A method for evaluating antiscalant retardation of crystal nucleation and growth on RO membranes

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ABSTRACT

An experimental method was developed for quantifying mineral scale nucleation and growth on RO membranes enabling comparison of the effectiveness of antiscalants in retarding mineral scale formation. Mineral scale growth and inhibition was evaluated, for calcium sulfate dihydrate (gypsum) as a model scalant, from direct visual observations of crystal growth on the membrane surface in a plate-and-frame RO cell. Comparison of membrane scaling with and without the use of antiscalants was carried out based on RO scaling tests conducted under identical operating conditions with respect to the initial flux and crossflow velocity, at identical initial concentration fields within the RO membrane channel and at the membrane surface. The range of gypsum saturation index (SI_g) at the membrane surface was 1.3–2.3 enabling determination of gypsum scaling for the above SI_g range from a single RO scaling test, given direct observation of crystal nucleation and growth on the membrane surface. The present work demonstrates that it is possible to distinguish antiscalants modes of scale inhibition and corresponding scale suppression effectiveness, over a reasonable range of solution supersaturation. The current approach introduces antiscalant crystal nucleation and growth retardation factors that can aid in the development, selection and dose optimization of antiscalants for use in RO desalination.

1. Introduction

Reverse osmosis desalination of inland brackish water sources is confronted with the challenge of requiring high product water recovery in order to decrease process cost (e.g., specific cost per volume of permeate) and the cost of brine management [1–5]. However, water recovery in RO desalination is typically limited due to fouling by colloidal matter [6,7], biofouling [8–10] and mineral scaling [5,11–14]. Mineral scaling, which is the focus of the present work, is of particular concern in the desalination of brackish groundwater [15,16], agricultural drainage water [3,5,17], as well as in water reuse applications [18]. Mineral salts that typically hinder RO desalination of brackish water at high recovery include calcium sulfate, calcium carbonate, calcium phosphate, barium sulfate, and silica [5,11,19]. As permeate recovery is increased, the concentrations of mineral salt ions increase above their saturation levels leading to membrane mineral scaling (by sparingly soluble mineral salts) due to both heterogeneous crystallization onto the membrane surface and surface deposition of crystals formed in the bulk solution [5]. Mineral scaling results in blockage of the active membrane surface area [12,20,21] leading to flux decline, as well as potentially damaging the membrane, thereby increasing the overall cost of desalination [22].

Addition of antiscalant chemicals (typically consisting of formulations of polyacrylic acid, carboxylic acid, or phosphonates; [23,24]) to the RO feed is a popular method of reducing the adverse impact of membrane mineral scaling [3,11,24–30]. Experimental determination of antiscalant effectiveness have been generally limited to evaluations of bulk crystallization [24,28,30], quantifying scaling behavior based on flux decline measurements [13,31,32] or determining the extent of surface area coverage by mineral scale [4,26,33]. Previous studies have provided reasonable approaches to ranking antiscalant effectiveness [24,26,34,35] and establishing the minimum antiscalant dose required for a given desalination task [26]. However, efforts to date have not yielded quantitative information regarding the impact of antiscalants on mineral crystal nucleation and crystal growth kinetics at the single crystal level. It has been suggested that antiscalants can adsorb onto newly formed crystal facets, thereby retarding or halting further crystal growth [4,36]. It has also been hypothesized that antiscalants increase the surface energy of crystal nuclei, effectively slowing the rate of crystal nucleation [37]. Different antiscalant formulations could have different degrees of impact on crystal nucleation and growth [25,36,38]. Clearly, direct quantification of such modes of action

should provide a more fundamental and consistent means of comparing antiscalant effectiveness, thereby enabling more informed antiscalant selection and dose optimization.

The present study presents a methodology for quantifying the effect of antiscalants on mineral salt nucleation and growth of individual crystals directly on the membrane surface during RO desalination. Demonstration of the present approach is focused on calcium sulfate dihydrate (gypsum) as the model mineral scalant given its common occurrence in inland brackish water desalination and the tenacity of gypsum scale [33,39]. Nucleation and growth of gypsum crystals were quantified via a recently developed method of direct visual observation of the membrane surface [4,33,40] in a plate-and-frame RO (PFRO) membrane channel. Since nucleation and crystal growth are dependent on the local level of solution supersaturation [33], detailed mapping of the concentration polarization field (and thus the saturation level with respect to the scalant of interest) was achieved via a recently developed three-dimensional CFD model of the fully coupled fluid hydrodynamics and mass transfer equations in the PFRO channel [41]. Given that concentration polarization (and thus mineral salt saturation level) varies axially along the membrane channel [41,42], even for typical small laboratory PFRO channels, it was then possible to quantify mineral crystal nucleation and growth over a reasonable range of supersaturation [33], with respect to the target scalant, from a single RO desalting experiment at the desired hydrodynamic conditions (e.g., channel crossflow velocity). Accordingly, the present study presents a practical method that can be used for direct quantification (and comparison) of antiscalant effectiveness with respect to retardation of both surface crystal nucleation and growth.

