Journal of Membrane Science 345 (2009) 53–58

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Effects of antiscalants to mitigate membrane scaling by direct contact membrane distillation

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ARTICLE INFO

Article history:
Received 17 April 2009
Received in revised form 28 July 2009
Accepted 8 August 2009
Available online 15 August 2009

Keywords:
Antiscalant
Membrane distillation
Scaling
$CaCO_3$
$CaSO_4$

ABSTRACT

The effects of antiscalants on mitigating the potential for membrane scaling by calcite and gypsum, respectively, were investigated during the direct contact membrane distillation process (DCMD) implemented with porous hydrophobic polypropylene (PP) hollow fibers having a porous fluorosilicone coating on the fiber outside surface. The surface tension and the membrane breakthrough pressure were tested for different kinds of antiscalants. At room temperature, antiscalant solutions behave like tap water. Based on this result, DCMD scaling experiments with $CaSO_4$ or $CaCO_3$ as a scaling salt were conducted. The supersaturation indices of the scaling salts used correspond to sea water concentrated 5 times for $CaSO_4$ ($\sim$75 °C) or half of the maximum saturation index (SI) reached during the concentration of sea water to 10 times for $CaCO_3$ ($\sim$73 °C). The results show that antiscalants K752 and GHR could dramatically extend the induction period for the nucleation of gypsum and calcite, respectively; further they slow down the precipitation rate of crystals, even at a dosage of only 0.6 mg/L. By comparison, a larger amount of antiscalant could further slow down the precipitation and also extend the induction period for both calcite and gypsum systems. There was no sign of any drop in the water vapor flux nor any increase in the distillate conductivity. Concentrates or reject streams from reverse osmosis desalination processes containing antiscalants may therefore be conveniently concentrated further by DCMD.

1. Introduction

Like other thermal desalination processes, membrane distillation (MD) could achieve much higher water recovery than reverse osmosis (RO), given its lack of sensitivity to osmotic pressures. During such a membrane distillation process, the mineral salts, e.g., $CaSO_4$ and $CaCO_3$ may potentially cause severe membrane scaling due to their inverse temperature-solubility behavior [1–3]. Indeed such scaling is a major limiting factor to recovery in conventional thermal desalination processes. Any method to solve such a potential problem will be very helpful in terms of reducing downtime and cost. While it has been shown in our previous communications [4,5] that membrane distillation is more resistant to scaling than conventional thermal processes, there is still room for improvement. As reported in the literature [6–9], antiscalants are efficient in inhibiting scaling from deposits not only during the RO process but also during higher temperature processes, for example, multistage flash (MSF) desalination, multieffect desalination (MED) and also associated heat exchange processes. The application of antiscalants could potentially help prevent scaling in membrane distillation as well, if there is no problem of pore wetting caused by antiscalants. To our knowledge, no investigations of this application have been reported.

Commonly used antiscalants include condensed polyphosphates, organophosphonates, and polyelectrolytes. Effective polyelectrolyte inhibitors are mostly polycarboxylic acids, e.g., polyacrylic acid, polymethacrylic acid and polymaleic acid. The antiscalant technique is cost effective: in many cases scaling can be suppressed with less than 10 mg/L of the antiscalant due to physical mechanisms rather than chemical mechanisms [10]. Specifically, antiscalants can (1) force a crystal morphology selective nucleation, (2) add diffusion and adsorption resistances retarding the crystal growth velocity and (3) change the crystal surface properties and therefore its agglomeration tendency [11]. Because of their reported effects in modifying the surface energies of crystals, the possible impact of these antiscalants on the surface energy of the hydrophobic MD membranes should be evaluated.

We have recently initiated a series of studies on desalination by DCMD. These studies carried out in laboratory at two scales [12,13] as well as in pilot plant scale [14] employed porous hydrophobic polypropylene hollow fiber membranes having a porous fluorosilicone coating on the outside surface exposed to the hot brine.

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doi:10.1016/j.memsci.2009.08.021

In the present study, experiments were first conducted to determine whether the microporous hydrophobic PP membrane would be wetted by antiscalant solutions at possible working concentrations by measuring solution surface tension and membrane breakthrough pressure. Polar liquids, such as water, have strong intermolecular interactions and thus high surface tension. Organic molecules which are mostly apolar or have low polarity usually have a small value of surface tension. As reported [15], a hydrophobic porous membrane could easily become wetted by aqueous feeds containing organics. Breakthrough pressure is a critical penetration pressure, above which the liquid penetrates the membrane pores [16]. Membrane distillation operation can be difficult if the breakthrough pressure magnitude is low.

Next, the effects of different antiscalant solutions on mitigating potential membrane scaling in DCMD were investigated and compared. In each case, the induction period and the calcium precipitation rate of gypsum or calcite were measured via the change of calcium concentration with time. Since scaling caused by calcite precipitation could be easily inhibited by the addition of a dilute acid, e.g., HCl [5], the performance of antiscalants on mitigating gypsum scaling was given greater weight for the MD experiments. Prior to DCMD scaling experiments, five different kinds of commercial antiscalants were compared in a non-membrane system, so that the best antiscalant to inhibit the gypsum scaling was known. For both scaling salts, the effects of the antiscalant dosage on their nucleation were investigated.

