

# Fouling Prevention by Electrically Charged Thin Film Composite Forward Osmotic Membranes

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## **Abstract**

Forward osmosis provides a low energy alternative for waste water purification. One of the major issues facing this process is the formation of a foulant layer preventing fluid transfer across the membrane. In recent studies, a conductive layer added to the membrane surface allowing an electric charge to be present on the membrane, has been shown to decrease the rate of mineral fouling in reverse osmosis membranes. Through the application of a conductive layer made of carbon nanotubes on Hydration Technology Innovations, LLC. thin film composite membrane, the applicability of the charged surface and its effects on mineral fouling was explored for forward osmosis membranes. Extensive testing was done by placing both positive and negative charges on the membrane with varying voltage potentials. This method of fouling prevention was found to have little observable effect on the membranes resistance to mineral foulants.

Keywords: Forward osmosis, Fouling, Mineral Scaling, Charged Membrane Surface.

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Figure 2: Illustration of desired ion separation due to addition of a charged membrane surface. The separation created must exceed the distance in which the force of ion attraction and nucleation will form on the membrane surface. Under a strong enough electric charge the ions will form some distance away from the membrane thereby reducing membrane fouling.

Figure 2: Standard TFC shown (right) developed by HTI. (Left) HTI TFC membrane to which a conductive layer of Carbon nanotubes have been embedded into the membrane surface has been applied. Areas upon the conductive layers that appear to be light gray or white are areas in which the conductive layer has come off.

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Figure 5: Test System Design: The two individual flow paths for both the draw and feed solutions are illustrated. Both solutions are drawn out of a large container placed on the scale and pumped through a closed loop. As water transfers across the membrane from the feed to the draw solution a change in mass is recorded on the individual solution balances.

Figure 6: the membrane was tested for 20 hours. During this period roughly 10% of the water in the feed solution was removed. Throughout the test the membrane was placed under a 1.5 V charge. After 16 hours of operation crystal nucleation began. The test was then continued for several more hours to ensure that the best environment for crystal formation was present. The flux of the membrane as a function of the percentage of water removed from the feed solution was then shown for both the control membrane and the conductive membrane for multiple trials.

Figure 7: Crystal growth apparent by visual inspection for both the charged test cell (right) and the standard test cell (left). Crystal nucleation appears to have occurred primarily at both inlet and outlet flow channels.

Figure 8: Similar to the previous figure, the flux rate as a function of feed concentration is displayed. In this instance, the polarity of the charged was reversed. The voltage potential was also increased to 2.5 V and tested for a period of about 20 hours. A large difference in initial flux is apparent in the figure.

Figure 9: (right) scattered crystal growth on the membrane surface immediately following the test after a negative charge was applied to the membrane. (Left) uniform crystal growth across the cathode pate producing a sheet of crystal completely bock from view the plate underneath.

## 1. Introduction

Osmosis presents a low energy way to concentrate or dilute solutions. During osmosis, solvent molecules pass through a semipermeable membrane from a region of low concentration to high concentration. From this process two methods of filtration arise. In reverse osmosis (or RO), solutions are highly pressurized. This is done to overcome the osmotic pressure within a membrane in order to concentrate a waste water solution while removing high quality water. This process, although effective, consumes large amounts of energy in pumping costs. In forward osmosis (or FO), naturally occurring osmotic pressure draws solvent molecules from low to high concentrations [1, 2, 3]. Generally, in forward osmosis, low concentration solutions, called the feed solution, contain undesirable matter from which the solvent is drawn, to high concentration brine solutions, called the draw [1, 3]. The rate of osmosis is controlled by diffusion of the solutes on both sides of the membrane and within the membrane. This low energy process has become increasingly desirable and feasible as energy costs have increased, and as membrane technology has progressed [1, 2, 3].

