REAL-TIME NONDESTRUCTIVE CHARACTERIZATION OF MEMBRANE

COMPACTION AND FOULING

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INTRODUCTION

In practice, the single most critical problem limiting the application of membrane processes for liquid separation is fouling [1]. The flux decline which accompanies fouling affects the operational reliability and economics in microfiltration, ultrafiltration, and reverse osmosis [1]. Fouling occurs predominately on the membrane surface due to the deposition of one or more system constituents including organics, sparingly soluble inorganic salts dissolved in the feed stream, and colloidal and/or particulate matter. In addition, a gel layer can be formed from organic molecules in the system due to concentration effects adjacent to the membrane surface and compaction can occur when the operating pressure causes a decrease in membrane thickness. Although the occurrence of fouling is often inferred from a time-dependent decline in flux, the interpretation of results in such studies is complicated by the fact that during operation gel formation and compaction as well as fouling may all occur simultaneously [2]. Since each of these processes can produce a flux decrease [3], it is often impossible to distinguish the particular combination of phenomena associated with an observed overall flux decline [1, 4].

The development of real-time measurement techniques that can distinguish between and characterize the various phenomena underlying flux decline will lead to improved understanding and control of membrane-based separation systems. An important consequence of such knowledge is the potential for a significant increase in the useful lifetime of membranes utilized for separation applications. The present paper reports initial progress in the development of an ultrasonic technique to monitor both compaction and fouling in a system with an inorganic salt dissolved in the feed stream.

EXPERIMENTAL INVESTIGATION

In order to simplify the initial experiments, a model fouling system was chosen. Whereas compaction can be in relative terms a short-time phenomenon occurring in less than 60 minutes, fouling is typically observed over much longer time periods usually on the order of days or months depending on the particular conditions. In this preliminary study, conditions were selected to enable significant fouling to be obtained in less than 48 hours.

Dow SW-30 membranes were used in both the compaction and fouling experiments.
The membrane is a thin-film composite (TFC) type which consists of a 0.2 μm thick polyamide layer supported by a 40 μm thick polysulfone substrate. These TFC layers are in turn attached to 150 μm thick polyester web. Compaction experiments were performed in pure deionized distilled water and the fouling studies utilized an aqueous solution of calcium sulfate. The solution was prepared by adding calcium sulfate powder to deionized distilled water and stirring vigorously for between 24 and 36 hours to ensure that the powder was completely dissolved to give a ~90% saturated solution.

Apparatus

The compaction and fouling experiments were performed using a laboratory-scale high-pressure separation system whose operational characteristics have been described previously [5]. The test cell used a parallel plate "sandwich" geometry which is shown in schematic form in Figure 1. The membrane and a stainless steel porous support are set between two flat 316 stainless-steel disks (3.2 cm thick x 17.8 cm diameter). Spacers are cut into the disks to give a 2.1 mm fluid space above the membrane, and the unit is sealed with a dual O-ring sealing system such that the membrane area exposed to flow is 30.7 cm². The cell is held together using four 2 cm diameter bolts.

The calcium-sulfate feed solution was passed through a coarse cartridge filter and pressurized using a positive-displacement pump to 4.14 MPa (600 psi). The pressure was maintained using a back-pressure regulator. The pressurized calcium-sulfate solution then passed through a high-pressure stainless-steel 2 μm filter. A specially designed surge tank dampened pressure fluctuations in the system. The permeate from the test cell was collected so that flow-rate measurements could be made. In addition, the temperature in the cell was measured using a thermocouple; temperature variations during a typical 48-hour run were ±1°C.

The solution flow rate in the cell was monitored with a rotameter downstream of the cell and maintained at a maximum rate of 12±0.1 liter/hour. This ensured that flow over the membrane always remained in the laminar regime. During the experiments, the concentration of the feed solution was checked every hour and kept at a constant level (±1%) by adding fresh deionized distilled water.

Figure 1. High-pressure test-cell design.
Ultrasonic Measurement System

The ultrasonic system consisted of a 5 MHz, 12.5 mm diameter flat compression wave transducer, a pulser-receiver, and a Nicolet Pro 50 digital oscilloscope. The frequency utilized was the highest frequency that would propagate through the stainless steel cell-lid, giving usable signal amplitudes for the echo from the membrane-liquid interface. The transducer was selected so that the near-field length matched the thickness of the upper stainless steel plate. The transducer was attached to the top of the cell using an ultrasonic couplant.

