Tunneling Through Scaling Barriers with Tandem RO Process for Silica and Calcium Sulfate Super-saturation

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Abstract

Tandem RO process involves a brackish water RO, followed immediately with a high pressure RO. Attaining the overall 95-97% recoveries with brackish or wastewater are increasingly possible. Such a process is limited only by the commonly 1,000 psi operating pressure capability of RO equipment, and energy cost of overcoming the opposing osmotic pressures of concentrates reaching the total dissolved solids (TDS) concentrations of 70,000 to 80,000 mg/l .

Reactive silica concentrations above 120 mg/l in RO concentrates generally result in gradual flux reductions due to adherence of growing populations of high molecular weight non-reactive silica polymers resulting from spontaneous` silicic acid dehydration polymerization. By using silica and silicate polymerization inhibitors, reactive silica levels of 300 -320 mg/l in RO concentrates can be controlled. By using the tandem RO process however, the silica concentrations can be rapidly increased to the vicinity of 1000 mg/l. It has been observed that colloidal silica that formed at such high concentrations adhere less to the RO membrane, and can be washed off with simple cleaning like silt particles instead of deposition as a thin film of transparent hydrated gel. At intermediate concentrations of silica in RO concentrates, such gels that form severely reduce membrane flux, and require special silica dissolving cleaners to retrieve membrane productivity.

In studying maximum RO recoveries in Western Texas and New Mexico, super-saturation of calcium sulfate (gypsum) is more challenging than silica due to shorter induction times for scaling by gypsum. By using effective antiscalants and cleaners that would dissolve gypsum when it does occur, tandem RO process conditions can be optimized to avoid gypsum crystallization. Since high TDS increases solubilities of scaling salts, rapid attainment of maximum TDS favors stabilization of RO concentrates towards scaling. Due to the non-equilibrium conditions in the RO system and induction times needed for membrane fouling by silica and calcium sulfate, tandem RO process offers the advantage of "tunneling" through the scaling barriers by these two and other scales, to reach the high TDS concentrations that reduce fouling.

In this paper, we provide data on the operation of the secondary RO in a batch mode. These data have been reported as concerning Concentrate Enhanced Recovery Reverse Osmosis (CERRO) Process, in reports under grants from US Bureau of Reclamation, Texas Water

Development Board and El Paso Water Utilities. These studies in the batch mode allows for more detailed observations of the kinetics of several fouling factors: cross-flow velocity, permeate flux, concentration polarization, induction times, and antiscalants.

The first tandem RO process on the municipal scale of 10 mgd capacity has been built in East Cherry Creek, Colorado and operated successfully for over a year, at 95% overall recovery. Minimization of the 0.5 mgd reject for disposal still provides a significant incentive for process development work currently in progress.

Keywords: Reverse osmosis; tandem RO process; zero liquid discharge; concentrate minimization; recovery maximization; silica fouling; calcium sulfate scaling; cross-flow velocity; permeate flux; concentration polarization; induction time; antiscalant; high TDS benefits; CERRO process.

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1. Introduction

In the arid regions of Southwestern United States, municipal brackish water ROs are limited to a maximum water recovery of 80-85% due often to silica and calcium sulfate scaling [1-11]. To minimize the cost of concentrate disposal, to recover more usable water, or to attain zero liquid waste discharge, higher recoveries with a secondary high pressure RO is desirable. Initial efforts focused on least costly ways of softening the primary RO concentrate while simultaneously reducing silica concentrations before using a secondary RO [1,5,6,11,12]. Pilot studies [13,18] in El Paso Texas and New Mexico involved using silica polymerization inhibitors and antiscalants uniquely effective in controlling calcium sulfate (gypsum) scaling in secondary ROs, to attain over-all water recoveries in the 96% range. Silica concentrations in the secondary high pressure RO exceeded 1,000 mg/l without apparent membrane fouling [14].

Work continues on optimizing system design for tandem RO process for cost-effective water recovery and volume minimization of concentrate discharge. Well waters in the El Paso Texas area serve as good models for the arid regions of Southwestern US. We provide interim results from our work in this paper. The data shows that the non-equilibrium conditions present in the rapid concentration of brackish water in the tandem RO system allows for the “tunneling” through the scaling barriers of silica and calcium sulfate, to reach the more stable conditions of the concentrate at very high TDS concentrations. The tandem RO process takes advantage of solubility of scales and fouling potentials of polymerized colloidal silica, being more favorable to acceptable operation and maintenance of the system at the highest TDS levels..