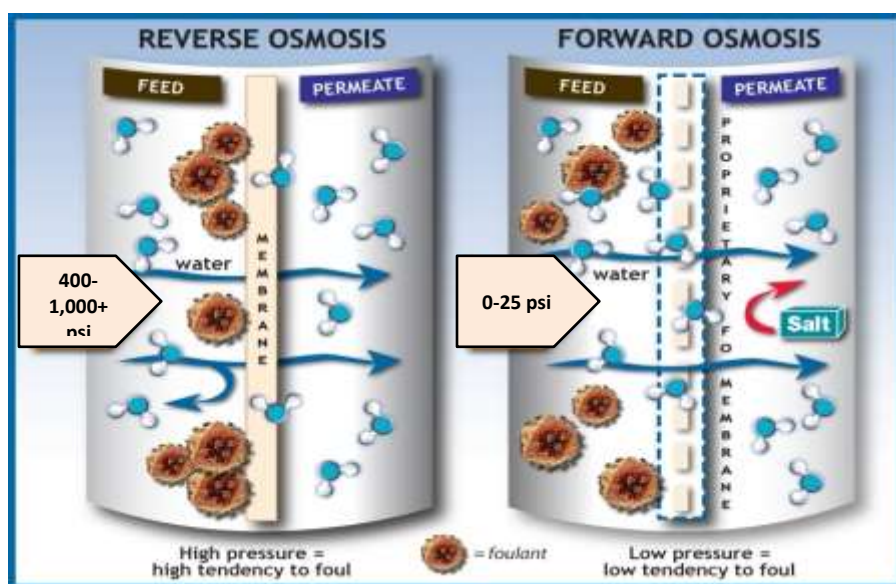


Figure 1: Illustration of RO and FO processes. The Reverse osmosis process, through the aid of large hydraulic pressures, forces water molecules from one side of the membrane to the other while preventing unwanted particulate transfer. Forward osmotic processes use naturally occurring osmotic pressure differentials created by separating a solution of high salt concentration from a solution of low salt concentration. The lower concentration solution, or feed solution, then transfers water from the low concentration to the high salt concentration region[1].

The rate of water transfer across the membrane is called flux, or is sometimes referred to as LMH (liter per square meter of membrane per hour). Foulants in the feed solution can begin to collect on the membrane surface and thereby impede water transfer across the membrane [1, 3, 4, 5]. Methods to remove foulants from the membrane are available, however the methods widely used act as a post-treatment requiring the FO system to be stopped and the membrane cleaned [4, 5]. Few methods have been presented in which the formation of a fouling layer has been prevented altogether. In order to produce a forward osmotic membrane with a consistent and constant high flux or LMH in the presence of foulants, the merits of the addition of a conductive membrane will be explored. The addition of this conductive layer to the membrane surface allows for the application of a charge [7, 8]. By applying an

electric charge to the membrane, crystals will form away from the membrane surface within the bulk solution [6, 8, 9, 10]. Because the crystals form away from the membrane they will not have a chance to adhere to the membrane, which would otherwise decrease the available surface area in which osmosis may occur [8, 9].

## 2. Theory

The movement of ions in a solution near a charged surface is known and is governed by the Poisson-Boltzmann[9, 10] equation:

$$\vec{\nabla} \cdot [\epsilon(\vec{r}) \vec{\nabla} \Psi(\vec{r})] = -\rho^f(\vec{r}) - \sum_i C_i^\infty z_i q \lambda(\vec{r}) e^{\left[-\frac{z_i q \Psi(\vec{r})}{k_B T}\right]}$$

Where  $\epsilon(\vec{r})$  is the dielectric constant,  $\Psi(\vec{r})$  the electrostatic potential,  $\rho^f(\vec{r})$  represents the charge density of the solute,  $C_i^\infty$  represents the concentration of the ion  $i$  at a distance of infinity from the solute,  $z_i$  is the charge of the ion  $q$  proton charge  $\lambda(\vec{r})$  is a factor for the position-dependent accessibility of position  $\vec{r}$  to the ions in solution.  $k_B$  is the Boltzmann constant,  $T$  temperature of bulk solution.

This equation is valid only for low potentials of about 200mv [9, 10]. In the experiments voltage potentials of 1.5 V were used, requiring, in order to model the reaction, that a Modified Poisson-Boltzmann equation be used. Using equations developed by Duan and Dudchenko et al, [9].

$$\vec{\nabla} \cdot [\epsilon(\vec{r}) \vec{\nabla} \Psi(\vec{r})] = \frac{-e N_A \sum_{i=1}^m C_i^\infty z_i q e^{\left[-\frac{z_i q \Psi(\vec{r})}{k_B T}\right]}}{1 + \sum_{i=1}^m \frac{C_i^\infty}{C_i^{max}} e^{\left[-\frac{z_i q \Psi(\vec{r})}{k_B T} - 1\right]}}$$

