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Membrane distillation for concentration of hypersaline brines from the Great Salt Lake: Effects of scaling and fouling on performance, efficiency, and salt rejection

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ABSTRACT

Membrane distillation (MD) is a thermally-driven separation process that utilizes a difference in vapor pressure across a porous, hydrophobic membrane as the driving force. MD may be applied to aqueous systems at concentrations up to and exceeding saturation of both sparingly soluble salts and soluble salts such as sodium chloride (NaCl), leading to potential application in high-recovery desalination processes that approach Zero Liquid Discharge (ZLD) operation, or as a concentration strategy for mineral recovery. Scaling and fouling is a significant risk for such processes, and knowledge of the effects of these phenomena on performance is essential to the evaluation of MD as a viable technology for these applications. The present study investigated the scaling and fouling behavior of a hypersaline brine collected from the North Arm of the Great Salt Lake (GSL), which was nearly saturated with respect to NaCl, and also contained high concentrations of dissolved minerals and organic carbon. Effects on water flux, thermal efficiency, and salt rejection were measured, and membranes used were analyzed before and after testing to evaluate potential causes of these effects. Scaling by NaCl crystallization on the membrane surface limited water recovery to approximately 10%, and also caused damage to the internal pore structure of the membrane when the temperature difference (ΔT) between the feed and distillate was higher than 20 °C. Analysis of the solution chemistry of the GSL water was effective in predicting the scaling tendency of NaCl, but inadequate in predicting the scaling tendency of other salts. Amorphous scaling structures on the membrane surfaces containing magnesium and oxygen were implied as the dominant factors contributing to performance decline at concentrations below NaCl saturation, and the result of fouling due to interactions between organic matter and magnesium. Operation at a maximum water recovery of 8% combined with intermittent reversal of the temperature gradient were effective strategies to prevent both scaling and fouling and maintain long-term performance.

1. Introduction

Desalination technologies are becoming increasingly important for the treatment of impaired water for drinking, agriculture, diverse industries, and for environmental protection. Due to increased water demand, technological advancements, and improvements in the cost-competitiveness of desalination, it is currently in a period of rapid growth and is expected to reach a global capacity of 100 million m^3/day in 2015 [1]. Although desalination may be a promising means of meeting fresh water demands in water scarce regions, it is rather energy intensive and produces a hypersaline reject brine that presents an environmental disposal challenge. Concentrated brines from seawater desalination are typically returned to the sea. In the case of inland brackish water desalination, where disposal to seawater is not an option, the brine must be disposed of by other means, including land application, which may adversely impact soil and groundwater [2].

Strategies to reduce the volume of brine generated during desalination could greatly reduce the environmental impact of desalination, particularly if they include mineral recovery from brine and approach a zero liquid discharge (ZLD) operation. These brines may contain minerals of economic importance, which could offset the increased cost of desalination. Naturally occurring hypersaline brines such as the water of the Great Salt Lake (GSL) and the Dead Sea [3] are already utilized commercially for recovery of minerals composed of the most concentrated ions, including sodium, potassium, calcium, magnesium, sulfate, and chloride. Mineral

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extraction from lower salinity brines has also been explored, including from some geothermal brines [4–6] and desalination brines [7]. Some brines have also attracted interest as a source of higher value minerals such as lithium [8–11]. However, most brines are composed primarily of common salts such as sodium chloride (NaCl), and concentration combined with salt removal is needed before the more valuable minerals can be recovered. This initial concentration is often accomplished using evaporation ponds that require large amounts of land area and time for evaporation, lose large amounts of water to the atmosphere, and experience seasonal variation in performance due to local climate conditions.

Separation processes that can desalinate water containing very high total dissolved solids (TDS) could potentially increase water recovery while serving as the primary concentration process for mineral recovery, which may improve overall process efficiency and reduce the footprint of combined desalination and mineral recovery operations. However, due to both inherent thermodynamic and physical limitations and high mineral scaling potential, high recovery desalination is difficult to achieve with existing technologies. Thermal desalination such as multi-stage flash distillation (MSF) and multiple-effect distillation (MED) are prone to mineral scaling of heat exchanger surfaces due to the high temperatures involved, and therefore they typically operate in the range of 10–30% water recovery for seawater desalination [12]. Reverse osmosis (RO) may achieve higher recovery, typically about 50% for seawater; however, it is also susceptible to organic and biological fouling [13,14] and experiences increasing energy demand with recovery due to the increased osmotic pressure of the feed solution as it is concentrated. Moreover, as concentration increases, the hydraulic pressure required to overcome the osmotic pressure eventually exceeds the mechanical limitations of the membranes and modules used, effectively restricting the maximum operating concentration.

