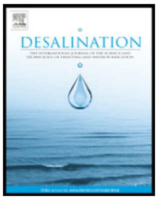
Desalination 374 (2015) 20–30

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Scale reduction and cleaning techniques during direct contact membrane distillation of seawater reverse osmosis brine

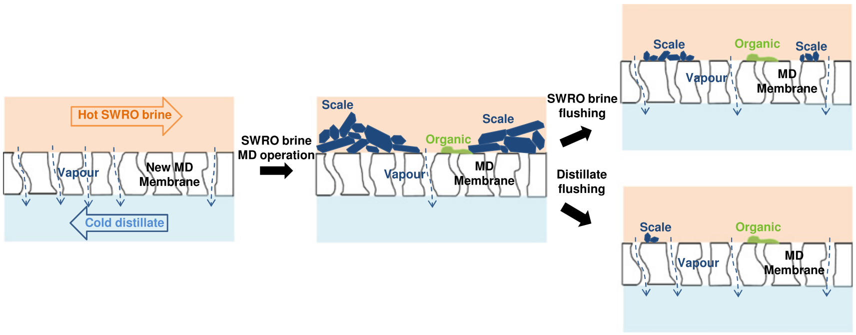
Po Zhang [a,b], Philipp Knötig [b], Stephen Gray [b], Mikel Duke [b]

[a] Osmoflo Pty Ltd, Adelaide, Australia
[b] Institute for Sustainability and Innovation, College of Engineering and Science, Victoria University, Melbourne, Australia

HIGHLIGHTS

- Reduction of distillate flux is primarily caused by precipitation of $CaCO_3$ and $CaSO_4$.
- Changing of pH in hot bulk brine provides early indication of scaling formation.
- Inline cartridge filtration improves DCMD operational time and water recovery.
- Antiscalant prolongs DCMD operational time by mitigating salts precipitation.
- SWRO brine and distillate flushings are effective in membrane cleaning.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form 1 July 2015
Accepted 2 July 2015
Available online 24 July 2015

Keywords:
Membrane distillation
Brine treatment
Scaling
Antiscalant
Membrane cleaning

ABSTRACT

Scale reduction and cleaning techniques were investigated for direct contact membrane distillation (DCMD) during processing of seawater reverse osmosis (SWRO) brine at feed and distillate temperature of 50 °C and 25 °C, respectively. The results showed that MD achieved distillate electrical conductivity (EC) of less than 5 μS/cm and good flux (above 20 $L/m^2/h$) prior to rapid flux reduction at a brine feed EC of approximately 160 mS/cm. Analysis by inductively coupled plasma (ICP) and scanning electron microscopy coupled with an energy dispersive spectroscopy (SEM–EDS) revealed that flux reduction was primarily caused by precipitation of $CaCO_3$ and $CaSO_4$. Titration results showed that concentrating brine feed water pH was linked to distillate flux, and further revealed the precipitation process of $CaCO_3$. Implementation of a 0.45 μm cartridge filter at the brine feed inlet extended water recovery from 45% to 60% due to the removal of precipitating salts. Simple chemical free membrane cleaning regime involving distillate flushing restored MD initial flux to 98%. Periodic raw SWRO brine feed flushing also restored membrane initial flux to 84% over 133 h of operation. Results also showed that possible organic fouling developed over long-term MD operation with constant EC of SWRO brine at feed.

1. Introduction

In the last decade, seawater reverse osmosis (SWRO) desalination has an increasingly important role to supply drinking water in many countries due to effects from climate change and population growth in coastal cities. SWRO requires high pressure pumping to force water molecules through a semi-permeable membrane against the osmotic pressure while rejecting salt ions. This process achieves 40% to 50% water recovery and the remaining 50% to 60% brine solution is usually discharged back to the sea. SWRO brine contains several chemical agents that are added during RO pre-treatment processes. Studies

---

E-mail address: mikel.duke@vu.edu.au (M. Duke).

http://dx.doi.org/10.1016/j.desal.2015.07.005
0011-9164/

suggested that SWRO brine has a strong potential to detrimentally impact costal ecosystem and species [1,2]. This has led to research on environmental friendly and economical viable SWRO brine management options [3].

Membrane distillation (MD) has become a promising technology for recovery of water from SWRO brine where waste heat can be utilized from a nearby power plant [4,5]. Mericq et al. reported that 89% water recovery could be achieved for synthetic SWRO brine treatment coupled with vacuum MD (VMD) [8]. However, scale formation and mitigation in the presence of antiscalant were not investigated in this study with real SWRO brine. Other water treatment technologies (e.g., crystallization) could be coupled with MD and eventually achieves zero liquid discharge of SWRO brine [6,7].

MD is a thermal membrane separation process that involves transport of vapor through microporous hydrophobic membranes and operates on the principle of vapor–liquid equilibrium as a basis for molecular separation [9]. Compared with other brine treatment technologies, MD has several advantages, such as lower operating pressure, moderate temperatures, potential for 100% rejection of non-volatile solutes and production of high purity distillate [10]. Another advantage of MD is its compact configuration compared to other thermal processes [11]. MD has been developed in four different configurations, including direct contact MD (DCMD), air gap MD (AGMD), vacuum MD (VMD) and sweeping gas MD (SGMD). Among those configurations, DCMD process has been considered as the simplest configuration for treating concentrated brines [12]. In DCMD brine treatment, the heated brine solution is in direct contact with one side of the porous hydrophobic membrane while the cold distillate flows on the other side of the membrane. Salts and non-volatile organic matter stay on the brine side of the membrane, while water vapor diffuses through the membrane pores and condenses on the distillate side of the membrane.