2. Concentrate Enhanced Recovery Reverse Osmosis (CERRO) Process

The CERRO process started as a pilot scale project designed to recover additional water from the silica-saturated concentrate from the Kay Bailey Hutchison Desalting plant in El Paso, TX. With an average silica concentration of 130 mg/L, the expectations of reaching high recoveries were low, but extensive testing showed that recoveries between 85 and 90% were achievable [15].

The CERRO process is designed to operate in a batch mode. The pilot unit used was a single-membrane system with membrane specifications shown in Table 1.

Table 1: SWRO Membrane Specifications

Parameter	Specifications
Membrane Dimensions	21” x 2.4” (53.3cm x 6.1cm)
Membrane Type	Polyamide Thin-Film Composite
Maximum Operating Temperature	113°F (45°C)
Maximum Operating Pressure	1,000 psi (69 bar)
Maximum Pressure Drop	15 psig (1.0 bar)
pH Range, Continuous Operation	2 - 11
pH Range, Short-Term Cleaning	1 - 13
Maximum Feed Silt Density Index	SDI 5
Membrane Area	13 ft^2 (1.2 m^2)

The unit is driven via a high pressure positive displacement pump with a capacity of 2.4 gallons per minute (9.0 L/min). The operating pressure was varied from 300 psi to 800 psi (20.7 bar to 55 bar), depending on the quality of the feed water, which was typically pretreated with acid to remove the alkalinity. The concentrate that served as the feed solution already had an antiscalant for silica, and an antiscalant for sulfates was added at 5 ppm to avoid calcium sulfate precipitation. During operation, the permeate was collected in a separate tank, but the concentrate was continuously recirculated back to the feed tank until a pre-determined recovery was reached as indicated by the concentrate conductivity.

3. Investigation of Factors Affecting Fouling in the Batch-Treatment CERRO Process

A distinguishing characteristic of a batch-treatment process is that it is a non-steady state system. Therefore, many of the operational parameters of conventional RO systems do not apply. In this section, we will investigate some of the operating conditions that affect fouling in the batch-treatment CERRO process.

3.1: Cross Flow Velocity

The cross-flow velocity in the CERRO process increases as the recovery of the system increases. This happens because the concentrate is returned to the feed tank, and because the system is operated at constant pressure, the osmotic pressure of the feed water increases, causing the permeate flux to decrease and the concentrate flow to increase as a function of time as shown in Figure 1 for one test run.

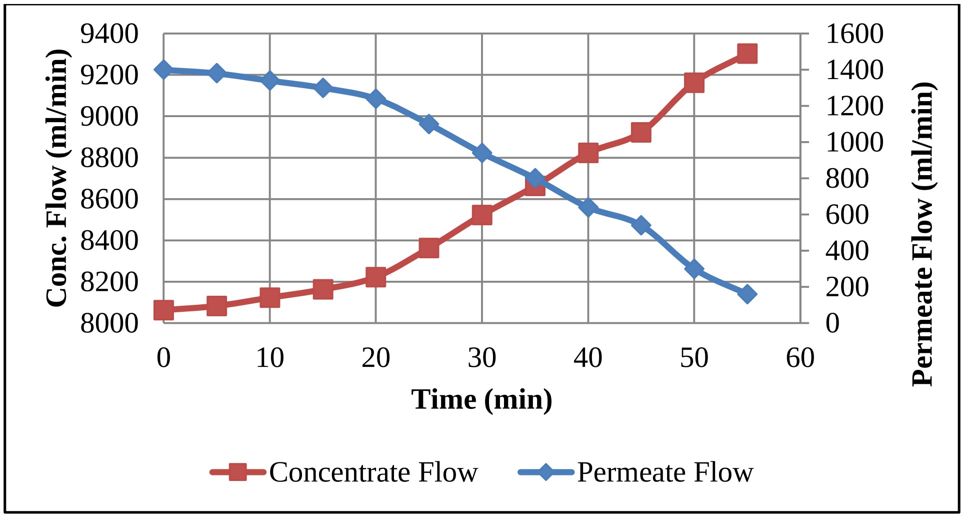

Figure 1: Permeate and Concentrate Flows versus Time for One Test Run

The cross-flow velocity was calculated by dividing the volumetric flow rate by the cross sectional area of the membrane. Figure 2 shows the permeate flow rate and the cross-flow velocity as a function of time for a test run.

