply higher quality water to the cooling tower. These treatment processes range from traditional processes like flocculation/coagulation followed by rapid sand filtration to more advanced membrane technologies like microfiltration (MF), ultrafiltration (UF), or reverse osmosis (RO). For treatment of BD water, integrated membrane systems (IMS) that incorporate both traditional and advanced treatment processes are capable of approximately 70% recovery of BD water (Buhrmann et al., 1999, Okazaki et al., 2000, Into et al., 2004, Wang et al., 2006). Some of these systems are even efficient enough to achieve zero liquid discharge when coupled with evaporation basins (Buhrmann et al., 1999). However, while IMS are capable of producing high quality makeup and recycled BD water, they are required to operate at high pressures and, therefore, require a more energy and robust systems. Alternatively, low energy treatment solutions could provide both energy and cost savings.

Various membrane processes can be used for treatment and reuse of unutilized waste streams from cooling towers. An overview of these technologies can be seen in Table 1. One such process is ultrafiltration (UF), which is a pressure-driven process that can produce water with high purity and low silt density. Industrial applications of UF include power generation, food and beverage processing, pharmaceutical production, and biotechnology. The operating pressure required for UF is typically between 10 and 70 psi. New ceramic membranes for UF make the process robust and reliable for use in industrial applications. For surface water contaminated with suspended solids, UF can be the ultimate treatment for cooling water conditioning or it can be the pretreatment for advanced membrane processes such as nanofiltration (NF) or reverse osmosis (RO).

NF and RO separation technologies can remove dissolved impurities from water through the use of a semi-permeable membrane. Higher pressure is used as the driving force for the separation. The membrane's operating conditions are fine-tuned to balance the water production rate (flux) with the specific rejection rates of contaminants, to achieve up to 99.8% salt rejection without compromising the integrity of the membranes (i.e., fouling and scaling). For surface and ground water loaded with high concentrations of dissolved salts, NF and RO are the ultimate treatment for cooling water production.

A more novel membrane process that could be used to treat BD water is forward osmosis (FO) which is an osmotically-driven membrane process that uses osmotic pressure differential across a semi-permeable membrane, rather than hydraulic pressure differential (as in NF and RO) as the driving force for transport of water through the membrane. The FO process results in concentration of a feed stream and dilution of an osmotic agent (i.e., a draw solute). The FO process has experienced renewed interest in recent years. New findings regarding the capabilities and benefits of FO in different fields of science and engineering clearly demonstrated that it has a significant merit for treatment of impaired water and for desalination. FO has been evaluated and is currently utilized for food processing, in drug delivery systems, and in very small water treatment systems for emergency situations. Integrating FO into existing RO or NF processes at facilities treating both reclaimed and saline water can substantially reduce the energy needed to operate pressure-driven membrane systems.

Another novel option for treatment of BD water is membrane distillation (MD). MD is a thermally-driven membrane process in which a feed solution at elevated temperature flows under very low pressure (close to ambient) on the active side of a hydrophobic, microporous membrane. In direct contact MD (DCMD), the configuration that is being tested in the current study, fresh cold water flows under low pressure on the product (permeate) side of the membrane. The temperature difference across the membrane is the source of a vapor pressure gradient that drives evaporation through the membrane pores; the hot feed solution evaporates at the interface with the dry membrane pore, the vapors diffuse through the membrane pores, and then condense directly into the cold stream on the permeate side of the membrane. Advantages of the DCMD process include exceptionally high rejection of ions, macromolecules, colloids, and other non-volatile compounds, and operation at very low pressure. In fact, low pressure must be maintained in order to prevent pore flooding, which would lead to degradation of product water purity (Lawson and Lloyd, 1997). But more importantly, MD can be effectively driven by sources of low-grade heat, a resource that is readily available in geothermal power plants and in most cooling towers. DCMD can achieve very high water recovery because, unlike other membrane processes, high salt concentrations have a minimal impact on the driving force; therefore, it produces a stream of highly concentrated brine to be disposed of.

One method for BD disposal at geothermal power plants is to blend the BD with the geothermal brine before injection into the geothermal reservoir. However, in order to protect well casings, the brine must be deoxygenated before injection. This deoxygenation is commonly done chemically. Alternatively, degasification can be accomplished with membrane processes; specifically, with a MD configuration called vacuum membrane distillation (VMD). In VMD, a warm feed solution flows on the feed side of a hydrophobic microporous membrane and vacuum is induced on the permeate side of the membrane. Because dissolved gasses in water are more volatile than the water itself, VMD can remove the gasses with minimal water flux. In VMD, the fluxes of both water and dissolved gases depend on feed temperature with higher fluxes expected at higher temperatures.

