Journal of Membrane Science 510 (2016) 293–305

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Calcium carbonate scaling of desalination membranes: Assessment of scaling parameters from dead-end filtration experiments

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
24 February 2016
Accepted 26 February 2016
Available online 2 March 2016

Keywords:
Incipient scaling
Dead-end filtration
RO membrane desalination
Modeling
Permeation velocity

ABSTRACT

Membrane desalination is associated with significantly increased ion concentration of rejected sparingly soluble salts (commonly of calcium, magnesium, barium, etc) right at the membrane surface, leading to undesirable membrane scaling. Optimization of desalination membrane-plant design and its operation strategy requires quantification of scaling evolution phenomena, through appropriate mathematical models involving experimentally determined system parameters. In recent years, a modeling approach based on heterogeneous nucleation-growth theory was developed for this purpose, and proven to be successful in the case of non-stirred dead-end desalination experiments but not in the case of cross-flow and stirred dead-end desalination. To resolve this inconsistency, new results from numerous sets of improved dead-end non-stirred experiments (some with controlled changes of imposed pressure difference during testing) are reported that provide useful quantitative information and insights regarding incipient scaling. The previous modeling approach is generalized considering non-classical nucleation. Moreover, the likely scatter of local membrane-surface properties is considered in a parameter estimation approach. The new modeling approach leads to estimation of a range of scaling-model parameters consistent with the experimental data. Such parameters can be employed in comprehensive modeling tools of membrane-modules, to simulate their operation for the particular type of membrane for which parameters are extracted.

1. Introduction

Various water treatment and desalination technologies have been developed, and are under development, to cope with the clean water scarcity at global scale [1–3]. Treated waste-water reuse and desalination of seawater or brackish water have emerged as reliable solutions to this serious problem [3,4]. In particular, reverse osmosis (RO) membrane desalination is the technology of choice for new desalination installations, mainly due to improvements of membrane materials and of overall process engineering [4], although maximization of clean-water recovery and minimization of specific energy consumption are still the major challenges in RO operation [3,5]. However, the concentration of sparingly soluble salts in the feed stream has an essential influence on permeate recovery in membrane desalination and water treatment processes [6]. These salts tend to precipitate on the surface of the membrane due to creation of local supersaturation (i.e. induced by the so-called concentration polarization) adversely affecting the desalination process efficiency (i.e. through reduction of permeate flux, increase in transmembrane pressure, product quality deterioration, membrane life shortening), economics and the environment [7]. Therefore, reliable prediction and prevention of salts precipitation in membrane systems is a key issue for their operation [8]; for instance, overprediction of brine scaling tendency leads in over-dose of the commonly used anti-scalants (with negative environmental and economic impact), whereas underestimation of the scaling potential results in salts precipitation and membrane degradation.

Although various salts have been found in membrane autopsy studies, calcium carbonate, which is studied in this paper, and calcium sulfate dihydrate are most commonly encountered in desalination of surface and ground waters [3,5,7]. Scale formation is reported to occur through two pathways; i.e. direct crystallization on the membrane surface, due to membrane active sites which favour nucleation and further nuclei growth and bulk precipitation with ensuing crystallite deposition [9–13]. Scaling in membrane systems is considered to be a combination of these two

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http://dx.doi.org/10.1016/j.memsci.2016.02.061
0376-7388/

mechanisms and is affected by membrane morphology and process conditions; however, there is uncertainty on the mechanisms and rate of nuclei (and/or deposit) development on the membrane surface during desalination. The literature on bulk precipitation of sparingly soluble salts [14–17] and on the heterogeneous crystallization on solid surfaces [18–21] is rather extensive. However, there are still significant gaps in understanding of incipient scale formation on solid substrates [22] and especially on surfaces of membranes used for water desalination. In addition, the discussion on existence of an induction period during membrane scaling is still open [23]. The usual procedure in the literature for the determination of the induction time is by monitoring fluid variables as turbidity, conductivity, Ca^{+2} concentration, pH or global variables as the permeate flux [10,12,14] that have low sensitivity in detection of incipient scale formation [23].

To address this problem systematically, one needs a comprehensive model/simulator of incipient scaling occurring in the spacer-filled membrane channels, based on a realistic physicochemical model with correctly estimated input parameters. The approach of performing (relatively short-duration) scaling experiments under controlled conditions in the experimentally convenient dead-end configuration and of ‘transferring’ the results to membrane-desalination modules (through appropriate modeling) has been proposed by Karabelas et al. [24]. Later, it was shown [25] that the flow conditions in dead-end filtration cells are different from those in membrane modules; yet, by carefully selecting the range of agitation rate (rpm) in the dead-end configuration, it is possible to have conditions rather similar to those of cross-flow membrane-module operation [26]. Recently, incipient scaling during dead-end desalination in pressure-cells *with agitation* has been studied [26]. However, whereas *the unstirred* dead-end scaling data were modeled successfully [25] using a classical nucleation-particle growth approach, this was not the case for data obtained in cross-flow tests (i.e., in a spacer-filled desalination-membrane test-section [23]) and in the stirred dead-end cell [26].