$Z$  is the valence of ions,  $e$  is the elementary charge,  $N_A$  is Avogadro's number,  $C_i^{max}$

is the maximum ion concentration allowable within a given region, the values of  $C_i$  and  $C_i^{max}$  can be further expounded upon by the following equations:

$$C_i = \frac{C_i^\infty e^{\left[-\frac{z_i q \Psi(\vec{r})}{k_B T}\right]}}{1 + \sum_{i=1}^m \frac{C_i^\infty}{C_i^{max}} e^{\left[-\frac{z_i q \Psi(\vec{r})}{k_B T} - 1\right]}}$$

$$C_i^{max} = \frac{p}{\frac{4}{3}\pi R_i^3 N_A}$$

Where  $p$  is a packing coefficient,  $R_i$  is the ionic radius.

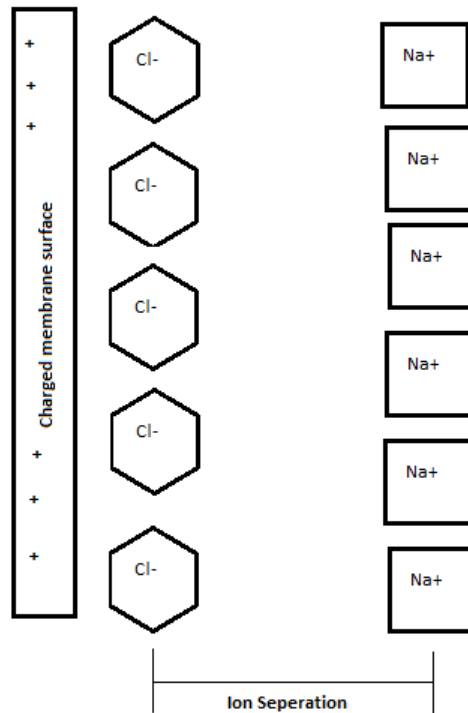


Figure 2: Illustration of desired ion separation due to the addition of a charged membrane surface. The separation created must exceed the distance in which the force of ion attraction and nucleation will form on the membrane surface. Under a strong enough electric charge, the ions will form some distance away from the membrane thereby reducing membrane fouling.

The separation of ions described by the modified Poisson-Boltzmann equation is illustrated in figure 2. Due to high solution concentrations found directly above the surface of the membrane and the porous nature of the membrane, crystal nucleation sites often occur on the membrane surface. By using the charge to cause ion separation, the nucleation site is then shifted away from the membrane surface thereby preventing flux impedance [9].

### 3. Methods & Materials

#### 3.1 Chemicals

Sodium Chloride (NaCl) was obtained from Sigma Aldrich (St. Louis, MO). Purified water and proprietary solutions containing high salt concentrations were obtained from Hydration Technology Innovations, LLC. (HTI, Albany, OR).

#### 3.2 Sample generation and characterization

Conductive thin film composite (TFC) membranes were commissioned and fabricated by HTI. Comparable nonconductive TFCs were also obtained from HTI for sample comparison. Of the membranes generated, samples were inspected with a scanning electron microscope, housed at Oregon State University (Corvallis, OR), to ensure a uniform application of the conductive layer was applied to the membrane. These membranes were then tested using 1M NaCl solutions in forward osmosis (FO), and pressure retarded osmosis (PRO) modes to check membrane quality.



Figure 2: Standard TFC shown (right) developed by HTI. (Left) HTI TFC membrane to which a conductive layer of carbon nanotubes have been embedded into the membrane surface. Areas upon the conductive layers that appear to be light gray or white are areas in which the conductive layer has come off.

Great difficulty was faced in the generation of the conductive membranes. As seen in the image of the conductive membrane in figure 2, small variations of the conductive layer are present. Thinner portions in the conductive layer apparent in the gray and white regions of the membrane are areas in which the conductive layer has come off due to light abrasion. As the conductive layer would come off the



membrane itself would be damaged and become unusable. The fragility of this membrane is in stark contrast with the durability of the standard HTI membrane. Durability of the conductive membrane would increase, however, when the membrane became fully hydrated after a ten minute soak in deionized water.