In order to assess the potential for water and energy savings through the treatment of unutilized BD waste streams, this study investigates the effectiveness of both conventional membrane processes (i.e., low pressure RO and NF) and more innovative membrane processes (i.e., DCMD and FO) for the treatment of BD water. The main objectives of the current study include the selection of appropriate membranes for the different processes and assessment of long-term process sustainability (i.e., fouling and scaling rates, and membrane cleanability). In addition, pilot-testing of NF and MD systems will be performed at a geothermal power plant in the summer of 2008. Finally, the different membrane processes will be compared to determine the strengths and limitations of each one. An additional objective of the study is to evaluate the feasibility of VMD for deoxygenation of concentrated BD water to be injected into geothermal reservoirs.

2. Experimental

2.1. Membranes

RO and NF membranes: Four NF membranes and two low-pressure RO membranes were tested. The NF membranes used were NF90 and NF 4040 (Filmtec, Midland, MI), TFC-S (KOCH, Wilmington, MA), and XN45 (TriSep, Goleta, CA). The RO membranes tested were XLE (Filmtec, Midland, MI) and ULP (KOCH, Wilmington, MA). All RO and NF membranes are thin film composite polyamide membranes with the exception of the NF4040, which is made of polypiperazine amide.

FO membranes: Although having similar characteristics to those of RO membranes, membranes for FO are unique and are currently manufactured by only one company in the US, Hydration Technologies, Inc. (HTI, Albany, OR). One type of cellulose triacetate (CTA) membrane was acquired from HTI and has been tested in this investigation.

Microporous membranes: Two flat sheet microporous, hydrophobic DCMD membranes were tested at the bench-scale. One of the membranes is a composite membrane made of a thin active layer of polytetrafluoroethylene (GE PTFE) on top of a more porous support layer. The effective pore size of the GE

PTFE membrane is 0.22 μm. The remaining DCMD membrane is a symmetric, isotropic membrane made of polypropylene (GE PP). The effective pore size of the GE PP membrane is 0.22 μm. All membranes were acquired from GE Osmonics (Minnetonka, MN). A polypropylene capillary membrane with a pore size of 0.2 μm and a surface area of 0.1 m^2 was used for all VMD experiments (MD 020 CP 2N, Microdyn-Nadir, Germany). A similar membrane with a surface area of 10 m^2 will be tested at the pilot-scale level in DMCD mode.

2.2. Experimental Setups (DCMD, VMD, FO, RO/NF)

An NF/RO apparatus was designed and assembled. Two original SEPA-CF membrane test cells (GE Osmonics, Minnetonka, MN) were used in parallel for all RO and NF experiments. Each cell holds a small membrane coupon, 139 cm^2 in surface area. A high-pressure positive displacement pump was used to circulate water through the membrane cells (Figure 2). During the experiments product water samples were collected for analysis and water flux was measured.

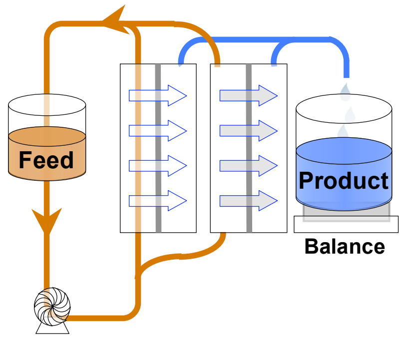

Figure 2. Bench-scale experimental apparatus for RO and NF.

An FO bench-scale apparatus was designed and assembled using a modified SEPA-CF membrane cell. The membrane cell consists of two flow channels, a feed channel where feed solution flows under very minimal pressure on the active side of the FO membrane, and the permeate channel where a draw solution (DS) with a concentration of 50 g/L NaCl flows on the support side of the membrane. Water is circulated through the system under very low pressure using two gear pumps. The membrane (139 cm^2) is held between the two sides and water diffuses through the membrane due to the osmotic pressure difference from the feed to the DS (Figure 3).