Membrane distillation (MD) is a unique membrane process that utilizes a partial vapor pressure difference across a hydrophobic, microporous membrane to induce vapor transport through the membrane pores [15]. The most common configuration, known as direct contact membrane distillation (DCMD), involves both the feed solution and distillate in direct contact with the two membrane surfaces, and vapor pressure difference is established by maintaining the feed solution at a higher temperature than the distillate. In principle, mass transport occurs in the vapor phase only, allowing for the separation of highly purified water from brines containing primarily nonvolatile solutes such as those present in seawater, brackish groundwater, or saline lake water. Because the feed solution and distillate are separated by a vapor phase, the difference in osmotic pressure between the feed and permeate streams does not affect the process; and because the partial vapor pressure of water is only slightly affected by the presence of dissolved ions, very high salinity streams can be desalinated with MD. Only minimal flux decline is observed when using MD to desalinate water having high NaCl concentrations [16–19], and because of this, MD is believed to have great potential as a desalination process for brines, including concentrates from RO [20–24] and nanofiltration (NF) [25–27], and hypersaline streams such as water from the GSL [28].

The unique capabilities of MD at high salt concentrations have led to interest in its potential for integration with crystallization and mineral recovery in a combined membrane distillation crystallization (MDC) process, and has been effectively demonstrated at the laboratory scale for the recovery of various salts commonly found in natural and industrial brines, including NaCl [25,29–32], $CaCO_3$ and $MgSO_4$ [25], and Na_2SO_4 [26,32]. For the most part, efforts to date have used synthetic solutions, which may perform quite differently than natural brines. For example, in an MDC study using RO concentrate from natural seawater, Ji et al. [20] reported reduced transmembrane flux, a 20% reduction of salts crystallized, and a 15–23% reduction in crystal growth rate (compared to artificial concentrates) due to dissolved organic matter.

As in other desalination processes, mineral scaling and organic fouling may be significant problems for MD; and the potential for MDC to become established as a viable treatment strategy is in part dependent on a more comprehensive understanding of crystallization behavior of natural hypersaline brines concentrated with MD. Scaling by sparingly soluble salts such as $CaCO_3$, $CaSO_4$, and silica [33–38] are known to cause substantial flux decline; however, in some cases it has been shown that the scale layer formed on the feed side of MD membranes is relatively porous and does not completely prevent water flux [37] and may be removed with simple cleaning processes [28,35,39]. Also, employing management strategies such as periodic flushing of the membrane with DI water [36] or periodic reversal of the driving force, which reverses the direction of water transport [28], can interrupt the crystallization process before sufficient induction time has passed and may mitigate scale formation. While scaling by sparingly soluble salts typically forms on the membrane surface only and does not affect salt rejection, scaling by NaCl on the membrane surface itself has been shown to aggravate pore wetting [29,39], which reduces water flux due to the loss of driving force and can also reduce salt rejection, and may lead to crystallization inside the pores themselves [30]. Crystallization on membrane surfaces may also affect membrane properties such as surface hydrophobicity and mechanical strength [40].

In this study we investigated membrane scaling and fouling behavior of the MD process applied to the concentration of hypersaline brine obtained from the North Arm of the GSL, which is nearly saturated with respect to NaCl and contains high concentrations of calcium, magnesium, potassium, sulfate, silica, and natural organic matter. Experiments and analyses were performed to isolate the effects of scaling by the different salts at high concentration factors, to identify dominant scaling and fouling mechanisms, and to characterize the short-term and long-term effects on membrane performance. Strategies for preventing and mitigating these effects were also investigated.

2. Mass and heat transfer in MD

Water flux (J) in the MD process is proportional to the vapor pressure difference between the feed and distillate streams [41]:

$$J = C_m(p_{f,m} - p_{d,m}) \tag{1}$$

where $p_{f,m}$ and $p_{d,m}$ are the vapor pressures of the feed and distillate streams at the membrane surface, respectively, and C_m is a mass transfer coefficient that is characteristic of the system. C_m is a function of the membrane physical properties (i.e., thickness, porosity, pore size, and pore tortuosity), and the temperature and pressure of the gaseous phase within the pores. In the DCMD configuration, vapor pressure differential is accomplished by maintaining a higher feed stream temperature (T_f) than distillate stream temperature (T_d). For pure water or very dilute solutions, vapor pressure of water at the membrane surface is a function of the mean membrane temperature (T_m) in accordance to the Antoine equation:

$$p = \exp\left(23.238 - \frac{3841}{T_m - 45}\right) \tag{2}$$

where $T_m = (T_f + T_d)/2$. At relatively low temperature difference between the feed and distillate streams, water flux may be expressed as a function of temperature:

$$J = C_m \frac{dp}{dT}\Delta T \tag{3}$$