Like other membrane processes, the formation of crystal deposits on the membrane surface causes an operational problem that dramatically impacts on performance and long-term operation [13]. Uniquely for MD, both temperature and concentration polarization occur due to heat and mass transfer processes associated with its operation. Sparingly soluble salts such as $CaCO_3$ and $CaSO_4$ exist in SWRO brine and have inverse solubility with temperature. These salts are likely to form crystal deposits on the membrane surface due to hot bulk brine solution. Water vapor flux is also expected to create a high level of supersaturation of salts near the membrane surface, which also aggravates salt precipitation [14]. The deposits not only reduce the MD membrane effective operational area but also increase the heat resistance between the bulk side of brine solution and membrane surface which inhibit vapor flux transfer through the membrane [15]. Several studies have revealed that the salt deposits can cause severe wetting of membrane pores that eventually contaminates the distillate and significantly increases distillate electrical conductivity (EC) [14]. Gryta reported in 2008 that $CaCO_3$ scaling was formed inside polypropylene (PP) membrane pores and could be dissolved by 3 wt.% HCl rinsing solution, but this also led to wetting of adjacent pores [16]. During long-term MD operation, water evaporation takes place on wetted crystal surfaces and creates the possibility of heterogeneous crystallization and the growth of crystallites in the direction of the vapor phase. As a consequence, a new area of pores will be wetted and the total area of wetted pores grows. This process was described as the "water-logging" mechanism by Gryta [17]. Exploring cleaning techniques for MD are therefore not only important to minimize flux loss, but also to avoid membrane wetting due to scale intrusion into the pores.

Although MD membrane cleaning has not been extensively studied in the past, some recent cleaning trials have already shown growing interest in the development of efficient and cost effective cleaning regimes to achieve long-term MD operation. Gryta [16] conducted DCMD on tap water and reported that rinsing with 3 wt.% HCl solution dissolved $CaCO_3$ deposits on capillary PP membrane allowing restoration of the initial membrane permeability. Similarly He et al. [18] studied $CaSO_4$ scaling on PP hollow fiber membrane in DCMD experiments, and showed that flushing scaled membranes with 0.06 M NaCl solution followed by a demineralized water rinse returned membrane water flux to the baseline value. Nghiem and Cath [19] also reported that a simple membrane cleaning regime involving membrane periodic flushing with demineralized water proved to be effective for controlling $CaSO_4$ scaling on polytetrafluoroethylene (PTFE) flat sheet membrane.

Antiscalants are also utilized to combat scaling in process equipment. Antiscalant is considered effective in inhibiting crystal deposit build up during RO processes and for high temperature processes such as industrial boiler applications. Antiscalant mitigates membrane scaling by selecting crystal morphology nucleation, retarding the rate of crystal growth and changing the agglomeration tendency of crystals [20]. Commercial antiscalants that are used in RO processes generally contain polyphosphates, organophosphonates, and polyelectrolytes [21]. In RO application, antiscalant is dosed (1 to 10 mg/L) in RO feed to postpone salt precipitation, keeping salts in a supersaturation condition as brine leaves the process. For the application of MD on RO brine, the antiscalant is typically present in the RO brine being fed to the MD and could potentially influence MD performance. Limited studies have been undertaken on MD scaling inhibition with antiscalant dosing commonly used in RO processes. Gryta [21] conducted a study on $CaCO_3$ scaling in MD with mixing of polyphosphate based antiscalcant. It was discovered that polyphosphate prolonged the $CaCO_3$ precipitation process and changed the morphology of crystal deposits on the membrane. Periodic membrane flushing with diluted HCl solution was able to remove amorphous deposits that formed during 200 h of operation and restored the membrane initial flux. He et al. [22] reported that commercial antiscalant contains organophosphonate compound was effective to mitigate scaling in DCMD at 75 °C under a supersaturated $CaSO_4$ solution which corresponds to 8-fold concentrated sea water. Ketrane et al. [23] studied five commercial antiscalants on inhibiting $CaCO_3$ precipitation from hard water, and it was found that scale inhibiting capacity of phosphonates remained unchanged in the range temperature 20 °C to 50 °C. It also suggested that phosphonates are better inhibitors than polycarboxylates or polyphosphates.

In a recent work, the use of a cartridge filter was found to be effective at reducing scaling during the treatment of a real groundwater RO brine by placing the filter in the hottest region of the hot cycle (after heat exchanger, but before membrane) which inhibited $CaCO_3$ scale formation on the membrane enabling much higher water recoveries to be achieved [24]. Previous studies have explored scaling mitigation approaches during MD treatment of RO brine primarily using synthetic solutions. Limited studies have undertaken at the scale formation mechanism and membrane cleaning regime with real RO brine and presence of antiscalant. The main objective of this present study was to investigate the scale formation behavior on MD membranes when treating SWRO brine. Techniques to manage scaling including non-chemical cleaning, antiscalants and filtration will be studied to weigh up the best strategies to manage membrane fouling.

2. Experimental

2.1. DCMD bench scale apparatus

The flow diagram of the DCMD apparatus is shown in Fig. 1. The apparatus contained a feed water section and a distillate water section. Feed water was withdrawn from the feed container (6) and transferred to the DCMD module (3) through a heating unit (2). The heating unit consisted of a water bath and coil. The hot water bath temperature was set at a fixed value during experiments. The coil was made of 1/4 inch 316 L stainless steel tube and was submerged inside the water