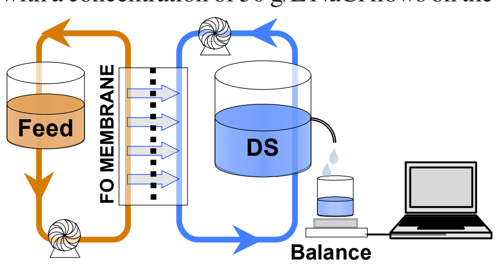

Figure 3. Bench-scale experimental apparatus for FO.

For the DCMD bench-scale testing, an apparatus similar to that used for the FO experiments was used. The main differences include recirculation of cold, fresh water on the support side of an MD membrane rather than DS and temperature control systems installed in the feed tank (heater) and in the cold reservoir (chiller). Water is circulated through the system under very low pressure using two gear pumps (Figure 4).

The DCMD apparatus was altered to perform the VMD experiments. A polypropylene, capillary membrane module was used for all VMD experiments. Feed solution at elevated temperature flow on the feed side of the membrane (bore side of the capillary membranes) and the permeate side of the membrane (shell side) was connected to a vacuum pump which induced the necessary vacuum on the permeate side of the membrane (Figure 5). A heat exchanger on the vacuum line between the membrane element and the pump condenses any water vapor that has diffused with the dissolved gas across the membrane. This condensate is collected and measured in a graduated cylinder.

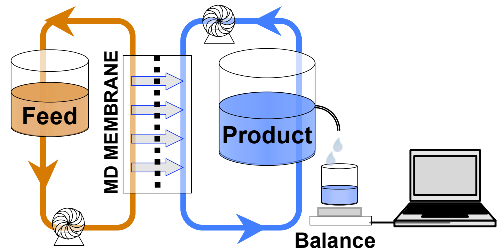

Figure 4. Bench-scale experimental apparatus for DCMD.

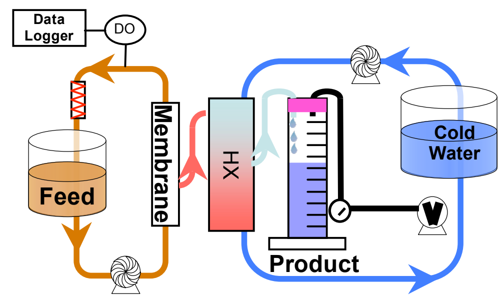

Figure 5. Bench-scale experimental apparatus for VMD.

2.3. Sample Collection and Analysis

BD water was collected in 5-gal containers from the bottom of the cooling tower at the Ormesa 1 power plant in Imperial Valley, CA. Elemental analysis was performed on the water using ion chromatography and inductively coupled plasma. Major constituents in the water included Ca, K, Mg, Na, Cl, HCO_3, and SO_4. Turbidity was measured using a Hach model 2100A turbidimeter.

Silt density index (SDI) was measured according to the ASTM D 4189-82 standard method, but SDI values could not be calculated because the suspended solids concentrations were too high. The high SDI of the BD water indicates high fouling potential. As such, pre-treatment must be performed to remove suspended solids if membrane processes such as RO, NF, FO, or MD are to be utilized.

2.4. NF/RO Experiments

2.4.1 Pure Water Baseline Flux Experiments

Preliminary experiments were conducted for six NF and RO membranes on the NF/RO apparatus using pure water feed. Pure water flux was then determined at feed pressures of 70 or 150 psi. These pressures were selected because they are typical pressures for low-pressure RO and NF processes and produce water flux in the range that is recommended by most membrane manufacturers.

2.4.2. Performance and Cleaning Experiments

Performance experiments were conducted using 4 L of pre-filtered BD water. The operating pressure for each membrane was determined so that all membranes would have an initial flux of approximately 20 LMH. Water flux, flux decline, and salt rejection were measured. Experiments were terminated when the flux dropped below 5 LMH. At this point, the membranes were cleaned with a solution of EDTA and NaOH that was circulated through the system. To evaluate the effectiveness of the cleaning procedure, flux experiments were performed again using 2 L of fresh BD brine.

2.5. DCMD Experiments

2.5.1. Initial Flux Experiments

The DCMD process was tested using pre-filtered (0.5 µm) BD water. The experiments were performed with BD water temperature of 40 or 50°C and permeate stream temperature of 20°C. In order to assess the long-term performance of the DCMD process for BD treatment, the membranes were repeatedly fouled/scaled and cleaned. BD water was filtered through a 0.5-µm cartridge filter and then concentrated until 60% water recovery had been achieved with a feed temperature of 40°C and a permeate temperature of 20°C. After the membrane was fouled/scaled, the system was emptied of all water and a solution of 0.1 wt% NaOH and 1 wt% Na_4EDTA (pH ~ 12) was circulated through the system. After cleaning, the system was thoroughly rinsed with DI water. This concentration-clean cycle was repeated three times and a small amount of water was circulated through the system a fourth time to measure a final maximum/initial water flux.