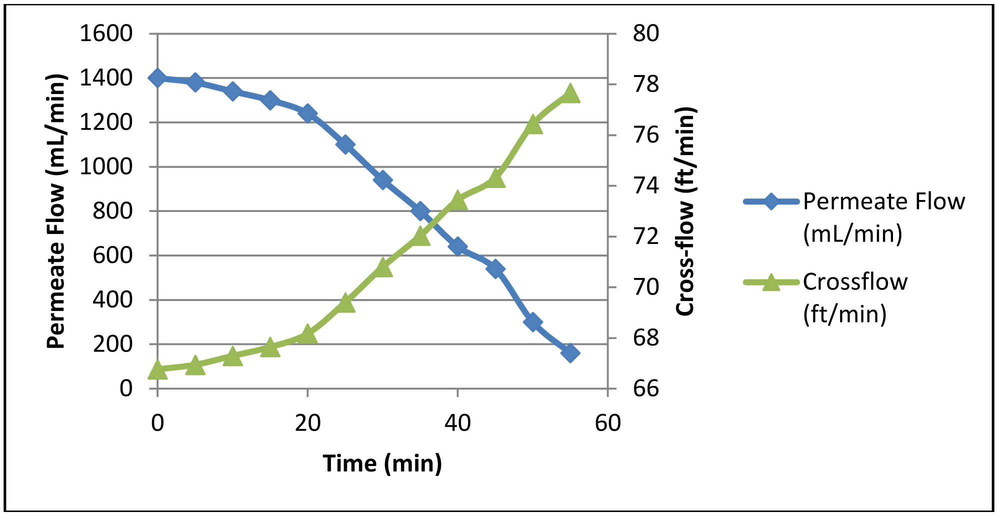

Figure 2: Permeate Flow Rate and Cross-flow Velocity versus Time

Note that there is an increase in the cross-flow velocity of about 16% during the batch run time due to the decrease in the permeate flow rate. The increased cross-flow velocity has a beneficial effect on concentration polarization as discussed a following section of this paper.

3.2 Permeate Flux

The permeate flux can be calculated by dividing the permeate flow by the active area of the membrane. The seawater RO membrane used in this project had an active membrane area of 13 ft^2, with a recommended flux of 13 gal/ft^2-day [21]. Figure 3 shows the results of the permeate flux calculations during one batch run. It can be seen that the flux in the CERRO process is higher during most of the batch than the recommended flux given by the manufacturer. The problem with having a high flux is that the concentration polarization in the surface of the membranes is high and there is a latent risk of fouling the membranes due to precipitation and or polymerization of some minerals.

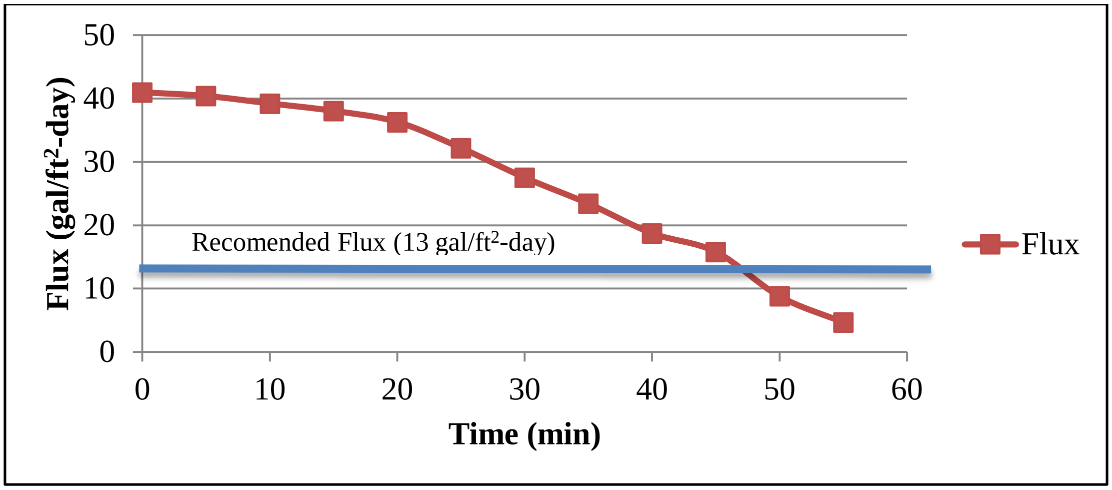

Figure 3: Flux Change versus Time

It can be seen that the flux in the CERRO process is much higher during most of the batch run than the recommended flux given by the manufacturer. Despite this condition, there was never any membrane fouling through hundreds of test runs over several years of testing.