2. Experimental

2.1. Materials and methods

Calcium chloride ($CaCl_2 \cdot 2H_2O$), barium chloride ($BaCl_2 \cdot 2H_2O$), magnesium sulfate ($MgSO_4 \cdot 7H_2O$), and anhydrous sodium sulfate (Na_2SO_4) were used for preparation of the RO feed solution (Table 1). All inorganic chemicals were reagent grade obtained from Fisher Scientific (Pittsburgh, PA). The feed solution composition detailed in Table 1 was selected as a model solution to mimic the composition of RO concentrate from desalting of Colorado River water at ~85% recovery [23], to illustrate the present methodology of assessing antiscalant effectiveness and mineral scale development. Bicarbonate was excluded from the model solution in order to focus on gypsum scaling [4]. It should be noted that while the saturation index for barite in the feed solution was high (Table 1), previous work has shown that barite would not precipitate on the membrane surface for the present range of experimental conditions [23].

RO membrane scaling tests were performed with the above model solution using TFC-ULP membrane obtained from Koch

Membrane Systems (San Diego, CA), reported to have a root mean-square surface roughness of 54.2 nm, $L_p = 12.3 \times 10^{-7}$ m bar^{-1} s^{-1} and nominal salt rejections of 97% and 93% for $CaCl_2$ and $NaCl$, respectively [26]. Two different commercial antiscalants, PC-504T (Nalco, Naperville, IL) and Flocon 260 (BWA, Tucker, GA), designated hereinafter as AS1 and AS2, respectively, were used to illustrate the present approach of evaluating and comparing antiscalant effectiveness.

The feed solution (Table 1) was prepared such that it was nearly saturated with respect to gypsum. The level of saturation of gypsum was quantified by the saturation index, defined as:

$$SI_g = \frac{(Ca^{2+})(SO_4^{2-})}{K_{SP}} \quad (1)$$

where (Ca^{2+}) and (SO_4^{2-}) are the activities of the calcium and sulfate ions, and K_{SP} is the equilibrium constant for gypsum. The saturation index values were calculated using the multi-electrolyte OLI simulator [43].

2.2. Membrane scaling experiments

Membrane scaling tests were carried out using the TFC-ULP membrane using a laboratory plate-and-frame RO (PFRO) membrane system (Fig. 1). The PFRO unit consisted of a transparent test cell with an active membrane surface area of ~26 cm^2 (3.16 cm × 8.24 cm) and channel height of 2.56 mm. The polyethylene feed reservoir (18 l) was magnetically stirred and temperature controlled ($25 \pm 1\,°C$) using a refrigerated recirculation system (model 625, Fisher Scientific, Pittsburgh, PA). The feed solution was delivered to the RO cell via a 1/2 hp positive displacement pump (Hydra-Cell, Wanner Engineering, Minneapolis, MN). Transmembrane pressure was adjusted using a back-pressure regulator (US Paraplate, Auburn, CA), and a pressure transducer (model PX303-500G5V, Omega, Stamford, CT), installed before the membrane channel entrance, was used for monitoring pressure. Feed flow rate was monitored using a flow meter (model K-32002-38, Cole-Parmer, Vernon Hills, IL) connected at the PFRO retentate stream. The permeate flow rate was monitored by a digital flow meter (Model 1000, Fisher Scientific). As a precautionary measure, a cartridge filter of nominal rejection size of 0.2 μm (MNY92 10 in. cartridge filter, GE Water & Process Technologies, Minnetonka, MN) was installed at the retentate side of the membrane module in order to trap and remove from circulation any crystals that may have formed in the bulk solution in the membrane channel or detached from the membrane surface.

Prior to the start of each scaling test, the membrane was conditioned for a period of 4 h by pumping a feed solution composed of all salts (Table 1), except $CaCl_2 \cdot 2H_2O$ and $BaCl_2 \cdot 2H_2O$, through the membrane module at a permeate flow rate set at 1.2 ml/min. Subsequently, predetermined volumes of stock calcium chloride and barium chloride solutions were added to the feed reservoir to obtain the desired concentration of salt ions in the feed solution (Table 1). All scaling tests were carried out in a total recycle mode (i.e., permeate and retentate streams continuously recycled to the feed reservoir). In this manner, the composition of the feed solution remained essentially constant throughout the scaling experiments. Although there may have been some loss of calcium, barium or sulfate ions due to crystallization, previous studies have shown that this loss was negligible for the present small PFRO channel and range of operating conditions [17,26]. It is important to note that bulk crystallization of gypsum (the majority scalant) did not occur over the course of the experiments given that the gypsum saturation index was just below unity (Table 1). Therefore, gypsum scaling in the present study was essentially in the surface crystallization regime [27].

Table 1
Composition and properties of feed water solution.

Feed solution		
Na^+	630	mg/L
Ca^{2+}	680	mg/L
Mg^{2+}	275	mg/L
Ba^{2+}	1.4	mg/L
SO_4^{2-}	2410	mg/L
Cl^-	1200	mg/L
TDS	5200	mg/L
Osmotic pressure	266.7	kPa
SI_{Barite}	156	
SI_{Gypsum}	0.99	