2.5.2. SEM Analysis

BD water was concentrated in the DCMD apparatus until 80% water recovery had been achieved. After the experiment, the scaled membrane was dried and two sections were cut from the membrane, one to investigate scaling of the membrane surface and another to examine a cross section. Both samples were analyzed using a scanning electron microscope (SEM) (FEI Quanta 600, FEI Company, Hillsboro, OR). In addition to visualizing the surface and cross section of the scale layer, an Energy dispersive X-ray spectrometer (Princeton Gamma-Tech, Inc., Rocky Hill, NJ) was used to analyze the chemical makeup of the foulant crystals.

2.6. VMD Degasification

The VMD apparatus was tested using DI water. Oxygen and water fluxes were used as performance parameters. Feed temperature was either 40°C or 20°C for these experiments. The vacuum pump induced negative pressures ranging from 22.5" and 25" Hg (125-189 mmHg abs.) The feed tank was topped of, leaving no headspace (approximately 21 L) in order to avoid continuous re-oxygenation of the water.

BD concentrate from the DCMD experiments, which is 60% more concentrated than the initial BD water, was used for performance VMD experiments. After deoxygenating the BD water, a final experiment was carried out with pure water to assess if any degradation in the membrane had occurred.

3. Results

3.1. NF/RO Experiments

Results from the bench-scale experiments performed with six NF and RO membranes are summarized in Table 2. Reported parameters include operating pressure, flux before and after cleaning, and product water conductivity before and after cleaning. Flux decline was qualitatively assessed over 15 hrs of operation and is indicated by a high, medium, or low decline. A low flux decline is defined by a flux decrease that is less than 25%, a medium flux decline is 25-75%, and a high flux decline is greater than 75%. Results have demonstrated the NF membrane can be effectively used for treatment of surface water for cooling towers. NF membrane can provide high quality water at low operating pressure and energy cost. Based on these results, two NF membranes were chosen for pilot testing that will be carried out in summer 2008.

Table 2. Summary of Membrane Performance for NF/RO experiments.

Membranes	Operating Pressure (psi)	Initial Flux (LMH)	Flux Decline	Flux After Cleaning (LMH)	Initial product Conductivity (µS)	Conductivity After Cleaning (µS)
NF90	48	19	Medium	17	145	211
4040	44	17	Medium	22	1370	1910
XLE	50	21	High	20	206	1180
ULP	66	20	High	20	178	not available
TFCS	50	16	Medium	16	340	260
XN45	35	20	Low	24	2690	2980

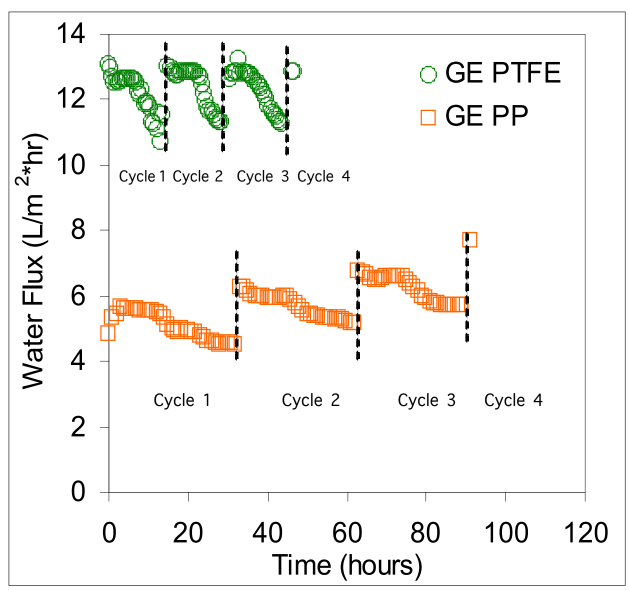

Figure 6. Results for DCMD performance experiments with GE PP and GE PTFE membranes. 60% recovery was achieved in each cycle. Dotted lines denote when cleaning was carried out.