As reported in literature [17], partial pore wetting will decrease the water vapor flux. The entrance of a saline solution into the membrane pores [18] resulting from pore wetting by an antiscalant may cause an increase in the distillate conductivity. Here we used the parameters of water vapor flux and distillate conductivity to determine whether there was any problem with antiscalants on the performance of DCMD through pore wetting.

2. Experimental procedure

The antiscalants studied in this paper are listed in Table 1. Surface tensions of antiscalant solutions having concentrations of 0.6, 20, 50 and 70 mg/L were tested with the Kruss K-8 Surface Tensiometer (with Du Noūy Ring) (KRÜSS USA, Matthews, NC) at ~23 °C. For breakthrough pressure tests, a piece of a 25 μm thick porous hydrophobic polypropylene flat membrane (Celgard 2400, Celgard, Charlotte, NC) was used in a test cell. The gas N_2 from a cylinder was used to push the antiscalant solution inside a pressure vessel to flow over one side of the membrane. The outlet of the test cell on this side of membrane was blocked. Breakthrough was checked by whether water came out from the other side of the test cell. Within 24 h if no breakthrough happened, the pressure measured by a test gauge was increased to a higher value till 997.6 kPa (130 psig) was reached. Breakthrough pressures of antiscalant solutions were tested for different concentrations in the following order, e.g., 0.6, 2, 4, 8, 14, 20 mg/L. Before testing another series of antiscalant solutions, the test cell and the flat membrane were thoroughly washed/flushed with DI water and dried in air.

The following procedure was adopted for $CaSO_4$ scaling studies with antiscalants without any membrane. At room temperature Na_2SO_4 solution was added into the mixed solution of $CaCl_2$ solution and antiscalants. The mixed solutions were stirred for 20 min (Corning magnetic stirrer, Lowell, MA) before being heated up to the MD operating temperature under a fixed heating procedure and stirring rate. The time to achieve a full turbid white solution was recorded for each of the tested mixed solution.

The experimental apparatus developed to study the effects of antiscalants on mitigating scaling during the DCMD process was similar to that employed in our previous scaling studies [4,5] except that the filter holder was removed. The properties of the membrane modules employed are shown in Table 2. The hot brine and the cold distillate were pumped respectively through the shell side and lumen side of the hollow fiber DCMD membrane module. In each experiment the inlet temperatures of both brine and distillate were kept constant. To keep the feed concentration stable, the liquid level was maintained between two level probes. By recording the amount of make-up water for each refill (noted as m_m, mg) and the time difference between two continuous make-ups (noted as t, min), the water vapor production rate could be calculated from $\dot{m}_v = m_m/t$. Alternatively it could be calculated from the local slope of the total make-up water weight vs. time.

Supersaturated solutions of calcium sulfate (or calcium carbonate) were prepared by mixing equimolar solutions of $CaCl_2$ and Na_2SO_4 (or $NaHCO_3$). The antiscalant solutions were dosed and mixed with the supersaturated Ca solution for 20 min before the feed solution was heated up. The methods of sample-taking, sample-preparation, atomic absorption (AA) analysis for [Ca] in the brine tank and Ion Chromatograph (IC) analysis for the anion in the distillate tank were as described in [4,5].

3. Results and discussion

3.1. Surface tension of antiscalant solutions

For all of the tested antiscalant solutions having concentrations varying from 0.6 to 70 mg/L, the value of surface tension was found to be 71.5 mN/m, which is very close to that of tap water (71.8 mN/m). It means that, at the experimental concentrations, the solutions of antiscalants, K752, K797, GHR, GLF and GSI show a water-like polar property and negligible surfactant effects.

Table 1
Information on antiscalants[a] studied.

Antiscalants	Chemical name	Weight % less than	pH	Recommended conditions		
				Dosage (mg/L)	$CaCO_3$	$CaSO_4$
K797[b]	Water	50	2.4–3.0	N/A	N/A	N/A
	Acrylic terpolymer/Solids	50				
K752[b]	Polyacrylic acid	47	2.2–3.0	N/A	N/A	N/A
	Water	37				
	Sodium polyacrylate	16				
GHR[c]	Aqueous solution of a nitrogen containing organo-phosphorus compound	N/A	1.8–2.0	0.4–0.8	Best choice	Effective
GLF[c]	Aqueous solution of an organo-phosphorus compound	N/A	9.8–10.2	2–4	Best choice	Effective
GSI[c]	Synergistic blend of antiscalants based on neutralised carboxylic and phosphonic acids	N/A	9.8–10.2	2–5	Effective	Effective

[a] Provided by manufacturers.

[b] From Noveon Inc. (Cleveland, OH).

[c] From Genesys International LTD. (Minneapolis, MN).