Understanding concentrations, saturation indexes, and induction times of a batch reverse osmosis system

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Abstract:
Reverse osmosis (RO) is one of several methods for water desalination. Over the years the energy efficiency of these systems have increased greatly and many variants of RO have emerged. The method that provides the most energy efficient system is batch RO. Batch RO provides the ability to recycle the retentate that is produced until it reaches a concentration where it can no longer be used. Additionally, batch RO can keep the pressure and osmotic pressure of the system balanced to prevent the need of external energy recovery devices. One challenge about this system is the supersaturation levels which can occur in the recycled retentate. With a high enough concentration nucleation will begin to occur causing scaling in the membrane reducing system efficiency. In this study, a 15-hour batch cycle is observed to analyze the concentration of calcium sulfate at the membrane, the saturation index of gypsum, and the potential induction times over the trial. After the sixth hour in the trial, a batch developed a concentration at the membrane of about 10 mM higher than any other batch creating a supersaturation solution with an induction time near the length of time the batch ran for. Subsequent batches revealed that each took almost twice as long to complete, suggesting that scaling of the membrane had occurred during the batch with the highest saturation index. These results help explain why: concentration at the membrane, saturation index, and induction times are important metrics to consider to run a batch RO system more efficiently.

1. Introduction

Reverse Osmosis (RO) desalination is a process which drives a feed of water across a membrane to produce permeate, clean water. In all RO systems a driving pressure is used to push the feed through the semipermeable membrane. As the feed passes through the membrane, the membrane repels the salts ions which leads to the production of two different water streams. The stream that passes through the membrane is the low-salinity stream, which is the permeate. The higher salinity stream is the rejected stream of water called, retentate or brine which will continue to flow through the RO system to be further processed. [1]

In this study, a batch RO system is utilized rather than a continuous RO system. In a continuous RO system, the brine produced only gets treated once and it is done. In a batch RO system, the brine is cycled through the system several times, which causes the concentration of the brine to increase over time. This leads to an increase of concentration which allows for a higher possibility in scaling at the membrane/crystallization of the ions. This crystallization, although uncertain when, begins the fouling of the membrane which hinders the production of permeate. The moment before the ions in the brine start to crystalize is called the nucleation induction time. This study analyzes the data from an experimental batch RO system to determine when nucleation is expected to occur based on the saturation index and the concentration of calcium sulfate.

Nomenclature

RR_i	Instantaneous recovery rate
C_f	Initial conductivity
t	Time
C_r	Retentate conductivity
Z_m	Membrane concentration
Z_i	Initial concentration
SI	Saturation index
T_{ind}	Induction time
N_{prob}	Nucleation probability
t_{step}	Time step

The water solution used for this experiment is a concentration of sodium sulfate ($NaSO_4$) and calcium chloride dihydrate ($CaCl_2 * 2H_4O_2$), which produces the salty solution of Na-Ca-Cl-SO4 which can potentially precipitate calcium sulfate ($CaSO_4$).

We chose to use a solution for calcium sulfate to best model a solution of salty sea water.

2. Methods

2.1 Calculating the Recovery Rate and Calcium Sulfate Concentration at the Membrane

This research analyzes the reverse osmosis systems developed at Olin college of engineering for studying scaling. This RO system produces data that measures the feed flowrate, permeate flowrate, feed conductivity, and flux. The RO system directly sends these measurements to Matlab. To calculate the induction time, first the concentration of the calcium sulfate at the membrane has to be calculated. As the production of permeate increases over time and is collected outside the system, the brine circulating within the systems becomes more concentrated over time. This increasing concentration can be proved by measuring the electrical conductivity of the brine. Since conductivity of water is the ability for water to pass an electric current due to the ions in the water [2], as the brine increases in salinity so will the conductivity. This relationship between the conductivity of the initial feed and the conductivity over time, assuming minimal salt permeation through the membrane, provides an estimate for the instantaneous recovery rate with this equation [3]:

$$RR = 1 - \left(\frac{C_f}{C_r(t)}\right)$$

The recovery rate explains the percentage of how much concentration from the feed is being extracted away from the permeate. The recovery rate can be used to estimate the concentration of calcium sulfate at the membrane using the formula[1]:

$$Z_m = \frac{1}{\left(1 - \frac{RR}{100}\right)} * Z_i$$

Where Z_m has the units of mM.