This work is motivated by the need to clarify these important issues and it is part of a systematic study aiming to develop an approach whereby (using facile bench-scale tests) one can obtain incipient scaling parameters that would enable modeling and reliable predictions of scaling phenomena in a real desalination-membrane module; the framework of such global modeling efforts is reported elsewhere [27,28]. To this end, the following main steps were taken in the present work: Improved unstirred dead-end experiments were performed (keeping the feed-water pH constant during the test); in these experiments different trans-membrane pressures (leading to different fluxes) were imposed to get more insight into the scaling process. A simplified model of the scaling process was developed, involving an extension of the classical nucleation theory, to analyze the new data and to facilitate a generalized modeling approach along the lines indicated above. The main idea of this approach is not to replicate the actual conditions of industrial SWM modules. The scope is to develop a tool that can provide accurate experimental data, taken under well-controlled and easy to implement conditions (in dead-end mode), in a time scale much shorter than that of the real process. Then fundamental quantities such as growth rate constant and nucleation related properties of membrane will be derived through appropriate mathematical modeling of the dead-end experiments. Finally, the above parameters (i.e. properties of membrane and solute only) will be employed in a SWM module model/simulator to predict evolution of scaling as discussed elsewhere (e.g. [27]).

The present publication is structured as follows: In the next section, experimental set-up and procedures are described in detail. Then, the experimental results are presented and discussed. Model development of the incipient scaling process follows. Finally, the experimental results are analyzed, in conjunction with the new model, and the findings are extensively discussed.

2. Experimental part

2.1. Equipment, materials and methods

The effect of permeation velocity on calcium carbonate crystallization on membrane surfaces was studied by conducting experiments in dead-end filtration high pressure test cells, with effective area of membrane specimen 9.1 cm^2, without agitation. The set-up employed for these tests is described in detail elsewhere [24,29]. Pressure, in the range from 80 to 150 psi, was imposed by a nitrogen cylinder of high pressure, in order to obtain the desired permeation flux through the membrane. Constant temperature was maintained (at $25\ °C \pm 0.5\ °C$), by immersing the test-cell in a bath, with temperature controlled by an external unit (Polyscience, USA, Model 9106). There was also continuous recording of the permeate mass produced for permeate flux determination. Scaling tests were performed by using membrane discs (of appropriate dimensions) obtained from a spiral wound element for brackish water applications (CPA2, Hydranautics), with a thin film composite polyamide membrane. It should be pointed out that for each experiment a new membrane sample was employed, because the scaled specimen SEM examination did not allow its reuse. Moreover, even if one wanted to reuse a certain specimen, by chemically treating it to remove the scale, likely structural modifications of the membrane surface [e.g. ([30,31])] would lead to a different surface topography and property distribution compared to the original one; therefore, use of a new coupon for each test was inevitable.

The test fluid was prepared by mixing solutions of $CaCl_2$ and $NaHCO_3$ of specific concentrations, according to the protocol described in [24]. The feed water pH was adjusted by adding 0.1 N HCl solution to obtain the various supersaturation ratios, while it was allowed to be in contact with air for equilibration with the atmospheric carbon dioxide. For each filtration test, the feed solution characterization consisted of pH, conductivity, calcium concentration, total dissolved solids (TDS), turbidity and total alkalinity measurements [32]. Turbidity measurements were considered necessary to verify that there was no bulk nucleation. Determination of the feed solution supersaturation ratio was accomplished by the thermodynamic code PHREEQC (computer program, version 2.15.07) [33]. For these calculations, the database “*minteq.v4.dat*” was employed, which is considered as the most complete such database available at present [34].

Experimental protocol implementation started with the membrane conditioning/ compaction step, using milli-Q deionised water, followed by the scaling test; initially, the dead-end pressure cell was filled completely with approx. 300 mL of synthetic feed water solution (thus eliminating the free air volume above the aqueous solution, for keeping constant the feed water pH during the scaling test), fully characterized beforehand. The feed water chemical composition remained practically constant throughout the filtration period because the total permeate recovery was very low (up to 3%) for all experiments.

For each supersaturation ratio examined, six (6) separate experiments were conducted according to the following protocol. Two experiments were performed by applying relatively low pressure (80 or 100 psi) for 30 and 60 min, respectively, and two experiments at a higher pressure (150 psi) for 30 and 60 min. The last two experiments were performed as follows: at the beginning the lower pressure (80 or 100 psi) was imposed for 30 min and after that the applied pressure was increased up to 150 psi for the same duration (30 min), while one more experiment took place by