A series of pulse-echo (Time-Domain Reflectometry - TDR) measurements were made in which the pulser-receiver was used with maximum power and minimum damping. The sampling rate for the digital oscilloscope was 5 ns, and 1000-point long records were obtained and stored on either a floppy disk or, for extended runs, on the 80 Mbyte system hard drive. At the end of a run digitized signals were then transferred to a 486-PC for display, analysis and output.

Compaction Experiments

In each compaction experiment the system was operated in a no-flow condition. After ensuring that the cell was filled with fluid, the outlet on the downstream side of the test-cell was sealed. Nitrogen gas was used to pressurize the water. The pressure was typically increased in increments of 69 kPa (10 psi) every five minutes until a maximum pressure of 2.76 MPa (400 psi) was reached. During the 60 minutes required for a typical experiment, the temperature remained reasonably constant 25±0.50°C.

As shown in the schematic of Figure 2(a), a time-domain shift can be expected during compaction for the echo from the membrane-water interface. Analysis of ultrasonic traces from the experiment indicated that the first echo from the membrane-water interface moved to progressively later times due to an increasing water-path length and membrane-thickness reduction. Using the speed of sound in constant temperature water, the movement of the membrane surface and hence change in thickness can be quantified by means of the following equation:

$$2L = U \Delta t \tag{1}$$

where $L$ is the distance from the bottom of the top steel plate to the membrane-solution interface, $U$ is the velocity of sound in water (1482 m/s at 20°C) and $U \Delta t$ is the change in arrival time or the time-domain shift. Assuming constant thickness in all other system components, the increase in $L$ is equal to the decrease in the thickness of the membrane. The pulse-echo TDR data showed the expected time-dependent exponential decrease in

![Figure 2](image)

Figure 2. Expected high-resolution time-domain response to an acoustic signal input for the case of (a) compaction and (b) fouling.
membrane thickness (Figure 3). As indicated in Figure 3, the membrane thickness response closely follows the applied pressure ramp such that the membrane compacts from an initial thickness of 150 μm and asymptotically approaches the final thickness value of 135 μm. Since the observed change in thickness exceeds that of the 0.2 μm polyamide layer, compaction occurs primarily within the porous support layer.

Fouling Experiments
A typical series of fouling experiments consisted of several runs using the same solution but at different flow rates. For each run the 90% saturated feed solution was circulated through the test cell at a fixed input pressure (4.14 ±0.035 MPa). The desired flow rate was maintained until a significant flux decline was observed. The feed-flow rate through the test cell in a typical experimental series was systematically varied such that three conditions were considered: (1) no flow, (2) 7.2 liters/hour and (3) maximum flow of 12 liters/hour. Two series of experiments were conducted using an aqueous solution of calcium sulfate. The experimental conditions for a typical three-run series are summarized in Table 1. As fouling develops, a new layer is formed on the membrane surface. When this layer reaches a critical thickness, a new ultrasonic echo can be expected from the

![Figure 3. Representative compaction response of the polymeric membrane due to applied pressure ramp: (a) pressure-ramp characteristics; (b) membrane thickness change calculated from equation (1).](image)

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Initial Permeate Flux (g/cm²·s)</th>
<th>Pressure (MPa)</th>
<th>Axial Flow Rate (l/hr)</th>
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<tbody>
<tr>
<td>1</td>
<td>9.50 x 10⁻⁴</td>
<td>4.14</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>8.69 x 10⁻⁴</td>
<td>4.14</td>
<td>7.2</td>
</tr>
<tr>
<td>3</td>
<td>7.06 x 10⁻⁴</td>
<td>4.14</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1. Experimental conditions for a typical series of fouling experiments.
fouling layer-solution interface. As shown in schematic form in Figure 2(b), this should be
distinct in the time-domain from the fouling layer-membrane interface. Although such
behavior can be observed when the ultrasonic system has sufficient resolution, the fouling
layer-solution interface was not seen during the real-time fouling experiments in this study.
Reproducible changes were obtained in the peak-to-peak amplitudes of 5 MHz pulse-echo
signals from the membrane surface. This amplitude decreased or increased depending upon
the flow condition inside the cell. Representative results are shown in Figure 4 in terms of
the variation of the permeate flux with time and the corresponding variation in the signal
amplitude with time. There is a amplitude decrease for the no-flow situation while an
overall increase in amplitude occurs for the two flow situations. The time scale of the
ultrasonic response is quite similar to that of the permeate flux. At the completion of each
run when the flux had declined to a minimum steady-state value, the test cell was opened,
and crystals were observed on the membrane surface. These deposits adhered quite tightly
to the membrane. Following removal and visual examination, samples of the membranes
were then prepared for morphological analysis.