2.2 Calculation of the Saturation Index for Gypsum

Saturation index quantifies how supersaturated or subsaturated a solution is. In this research, the saturation index for gypsum was calculated by using the software PHREEQC[4]. The equation which was fit to the simulation results after running simulations for our desired concentrations of calcium sulfate (with twice that concentration of sodium and chloride) was:

$$SI = 0.527 \ln(Z_m) - 1.5073$$

This equation provides the opportunity to find the saturation index of gypsum for each timestep throughout the batch RO trial. The saturation index reading can now inform how subsaturated or supersaturated the brine in the system is.

2.3 Calculating the Induction Time

Induction time is the delay before salt crystals start to form in a supersaturated solution. When the brine starts increasing in concentration the ions will start to join. When the ions reach a critical mass, the ions will start to crystalize and form salt.[5] At this point of nucleation, the membrane this may begin fouling. Fouling is when the pores along the membrane start to be covered by the salt crystals. This decreases the overall flux of the RO system, leading to a decrease production of permeate. To prevent fouling in the membrane and the nucleation of ions, the nucleation induction time is calculated.

He et al. [6] studies the nucleation kinetics of calcium sulfate dihydrate and produces a dataset which obverses the relationship between the different concentrations of calcium sulfate and the induction times. An interpolation of the He et al. table 1, with NaCl (m) equal to 0, produces an equation to calculated for induction time which is used in this study as:

$$T_{ind} = (1.66 * 10^6) * e^{-0.174 * Z_m}$$

Applying the equation to this study produces the model in Figure 3, where T_{ind} has the units of hours.

2.4 Calculating the Nucleation Probability

Related to the nucleation induction time, nucleation probability is the probability that salt with crystalize. Since the nucleation of ions depends on the random conditions of the concentration of the brine, any inductions times cannot be taken as exact. To best estimate nucleation a probability calculation must be made. The probability of nucleation during a given timestep is [3]:

$$N_{prob} = \frac{1}{T_{ind}} * t_{step}$$

3. Results and Discussion

The Batch RO system operated for several trials over different days. The trial which produced the data best suited for this study was a trial ran for 14 hours in the lab. With the sensors throughout the system, the trial had raw data for feed flowrate, permeate flowrate, and feed conductivity. Additionally, a few parameters to this study were initial feed concentration and final permeate conductivity.

3.1 Analyzing Concentration over Time

Over the 14-hour trial, the concentration of calcium sulfate at the membrane was recorded as seen in Figure 1. From Figure 1 it can be observed that most of the batches of feed had similar behavior. Most batches started with a concentration around 9 mM of calcium sulfate and had an ending concentration of 21 mM. However, there are two outliers to this pattern which appear in the third and sixth batch of feed. The third batch has the lowest concentration overall throughout.

Observing batch six in Figure 1, the highest concentration during this batch is almost 10mM higher than the average peak. Observing a higher concentration increases the probability of nucleation. With a high nucleation probability comes scaling in the membrane. Scaling should be avoided as it decreases the flux of permeate and membrane permeability over time. The implications of a batch like the sixth shall be discussed in further detail later.

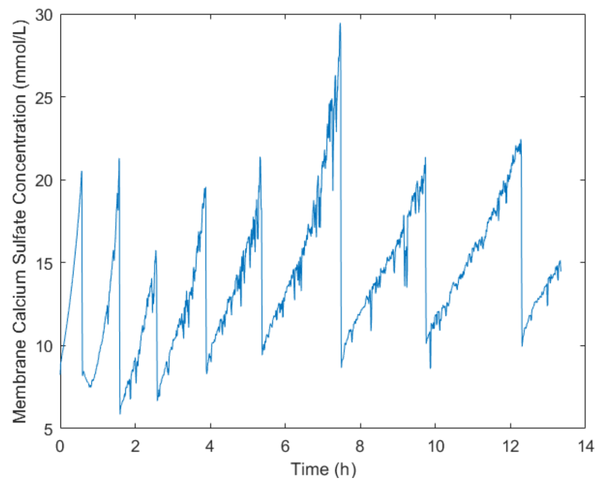

Figure 1: Concentration of calcium sulfate at the membrane of time. The different peaks in this figure represent the different concentrations rises in the several batches of feed ran over the 14-hour trial.

3.2 Analyzing Saturation Index over Time

In Batch RO desalination, since the retentate is being circulated back into the system this leads to an increase of concentration in the retentate. Since concentration is directly correlated to the saturation index of the solution, any increase in one will increase the other. As the saturation index increased the retentate will reach a point where the retentate becomes supersaturated. When the retentate reaches supersaturation the opportunity for the ions in the retentate to crystalize is present.

