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Sustainable operation of membrane distillation for enhancement of mineral recovery from hypersaline solutions

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ABSTRACT

Membrane distillation (MD) is an emerging desalination technology that has the ability to desalinate hypersaline brines, including those used in mineral production. MD can potentially replace evaporation ponds in conventional mineral production processes because of its small footprint and ability to utilize industrial low-grade heat. In the current study MD was investigated for sustained water recovery and concentration of hypersaline brines. Direct contact MD (DCMD) experiments were performed with water from the Great Salt Lake (> 150,000 mg/L total dissolved solids) as the feed stream and deionized water as the distillate stream. DCMD was able to concentrate the feed solution to twice its original concentration, achieving close to complete inorganic salt rejection. During experiments water flux declined to 80% of its initial value (from 11 to 2 L m^{-2} h^{-1}). Real-time microscopy revealed that precipitation of salts on the membrane surface was the main contributor to the decline in water flux. The application of novel scale-mitigation techniques was highly effective in preventing scale formation on membrane surfaces, sustaining high water flux and salt rejection, and eliminating chemical consumption used for membrane cleaning. MD was compared to natural evaporation and was found to potentially replace 4047 m^2 (1 acre) of evaporation ponds with approximately 24 m^2 (259 ft^2) of membrane area and to be nearly 170 times faster in concentrating hypersaline brines.

1. Introduction

As population grows, an increased stress is placed on natural resources [1]; thus, there is a need for more holistic approaches to process intensification, in which process waste is considered a resource. For example, in desalination, brine is considered a byproduct and treated as a waste stream, whereas in mineral production water is considered a byproduct and, as common practice, is evaporated to the atmosphere. Ironically, the waste stream of one process is the product of the other. Efficient utilization of brines and on-site energy resources could result in production of both water and high-value minerals for beneficial use, including potable water for urban areas and minerals for fertilizers or road deicing.

In mineral production, evaporation ponds are traditionally utilized for concentration of saline water and precipitation of minerals, which are then further processed in chemical plants. Evaporation ponds commonly use large areas, they are time and energy intensive, and when used, large volumes of valuable water are lost to the atmosphere [2]. In order to improve the efficiency of mineral recovery, replacement of evaporation ponds with desalination processes could minimize land use and increase water recovery from hypersaline streams.

Current engineered processes for desalination of brackish water and seawater include thermal distillation or membrane processes such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis (ED). Conventional thermal distillation processes are capable of achieving high water recovery, but they are limited by high-energy consumption needed to heat the feed stream [3]. While RO, NF, and ED are commonly utilized membrane processes for desalination [2], when feed solutions are highly concentrated or approach saturation, these processes are limited by operating pressures (RO and NF) or applied voltage (ED), and in many cases membrane scaling [4].

Alternatively, membrane distillation (MD) is a novel and unique membrane process that can synergistically assist in mineral recovery and simultaneously produce pure water. MD is a thermally driven membrane process in which the driving force for mass transfer of water is the partial vapor pressure difference across a microporous hydrophobic membrane. Thus, compared to hydraulic pressure and electric field driven membrane processes, MD is minimally affected by increased salt concentrations [5]. In direct contact MD (DCMD), a warm feed stream (e.g., brine) and a cooler fresh water stream (e.g., deionized water) are in direct contact with the active and support sides of the membrane, respectively [5]. In DCMD, water evaporates from the feed solution

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at the feed-pore interface on the feed side of the membrane, water vapors then diffuse through the membrane pores, and ultimately they condense into the distillate stream at the distillate-pore interface on the support side of the membrane.

1.1. Factors affecting DCMD process performance

While MD is a unique process that can be utilized for desalination of hypersaline streams, several transport phenomena may limit water flux through the membrane. These include decrease in partial vapor pressure, heat and mass transfer resistance across the membrane, and concentration and temperature polarization (or loss in heat transfer) across the membrane [5,6].

Heat and mass transfer dominate the vapor pressure driving force in MD. Because several phase changes occur during MD, the heat transfer resistances across the boundary layers of the membrane surface are often the rate-limiting step [5]. Although DCMD is considered one of the simpler configurations of MD, the conductive heat transfer across the membrane is greater than in other MD configurations [6,7].

Heat transfer across the MD membrane gives rise to temperature polarization (TP) in which the temperature of the feed solution at the feed–membrane interface declines and the temperature of the distillate at the distillate–membrane interface increases. Mass transfer across the MD membrane gives rise to concentration polarization (CP) in which the vaporization of water from the feed stream through the MD membrane results in an increased solute concentration and thus a lower partial vapor pressure of water at the feed–membrane interface. Similar to other membrane processes, CP can also induce membrane scaling, which further reduces process performance [8,9].