### 3.3 Testing Apparatus

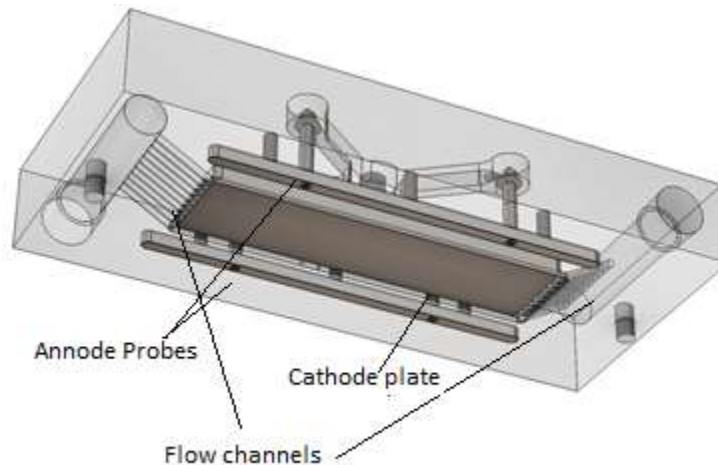


Figure 4: Conductivity test cell plate: One half of the test cell is depicted in the illustration above. In this instance the conductive surface of the membrane is faced towards the negative and positive plates of the test cell half. The other test cell half is then clamped to the underside of the cell with the membrane separating the cell plates. Two separate solutions are then pumped into the flow channels of the test cell, flowing across the membrane surface. The membrane acts as a barrier between the two solutions.

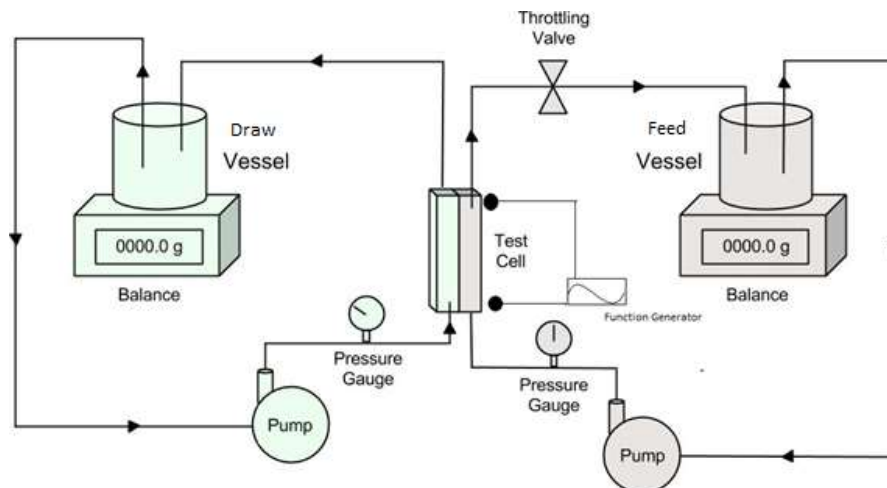


Figure 5: Test system design: The two individual flow paths for both the draw and feed solutions are illustrated. Both solutions are drawn out of a large container placed on the scale and pumped through a closed loop. As water transfers across the membrane from the feed to the draw solution, a change in mass is recorded on the individual solution balances[].

Using pre-existing HTI designs, a test cell (as seen in Figure 4) was developed with built-in electrical probes that would allow for the application of charge, but not impede membrane performance. The system design can be seen in Figure 5. As seen in this figure, the feed and draw are isolated from each other's flow path. The membrane is placed inside the test cell in Figure 5 separating the draw solution from the feed solution.

The plates within the test cell (Figure 4) were used for low positive DC voltages of about 1.5 V. When reversing the polarity of the wave the stainless steel plates would begin to degrade [3]. Thus, in order to test with higher voltage and allow for the reversing of the charge polarity, the plate was replaced with a corrosive resistant titanium plate.

In order to test the effect of a wide variety of signals an ATTEN ATF20B (Xili, Nanshan China) function generator was used. A Tektronix (Beaverton, OR) 2236A oscilloscope was used in order to ensure proper signal generation from the function generator. VWR (Radnor, PA) Lab Disc stir plates were added to the test-cell to ensure constant solution homogeneity during the test. Time, temperature, and mass transfer data were recorded digitally using a program developed by HTI.