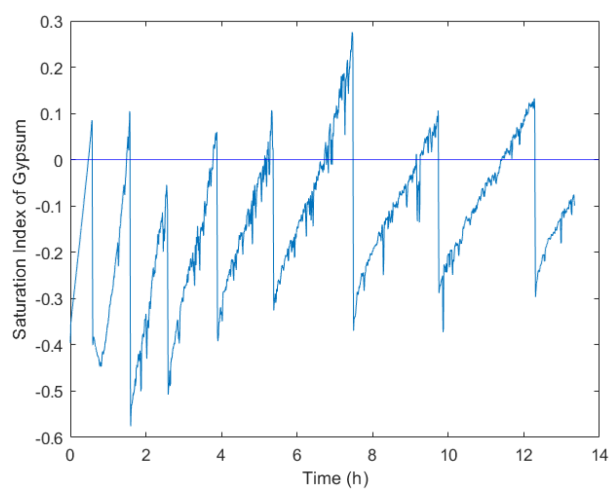

Figure 2: Saturation Index of Gypsum of several batches. The line for Saturation Index at zero represents the saturation limit.

In the first few batches of feed, as seen in Figure 2, the retentate only stays supersaturated for a short amount of time. However, starting from the sixth batch onward, when the batch reaches supersaturation, it stays there for longer. Since the batches are changed depending on the volume in the feed tank, the data indicates that from the sixth batch onward, for the same amount of feed being treated the retentate was much more concentrated for a longer period.

3.3 Analyzing Induction Time Over Time

Since induction times are closely correlated to saturation indexes, the more subsaturated a solution is, the closer the induction time is to infinity. On the other hand, once a solution reaches supersaturation, the probability that nucleation with occur is much higher, thus decreasing the induction time.

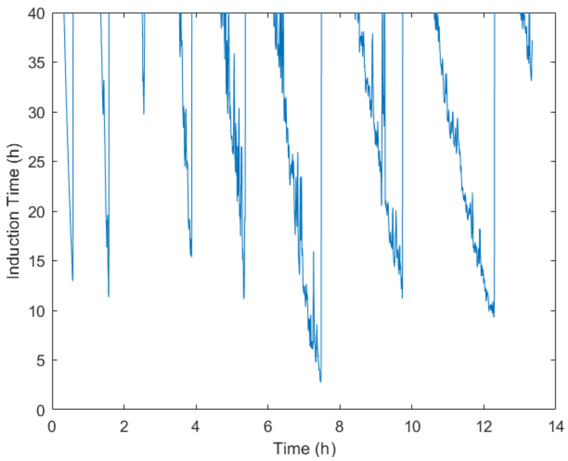

Figure 3: Induction time over time, representing the amount of time, in hours, which it would take for nucleation to occur if the solution remained at the current concentration.

Figure 3 reveals that in the first six hours the minimum induction times seem to be around 14 hours, meaning that nucleation will not be an issue since the trial time is still well before 14 hours. However, around the seventh hour of the trial, the supersaturated batch which had been seen in Figure 2 has the smallest induction time of around 2-3 hours. Considering that this supersaturated batch has been running for 2 hours and the RO system has already been running for 6 hours, it is possible that scaling at the membrane occurred during this batch.

This likelihood of scaling could explain why the batches after the sixth took longer. Salt crystals reduce membrane permeability which reduces the production of permeate and overall flux. Since our system currently depends on the volume of the feed to operate, if less permeate is being produced then less volume is being lost, thus taking more time to reach the desired volume for our system to start a new batch of feed.

To continue this study of scaling, the next steps would be to determine the nucleation probability of each batch of feed. If scaling were to occur, knowing the nucleation would give a better insight into when scaling occurs.

4. Conclusion

The batch RO system produced data that gave insight to the concentration at the membrane, saturation index of gypsum, and induction time, over a period of a 14-hour trial. For the first six hours the data appeared normal with little potential for scaling. However, after the sixth hour it could be observed that scaling was present since batches no longer took on average of one hour but two hours.

Although the RO system ran consistently for first few hours, the behavior in the brine that occurred after six hours is something that a volume reading can not account for. With the extraction and analysis of concentration, saturation index and induction time, future trials can be ran based on these three metrics rather than relying on a volume reading to create a more informed system.

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