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Ultrasonic sensor control of flow reversal in RO desalination. Part 2: Mitigation of calcium carbonate scaling

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ABSTRACT

The use of ultrasonic time-domain reflectometry (UTDR) in combination with statistically based analysis has been utilized to provide timely warning of the initial onset of local calcium carbonate scaling. The methodology was able to detect the onset of scaling in real time before any significant decrease in permeate flux was observed. Ultrasonic detection of scaling was confirmed via post-mortem examination of the membrane that showed the presence of aragonite crystals that were as small as 20 μm and covered less than 10% of the membrane surface. The ultrasonic methodology was then employed to trigger a change in flow direction (reversal of the concentrate and feed ends of the flow channel) when scaling was detected. When in forward flow, the upstream, midstream and downstream sections of the membranes had aragonite supersaturation values of $SI \sim 2.0$, ~ 5.3 and ~ 7.65, respectively; when the flow direction was changed, the *SI* values at the ends were switched but the *SI* at the midstream remained at $SI \sim 5.3$. Results indicated that flow reversal effectively mitigated scaling in downstream sections of the membrane even though they were periodically exposed to the highest supersaturation conditions. It was demonstrated that prompt intervention after an ultrasonic scaling signal improved the efficacy of flow reversal. The results reflect a significant advance in the use of UTDR in which the methodology is applied for active control of scaling mitigation rather than limited to passive detection of scale formation.

1. Introduction

Reverse osmosis has become a dominant method for desalination where waste heat or very cheap fossil fuel is not available. A major problem in achieving high-water recovery desalination is that as the concentration of rejected salts increases, sparingly soluble salts that greatly exceed their saturation limits begin to precipitate and cause scaling on the membrane. One of the most common salts encountered in scaling is calcium carbonate. Calcium carbonate can be controlled by a number of methods and processes including strategies for reducing the supersaturation level by changing the chemistry such as use of acid, ion exchange treatments [1–3] as well as precipitation softening of the feed [4] or the concentrate [5,6], or limiting the recovery. The most common method is to alter the kinetics by the use of antiscalants [7,8]. Recently, the novel process of flow reversal [FR] was proposed to control calcium carbonate scaling based on exploiting the finite times of nucleation kinetics [9].

However, all of these methods including the guidelines of commercial membrane and antiscalant manufacturers for controlling calcium carbonate depend on using the Langelier saturation index as a tendency for scaling [10]. This saturation index is solely based on the solubility product of calcite. However, there are three polymorphs of calcium carbonate: calcite, vaterite and aragonite [11] with calcite being the least soluble, and there have been questions regarding which polymorph correctly tracks scaling tendencies [12]. There is an expanding body of evidence that the polymorphs that precipitate can be affected by other ions in solution [13,14] as well as being inhibited by other minerals [11,15,16]. In addition, the tendency for precipitation and calcium-carbonate induction times can be affected by the membrane surface (table 6 in [14] and analogously for gypsum [17]). While "jar" tests can be done to rank antiscalants, they cannot cover all of the chemistries that must be considered, cannot account for real-time changes in feed chemistry, and they ignore surface effects on nucleation kinetics. Membrane flow-cell experiments based on flux decline or analysis of deposits can be conducted to determine safe recoveries and take into account surface effects, but cannot provide a control for real-time changes in chemistry and hydrodynamic effects. When these considerations are taken into account, the implication that arises is that the only way to

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know if conditions for calcium carbonate precipitation have actually been reached is by in-situ analysis of the surface susceptible to such scaling. A breakthrough in the in-situ detection of membrane scaling and fouling was the adaptation of ultrasonic time-domain reflectometry (UTDR) for noninvasively studying membrane scaling processes in real time [18,19]. The companion article [20] reviews the developments of this technology more extensively, especially as pertaining to calcium sulfate and shows how it can be used in real time for triggering effective interventions such as FR. UTDR allows early warning to be carried out on opaque, translucent and transparent conduits alike.

UTDR has been used to detect the presence of calcium carbonate ($CaCO_3$) scaling [21], but not as an early-warning system to enable effective intervention for mitigation and prevention of scaling. In the current study, we not only utilize UTDR to detect the onset of calcium carbonate scaling but also use the ultrasonic signals to trigger FR in a flat-sheet test cell. The test conditions were designed to simulate a range of recoveries, and the results showed significant mitigation of calcium carbonate scaling with the use of the combination of UTDR and FR. In addition, this study indicates that UTDR can serve as a direct measurement technique from which independent values of scaling induction time can be experimentally obtained.

2. Materials and methods

2.1. Materials

The membrane used in the experiments is LE-440 (Dow, Filmtec, Edina, MN), a polyamide-based extra-low energy RO membrane, which has a nominal water permeability of 6.5 $\text{kg h}^{-1}\text{ m}^{-2}\text{ bar}^{-1}$. The chemicals used are $CaCl_2 \cdot H_2O$ (analytic grade, CARLO ERBA, Rodano, Italy) and $NaHCO_3$ (analytic grade, GADOT, Haifa, Israel).