### **3.4 Procedure**

Two samples were selected and placed in identical test cells, save for the use of a function generator on one cell, and tested concurrently. Any portions of the solutions exposed to air were covered to minimize evaporative loss. Temperature was then fixed in the cell to 36°C. The draw and feed solution sides of the cells were run at 30 cm/s cross flow velocity (CFV) or 11 gph flow-rate [1]. A 4 psi. Pressure difference was held between both sides of the test cell with the draw and feed being held at 1 psi, and 5 psi, respectively [1]. Prior to introduction of the solution to the membrane a 1.5 V DC signal was applied to the conductive membrane. The charge was placed continuously on the membrane for the entire duration of the test. The test was then run until the feed solution had concentrated to the point of saturation. This was done so as to ensure the optimum environment for crystal formation on the membrane. The water transfer across the membrane (flux) was then recorded at 15 minute intervals for 72 hours.

For a higher voltage potential than 1.5 V, with a positive DC wave, the conductive surface of the membrane would be irreversibly damaged[3, 4]. The applied charge was reversed allowing for an increase of allowable voltages of 2.5 V and 7.5 V.

## 4. Results

### 4.1 Positively Charged Membrane

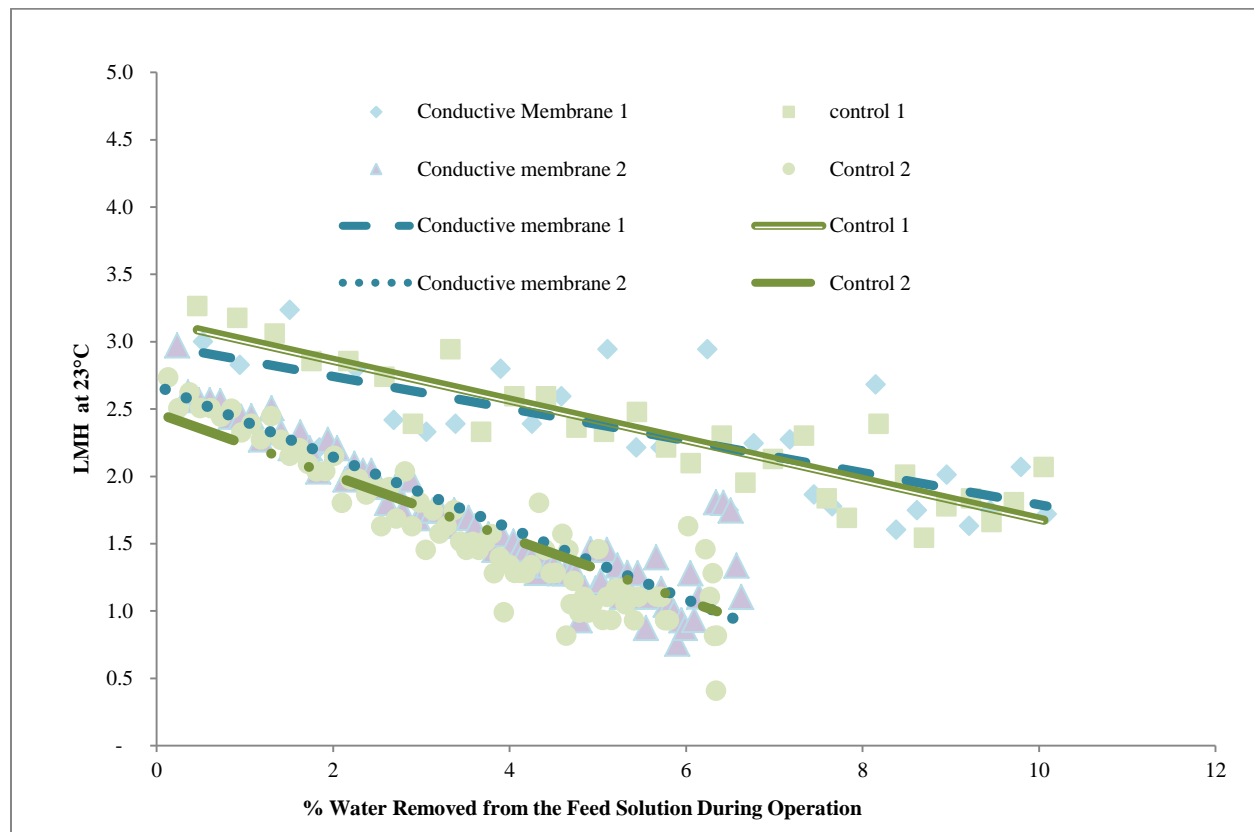


Figure 6: The membrane was tested for 20 hours. During this period roughly 10% of the water in the feed solution was removed. Throughout the test the membrane was placed under a 1.5 V charge. After 16 hours of operation crystal nucleation began. The test was then continued for several more hours to ensure that the best environment for crystal formation was present. The flux of the membrane as a function of the percentage of water removed from the feed solution was then shown for both the control membrane and the conductive membrane for multiple trials.