3.2. FO Experiments

FO has been shown to be a very robust pretreatment process for RO and NF. Recent studies have demonstrated that FO can be incorporated into RO systems to achieve more than 96% overall water recovery during desalination of brackish groundwater. FO was also very successful in pre-treating waste streams loaded with organic foulants (e.g., landfill leachate, anaerobic digesters). Performance experiments are underway and final results will be presented.

3.3. DCMD Experiments

3.3.1. Initial Flux Experiments

Eight blowdown water experiments have been carried out to date. Experiments with the GE PTFE and feed temperature of 40°C and 50°C (permeate 20°C) were repeatedly performed. Experiments with the GE PP at each temperature difference have been carried out one time. Being a thinner membrane, the GE PTFE has yielded higher water fluxes than the GE PP membrane (Table 3).

Table 3. Water flux comparison between GE PP and GE PTFE membranes. All units are in LMH.

Membrane	*ΔT = 20°C*	*ΔT = 30°C*
GE PTFE	14.18	25.85
GE PP	5.43	11.29

3.3.2. Performance and Membrane Cleaning Experiments

Performance experiments were carried out over three cycles of operation, fouling, and cleaning with a short fourth cycle to measure the initial flux after the third membrane cleaning. Water flux as a function of time during the four cycles is shown in Figure 6. Maximum water fluxes for the GE PTFE membrane were around 14 L/m^2-hr (LMH) which is comparable to water fluxes in RO. For the GE PTFE membrane, no irreversible flux loss was detected; water fluxes returned to initial values after each cleaning cycle. The initial fluxes in successive cycles for the GE PP membrane increased which is unexpected but still does not indicate irreversible fouling.

Possible reasons for flux increase at the beginning of each cycle include membrane wetting or damage, or temperature variation. However, the conductivity of the permeate stream remained low; indicating that the membrane was still rejecting all dissolved solids. Fluxes in the GE PTFE membrane were much higher than that in the GE PP membrane. Overall, DCMD can be effectively incorporated in the operation of cooling towers where readily available low-grade heat can be a very inexpensive driving force for water purification and reuse in the power plant. Efficient cleaning coupled with high water flux rates in DCMD suggests that once through membrane systems with high recovery and low residence time are feasible. Pilot testing of the MD process will also be conducted during summer 2008 using a large scale, once through DCMD apparatus, and results will be presented in the GRC.

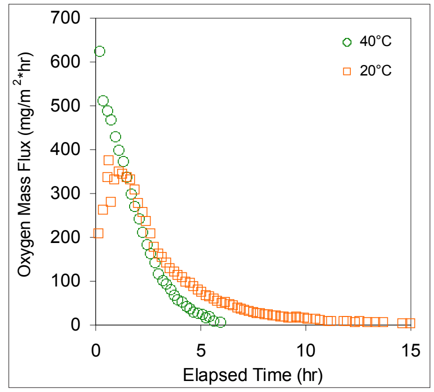

Figure 8. Oxygen flux for VMD pure water degasification experiments with feed temperatures of 20°CF and 40°C.

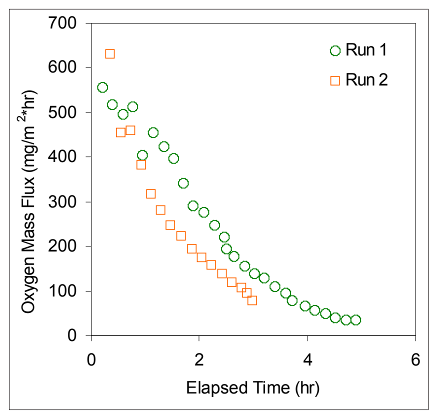

Figure 9. Two runs of oxygen fluxes for VMD, concentrated BD water degasification experiments with a feed temperature of 40°C.