2.2. RO test system

An RO flat-sheet system was designed for automatic FR triggered by signals obtained from ultrasonic sensors as well as continuous measurements of pressure, pH, permeate conductivity, temperature and permeate flow-rates. The flat-sheet cell was fabricated from polycarbonate and is similar in design to the one described in the companion article [20] except for the slightly increased width of the flow channel (8.6 cm). Three Panametrics model V111 (Waltham, MA) transducers (sensors) were used in this system, and installed as described in the companion article.

The flow loop (Fig. 1) is equipped with three pneumatically actuated valves to perform FR without water hammer effects by preventing sudden changes in flow direction. The valve opening sequence is presented in Table 1.

The flow system utilized two 20-L plastic tanks (labeled as FT1, FT2 in Fig. 1) containing aqueous solutions; the feed tank solution is stirred continuously with an aquarium pump (AP). The temperature is maintained within the range of 25–28 °C using an in-line coiled stainless steel heat-exchanger (HE) connected to a chiller in which the coolant flow is regulated by a thermal controller (type 94, Eurotherm Controls Ltd, England) with a thermocouple input. An in-line 1 μm filter (Filter) (10″ length, Hytrex II-type depth cartridge filter, GE-Osmonics, Minnetonka, Minn.) was installed to eliminate particulate in the bulk flow to the membrane. A high-pressure pump (Pump 2, model G20XDSGSHEHG, Wanner Engineering, Minneapolis, MN, USA) controlled by a frequency converter (FC) is used to recycle feed solutions through the flow loop at variable flow-rates between 30–200 L h^{-1}. This pump can supply a maximum pressure of 6.08 MPa (60 bar). A back-pressure regulator (BPR, model BP-3-1A11I5J111, GO Regulator, Spartanburg, SC, USA) is located at the outlet of the flow cell for maintaining the pressure. In sequence, the permeate from each of the collection ports is sent for a set time period to a collection vessel mounted on a balance (Bc, model TE2101, Sartorius, Edgewood, NY, USA) with a resolution of 0.1 g. The balance is connected via an RS-232 cable to a laboratory PC, and the weights are entered into a data file. The permeate is recycled directly to the feed tank when it is not collected on the balance. Routing of the flow from the permeate ports to the collection vessel or the feed tank is controlled by five three-way electrically actuated solenoid valves (S, model GEM b33, Baccara Geva, Kibbutz Geva, Israel), one on each permeate line. When the collection vessel fills, it empties automatically to the feed tank by an attached siphon. Two pressure gauges (PG) were installed before and after the flow cell to monitor the pressure drop across the cell. A pressure transducer (PT, model 1200, GEMS Sensors Inc., Plainville, CT, USA) is located after the first pressure gauge and before the flow cell. A flow-meter (FM) (UIL, Tel Aviv, Israel) is located on the outlet of the flow cell. The pH controller (TWT6222 with pH electrode CW711, El Hama, Mevo Hama, Israel) was used to monitor and control pH in the feed tank. The feed pH was adjusted by bubbling

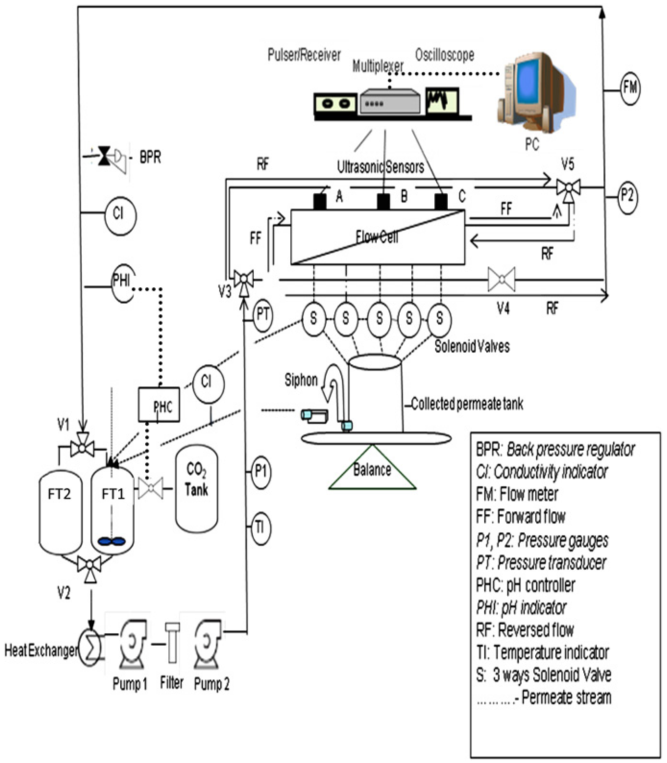

Fig. 1. Schematic of RO flat-sheet flow-reversal system. Dashed line: permeate stream and solid line: feed or retentate stream; dotted line - data acquisition and control.

Table 1
Valve operation during flow reversal.

Opening order after ultrasonic triggering	Function	Outcome
Valve 1 (V4)	Splitting the streams	Slowing
Valve 2 (V5)	Turn over the outlet to inlet	Dead end
Valve 3 (V3)	Turn over the inlet to outlet	Flow reversal