Flux rates for both charged and uncharged membrane were measured as a function of the water removed from the feed solution. As water was transferred across either membrane the osmotic potential of the draw solution declined as the concentration of the draw was decreased. The feed solution, due to the loss of water to the draw solution, was further concentrated and thus the osmotic potential of the feed solution was increased. These conflicting forces resulted in a general decline in flux as the feed solution was concentrated [1, 3]. The general trend of crystal formation within the system also resulted in flux decline. As is shown in Figure 6, the decline in both the conductive and nonconductive control membranes followed similar trends.

As the crystals continued to form with the system, the flow of the fluids would be impeded until the point in which system pumps were no longer capable of consistently pumping the solution. Once this

point had been reached the system was then turned off and the membrane was removed. Initial visual observations of both membrane test cells and both the control and conductive membrane crystal growth were then made. Following visual inspection the membranes were then observed under SEM imaging to determine crystal growth and verify membrane integrity. This testing procedure was then repeated several times to ensure reproducibility of the experimental results.

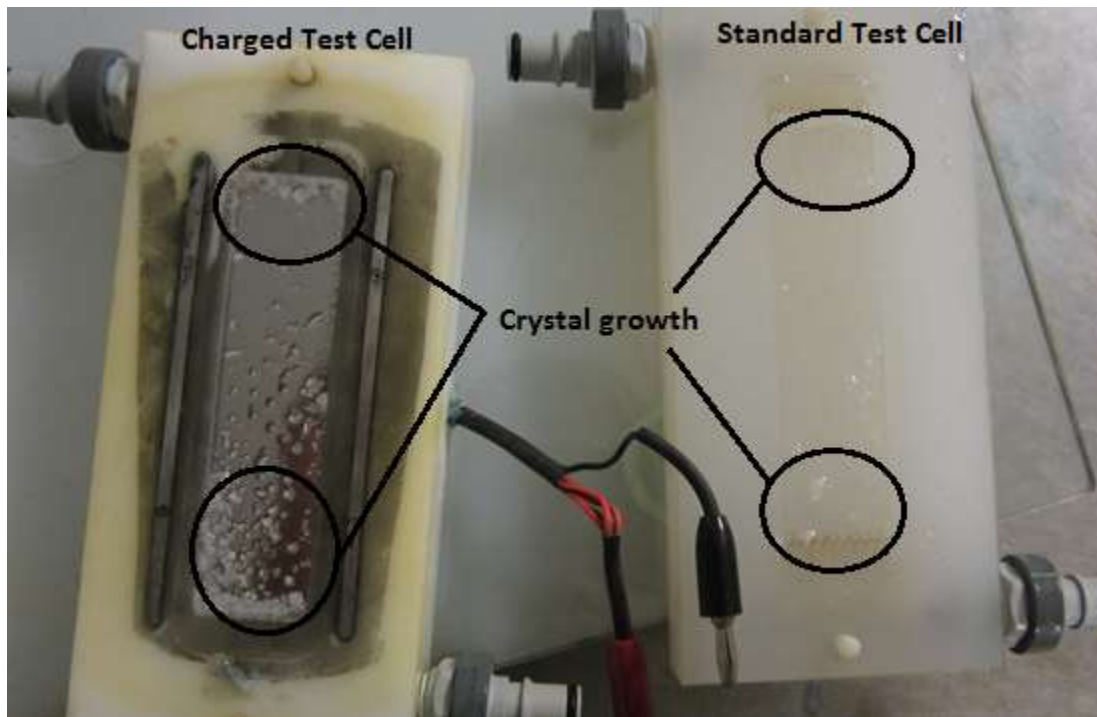


Figure 7: Crystal growth apparent by visual inspection for both the charged test cell (left) and the standard test cell (right). Crystal nucleation appears to have occurred primarily at both inlet and outlet flow channels.