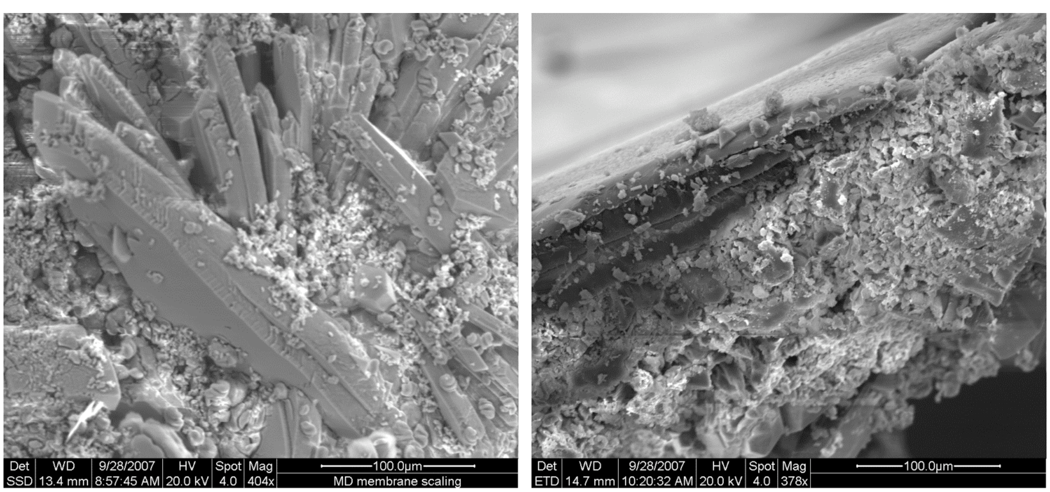

Figure 7. SEM images of GE PTFE membrane fouled with BD water filtered through a 0.5 μm filter. The left image is of the surface of the membrane and the right one is a cross section.

3.3.3. SEM

The SEM micrographs of the scaling on the DCMD membrane can be seen in Figure 7. Two major types of crystals can be seen in the images, large, well-formed geometric crystals, and smaller unconsolidated crystals. The spectroscopy confirmed that the larger crystals are $CaSO_4$ while the smaller ones are $CaCO_3$. Some NaCl crystals were also found but were assumed to have formed as water evaporated from the surface while the membrane was drying. In both the surface and cross-section views of the membrane, $CaCO_3$ and $CaSO_4$ crystals were randomly distributed indicating that there is no preferential precipitation of these salts and that their arrangement on the membrane surface is random. As precipitation of the major foulant crystals is random, no adjustments can be made to the way the experiments are done to augment the ratio of $CaSO_4$ to $CaCO_3$ fouling. Therefore, a cleaning agent that can dissolve both $CaCO_3$ and $CaSO_4$ must be used. Also, the depth to the geometry of the fouling shown in the SEM indicates that little to no pressure is exerted on the crystals as they are being formed. This allows for a more loosely arranged scale layer which may be more permeable than compacted scale layers seen in pressure driven membrane processes.

3.4. VMD Experiments

3.4.1. Pure Water Degasification

Once the headspace in the VMD apparatus had been removed, deoxygenation of the feed water was possible. Figure 8 shows the oxygen flux over time for the experiments conducted with feed temperatures of 20°C and 40°C. For all experiments, initial oxygen mass fluxes were high and decreased towards the end of the experiments. Initial oxygen flux was higher for the experiments conducted with feed at 40°C but flux decline occurred more quickly. DO concentrations followed a similar trend, declining to approximately 1 mg/L in all experiments. There was observable water flux for experiments at 40°C but none for experiments at 20°C. This indicates that during deoxygenation of BD water, more pure water can be produced for internal use in the cooling process.

3.4.2. Concentrated BD Water Degasification

Results for concentrated BD degasification experiments were similar to those for pure water feed. Results in Figure 9 illustrate the oxygen flux over time for the two concentrated BD experiments performed with a feed temperature of 40°C. Initial oxygen fluxes and flux declines were similar to those in the pure water experiments. Water fluxes were also similar to those in the pure water experiments. The similarity between the concentrated BD and pure water degasification experiments suggests that high salt concentrations in the concentrated BD water have little effect on the efficiency of the VMD process.

Using a preliminary model based on the results from the VMD experiments, a rough estimate of a large scale VMD treatment train for the degasification of concentrated BD water has been completed. Based on this model, a once through VMD system operating with a feed temperature of 40°C, a feed flow rate of 100,000 gallons per day, a vacuum of 360 mmHg, and using 16 membrane elements (4 parallel trains of 4 element in series) with a surface area of 14 m^2 per element could reduce DO concentrations from 8 to 1.2 mg/L. This minimal investment in membrane system has the potential to substantially reduce the amount of chemicals required to deoxygenate BD water before injection into the geothermal reservoir. Results from field testing will be used to fine tune the model and verify its accuracy.

4. Conclusions

Membrane processes are becoming popular for treatment of drinking water and wastewater. In many water reuse applications, including in industrial settings, membranes are the process of preference. With new membrane processes, and particularly thermally-driven membrane processes, more efficient use of water and energy in cooling towers of geothermal power plants can be achieved.

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