Membrane scaling occurs when inorganic salts precipitate and accumulate on the membrane surface, thus blocking the pores for vapor to diffuse across the membrane and subsequently lowering water flux. Scaling of sparingly soluble salts such as $CaCO_3$, $CaSO_4$, and silicates has been identified as a cause of flux decline when recovering water from natural streams, including brines from desalination processes [10–17]. Two types of membrane scaling can occur: homogeneous and heterogeneous scaling. Homogeneous scaling occurs when crystals that form in the bulk solution precipitate on the membrane surface, and heterogeneous scaling occurs when salts crystallize directly on the membrane surface [18–20]. Scaling can alter membrane surface properties (i.e., hydrophobicity), change membrane pore structure, and ultimately decrease process efficiency and potentially lead to wetting of the membrane pores [12,13]. In MD it is essential that the porous membrane maintains its hydrophobicity to prevent membrane wetting, which will allow passage of water in a liquid phase through the membrane pores [5]. Pore wetting of the membrane hinders water flux, lowers salt rejection, and further impairs membrane integrity (i.e., loss of hydrophobicity).

1.2. DCMD for concentration of supersaturated solutions in mineral production

Replacing traditional concentration methods with MD could produce high quality minerals and water, reduce land footprint of evaporation ponds, and eliminate the required pumping of water from pond to pond in mineral production sites. Recent studies have shown that MD consumes less energy than traditional thermal distillation such as multi-stage flash and multi-effect distillation, and can further concentrate brines from desalination processes such as RO, NF, and ED [10,13,15,16,21–23]. Furthermore, utilization of low-grade heat sources such as industrial heat emissions and solar energy can offset the overall energy consumption needed for MD [24–27].

Recent studies have coupled membrane processes with crystallizers to concentrate and recover minerals in hypersaline solutions [14,22,28–35]; however, none of these studies have effectively mitigated membrane scaling. While membrane scaling has been investigated [10–13,23,34,36–40], effective scale mitigation techniques for maintaining and restoring water flux and salt rejection when desalinating saturated solutions are still lacking. In the current study, DCMD was applied to concentrate Great Salt Lake (GSL) water. The main objectives of the study were to evaluate the performance of DCMD in concentrating hypersaline brines from the GSL, and in doing so, optimize operating conditions to maximize water recovery and mitigate membrane scaling. Several unique methods were developed and tested to identify and mitigate membrane scaling. Finally, the replacement of evaporation ponds with DCMD was assessed as a means to intensify the mineral production process.

2. Materials and methods

2.1. Membranes

Two hydrophobic microporous membranes were acquired from GE Water (Minnetonka, MN). The first membrane (TS22) is a composite membrane consisting of a thin polytetrafluoroethylene (PTFE) active layer and a polypropylene woven support layer. The overall thickness of the TS22 membrane is 175 μm, with an active layer thickness of 5–10 μm. The second membrane (PP22) is an isotropic membrane made of polypropylene (PP), and is approximately 150 μm thick. Both membranes have a nominal pore size of 0.22 μm and a porosity of approximately 70% [41]. After experiments, the membranes were rinsed with deionized water and stored in a desiccator until analysis. A new membrane coupon was used for each set of experiments.

2.2. Membrane cells

Experiments were performed with acrylic membrane cells fitted to test flat sheet membranes. The cells were fabricated with symmetric flow channels on either side of the membrane, allowing for parallel flow of feed and distillate streams on the opposite sides of the membrane. Nitrile rubber gaskets were used to form flow channels, approximately 2 mm deep, on each side of the membrane. Turbulent enhancing spacers were placed in the flow channels to reduce temperature polarization effects, increase water flux, and ensure that the membrane lay flat and centered in the cell [41]. Experiments were performed using a modified SEPA-CF cell with an effective membrane surface area of 139 cm^2. To prevent precipitation of salts on the membrane surface, the membrane cell was positioned horizontally with the feed side (active side) facing down. To observe real-time membrane scaling, an additional set of experiments was performed with a stereomicroscope (Stemi 2000, Carl Zeiss Microscope, Thornwood, NY) and a direct observation membrane cell that has a glass observation port (12.7 cm × 2.54 cm) and an effective membrane surface area of 89 cm^2. During these experiments, the feed side of the membrane was facing up.

2.3. Bench-scale system

Bench-scale experiments were performed to investigate water flux, salt rejection, and membrane scaling. A supervisory control and data acquisition (SCADA) system (LabVIEW, National Instruments, Austin, TX; and a LabJack UE-9 Pro, Lakewood, CO) was utilized to control the temperatures of the feed and distillate streams and collect data to calculate water flux and batch recovery.