3.3 Concentration Polarization

Concentration polarization (CP) refers to a build-up of solute near the surface of the membrane such that the concentration is higher than that in the bulk solution. There are a number of negative effects associated with concentration polarization, including a decrease in water flux and precipitation of solute, resulting in membrane fouling or scaling. There are many analytical and numerical models associated with concentration polarization in membrane systems. One way to evaluate the phenomenon is by calculating a concentration polarization factor, β, which represents the number of times more concentrated the solute is at the membrane surface than it is in the feed water [22]:

$$\beta = e^{J_w/K_{CP}} \qquad \text{Eq. 1}$$

where K_{CP} is the concentration polarization mass transfer coefficient which can be calculated using equation 2:

$$K_{CP} = 0.023\frac{D_L}{d_H}(Re)^{0.83}(Sc)^{0.33} \qquad \text{Eq 2}$$

Where:

D_L = Diffusion coefficient for solute in water
d_H = Hydraulic diameter of the feed channel
Re = Reynolds number
Sc = Schmidt Number

Since the diffusion coefficient (D_L) is different for each solute present in the water, the concentration polarization factor is different for each ion. In this analysis, the concentration polarization was calculated only for the Na^+, Ca^{+2}, Cl^-, and SO_4^{-2} ions. The diffusion coefficients for these ions were obtained from the Handbook of Chemistry and Physics [23]. Table 2 shows the diffusion coefficients for the respective ions.

Table 2: Difusion Coefficients

Ion	**Na^{+1}**	**Ca^{+2}**	**$SO4^{-2}$**	**Cl^{-1}**
D_L, m^2/s	1.33E-09	7.92E-10	1.07E-09	2.03E-09

Figure 4 shows the results obtained for the concentration polarization factors for these ions during the batch. It can be seen that the concentration polarization at the beginning of the batch for calcium is 2.23. This means that the concentration of calcium at the membrane surface is 2.23 times greater than the feed concentration at the start of the run. However, the concentration polarization factor decays during the run to 1.08, meaning that the concentration of calcium near the membrane surface is almost the same as its concentration in the final concentrate at the end of the run, due to the decay in the permeate flux and the increase in the cross-flow velocity during the batch treatment process. The same decrease is seen for the other ions.

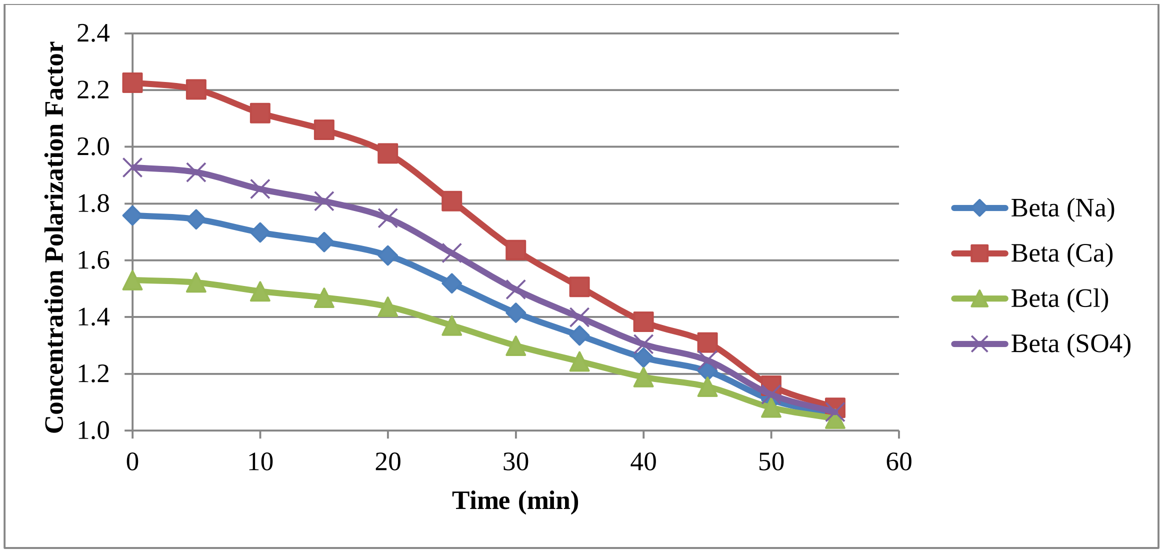

Figure 4: Concentration Polarization Factor for Different Ions

In order to investigate if calcium sulfate would precipitate in a non-recirculating (i.e., energy-efficient) system, a bypass valve was added ahead of the pressure vessel so that the cross-flow velocity could be reduced enough to simulate the flow that would be expected in a multi-membrane, single-pass system.