The minimal amount of crystal growth shown in Figure 7 within the test cells themselves generated little flow impedance within the cell. No crystal growth extended from the test cell to that of the membranes surface themselves for either the control sample or the conductive membrane. This pattern was consistent across the multiple tests performed under these conditions.

## 4.2 Negatively Charged Membrane

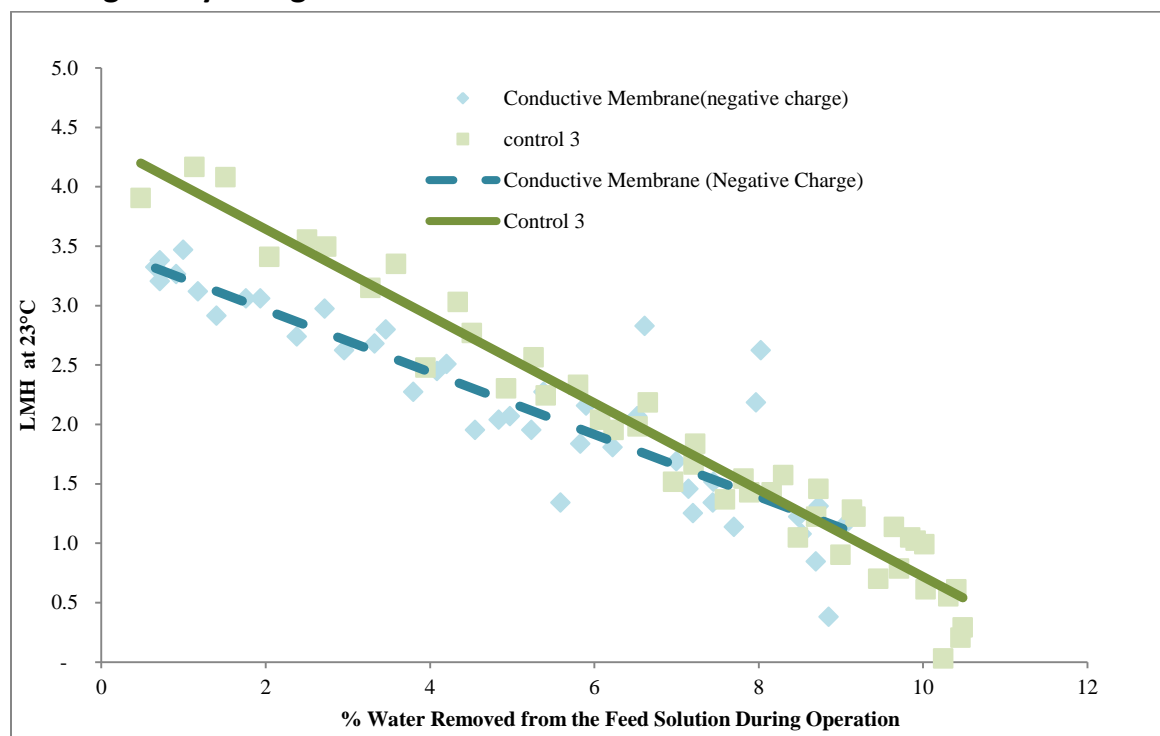


Figure 8: Similar to the previous figure, the flux rate as a function of feed concentration is displayed. In this instance, the polarity of the charged was reversed. The voltage potential was also increased to 2.5 V and tested for a period of about 20 hours. A large difference in initial flux is apparent in the figure.

By reversing the polarity of the applied charge, the charge applied to the membrane could be increased without fear of damaging the membrane. In doing so, however, an initial large drop in flux was apparent for the conductive membrane (Figure 8). This decline in flux for the conductive membrane fell at a slower rate than the decline in flux of the control.

Following the test, the conductive membrane and its respective test cell, under visual inspection had significant crystal growth (Figure 9). Scattered large crystal growth was evident on the membrane surface. A large crystal structure had formed uniformly across the cathode plate of the test cell, completely disrupting the flow path within the cell itself.