Deposit Characterization

Samples of all membranes were prepared for both scanning electron microscopy (SEM)
and acoustic imaging using a Hyscan 50 MHz acoustic microscope (AM). For SEM
samples the solution remaining on the membrane surface was carefully removed using a
lint-free tissue paper. The membrane was then stored in vacuum before morphological
characterization of the deposits. The AM samples were also blotted and carefully dried in
air. Wet storage in calcium-sulfate solution was avoided to prevent additional precipitation
while storage in pure water was avoided to prevent the dissolution of the calcium-sulfate
deposits.

The fouled membrane samples for SEM analysis were freeze-fractured in liquid nitrogen
and mounted on stubs using a two-sided carbon tape and coated with gold or chromium
before examination. Both the top (solution side) and the cross section of the membrane
were studied. Representative SEM micrographs for the no-flow and maximum-flow
conditions are shown in Figure 5. The same fouled-membrane samples were also studied

![Figure 4](image_url)

Figure 4. Influence of cell flow-rate on fouling behavior: (a) permeate flow-rate
characteristics; (b) corresponding changes in acoustic signal.
Figure 5. Representative cross-sectional SEM and top-surface acoustic micrographs (AM) showing morphology of calcium sulfate fouling-layer for the no-flow and 12 l/hr-flow conditions: (a) SEM for no-flow condition; (b) SEM for 12 l/hr-flow condition; (c) AM for no-flow condition; (d) AM for 12 l/hr-flow condition.
using acoustic microscopy. Membrane samples were placed in a container filled with calcium sulfate solution and C-scan images were obtained. Representative 50 MHz acoustic micrographs for the no-flow and maximum-flow conditions are shown in Figure 5.

Analysis of the SEM and acoustic images reveals fundamental differences in the fouling morphologies obtained in the two flow conditions. In the no-flow situation calcium sulfate appears to have crystallized very rapidly and produced a very uniform fouling layer which covers the entire membrane surface. Crystal colonies are packed very densely together making the top of the fouling layer very rough. The diameter of these colonies or "rosettes" is typically 100 μm, with a maximum thickness of approximately 60 μm. The platelets that constitute the rosettes have a relatively random orientation. In the maximum-flow condition the crystal colonies are typically 200-300 μm in diameter and randomly distributed over the surface. These crystals appear to grow in two distinct morphologies consisting of long, flat radiating platelets where one face rests on the membrane surface and also as flower-like growths protruding above the surface in which the platelets have a preferred orientation. We believe that the rapid initial ultrasonic amplitude decrease in the no-flow experiments is due to scattering from the randomly oriented platelets, whereas the increase in amplitude in the intermediate- and maximum-flow experiments is related to the growth of the protruding and oriented rosettes. The amplitude increase requires an increase in acoustic impedance to increase the reflection coefficient at the membrane-solution interface. Further analysis at intermediate run times is required to clarify the growth in the fouling and provide a correlation with an ultrasonic scattering model.

CONCLUSIONS

Compaction and fouling can now be characterized in-situ, in real-time using a noninvasive and completely nondestructive ultrasonic technique. Results indicate that the ultrasonic measurements are sensitive to the flow conditions in the separation cell and the fouling morphology on the membrane surface. Changes in the values of the ultrasonic parameters occur on the same time scale as the permeate rate-change data.

There is no accepted theory that accounts for the morphology of the fouling layer developed during desalination. This study provides an important tool whereby the real-time information obtained will enable new models and theory for fouling to be developed.

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REFERENCES