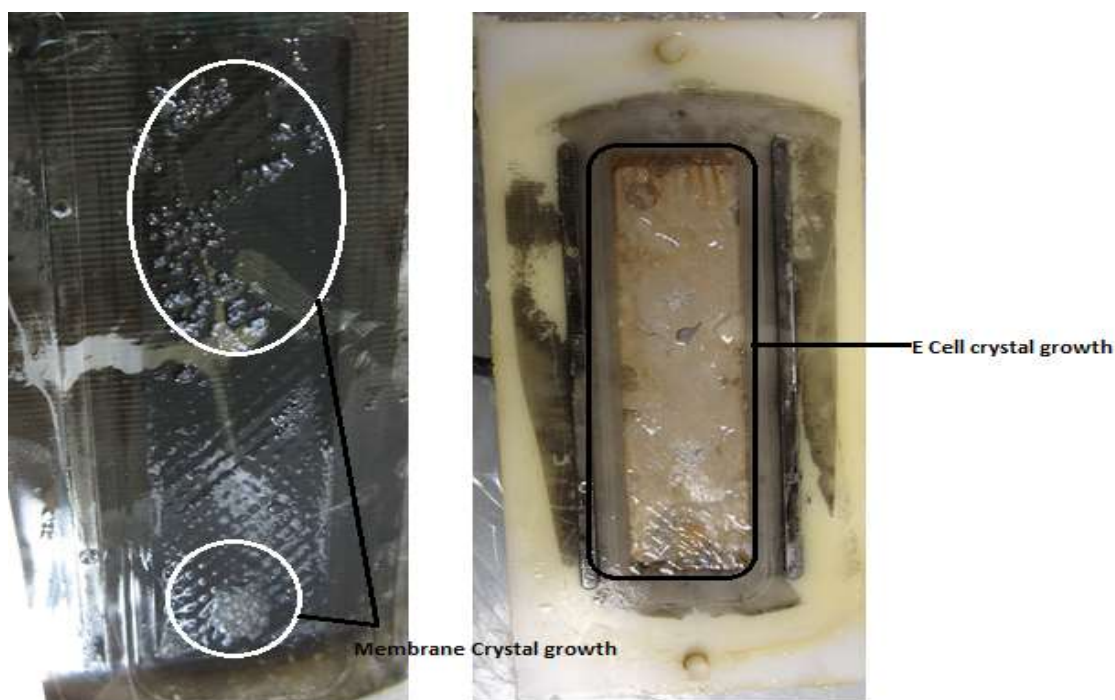


Figure 9: (Left) scattered crystal growth on the membrane surface immediately following the test after a negative charge was applied to the membrane. (Right) uniform crystal growth across the cathode plate is visible, producing a sheet of crystal completely blocking the plate underneath from view. Compare with Figure 7.

## 5. Discussion

The overall difference in flux loss for both samples of conductive membrane and their respective control samples (Figure 6) are consistent with each other. Slight variations between the rate of flux decline between the conductive membrane and control are too small to be considered a result of the desired fouling prevention when the membrane is positively charged. This lack of an effect is supported by the similarity of the crystal growth in the test cells.

In the case in which polarity of the charge is reversed, a large drop in the initial flux was evident. That, viewed with heavy crystal formation on both the conductive membrane and the conductive membrane test cell (Figure 9), could describe the change in membrane performance between the two tests. Assuming that the initial flux drop was a result of rapid crystal nucleation near the membrane, the flow rate of the solution within the cell would be impeded by the presence of large crystalline structures [4, 5]. This would most likely cause a decrease in the cross flow velocity within the test cell. Flux rates are strongly connected to cross flow velocity [1]. As cross flow velocities are decreased the flux generally

decreases. Rapid introduction of large crystals (figure 9) would therefore likely lead to a large drop in membrane flux.

The use of a charged membrane surface to prevent membrane fouling was not readily apparent given the data recorded. This could be a result of the ionic forces of attraction leading to crystal nucleation overcoming the force of separation within the cell due to the charge[8, 9]. This would cause the nucleation site to shift above the membrane, but not far enough.

Due to the difficulty in the generation of a uniformly conductive membrane sample, and with the current lack of evidence to support fouling prevention, this method of fouling prevention is not currently feasible at this time. Although theoretically possible, the method of using an electrically charged membrane presented little evidence for the prevention of crystal formation on the membrane surface. Moving forward, new developments in the generation of the conductive layer and research into other ionic crystal foulants are recommended.

## 6. Appendix

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