Table 3 shows the cross-flow velocity and flux where the feed flow was reduced by 60% by opening the bypass valve (the pressure had to be raised in the middle of the experiment due to improper initial adjustment of the concentrate valve).

Table 3: Cross-flow Velocity and Flux at Low Feed Flow

Time (min)	Permeate Flow (ml/min)	Concentrate Flow (ml/min)	Cross-flow Velocity (ft/min)	Flux (gal/ft^2-day)
0	1200	2,400	21.1	35.1
5	1,170	2340	20.6	34.2
10	1,230	2220	19.5	36.0
15	1,110	2,640	23.2	32.5
20	1,035	2,700	23.7	30.3
25	975	2,730	24.0	28.5
30	780	2,800	24.6	22.8

The results showed a reduction of 63% in the cross-flow velocity compared with the non-bypass set-up, but the permeate flux remained relatively the same and about 2.5 times higher (for most of the test run) than the manufacturer's recommended flux of 13 gal/ft^2-day.The concentration polarization factor (β) was calculated for the same four ions as before, and the results are shown in Figure 5.

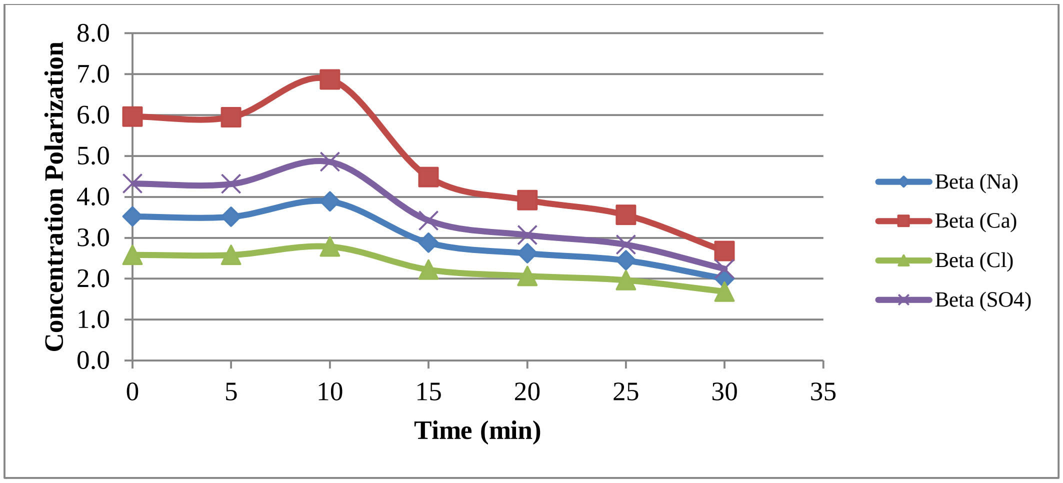

Figure 5: Concentration Polarization Factors at Low Cross-flow Velocity

Chemical equilibrium analysis using the software Visual MINTEQ showed that there was silica super-saturation from the beginning of the batch and super-saturation of calcium sulfate from 5 minutes through the end of the batch run. No precipitation was observed prior to discharging the concentrate (immediately after the 30 minute treatment time), and there was no membrane fouling per the post-test flush results. Calculation of the mass transfer coefficient also indicated that there was no fouling (i.e., the same value was obtained as in all previous test runs). Thus, the reduced cross-flow velocity and concomitant increase in the concentration polarization factor did not appear to adversely affect the performance of the CERRO process.

3.4 Induction Time

Induction time is arguably the most important parameter in batch treatment systems. In this context, induction time refers to the time period between super-saturation of a substance and the formation of a precipitate, scaling substance, or other foulant. The substances of concern in this investigation were silica and calcium sulfate. Previous work concerning silica during batch treatment of RO concentrate from the KBH Desalting plant in El Paso, TX showed that reactive silica concentrations starting at 115 mg/L routinely reached concentrations in the range of 800 mg/L at recoveries of 85%, with one run showing a concentration of 1,325 mg/L at a recovery of 92% [15]. The results are reproduced in Figure 6.

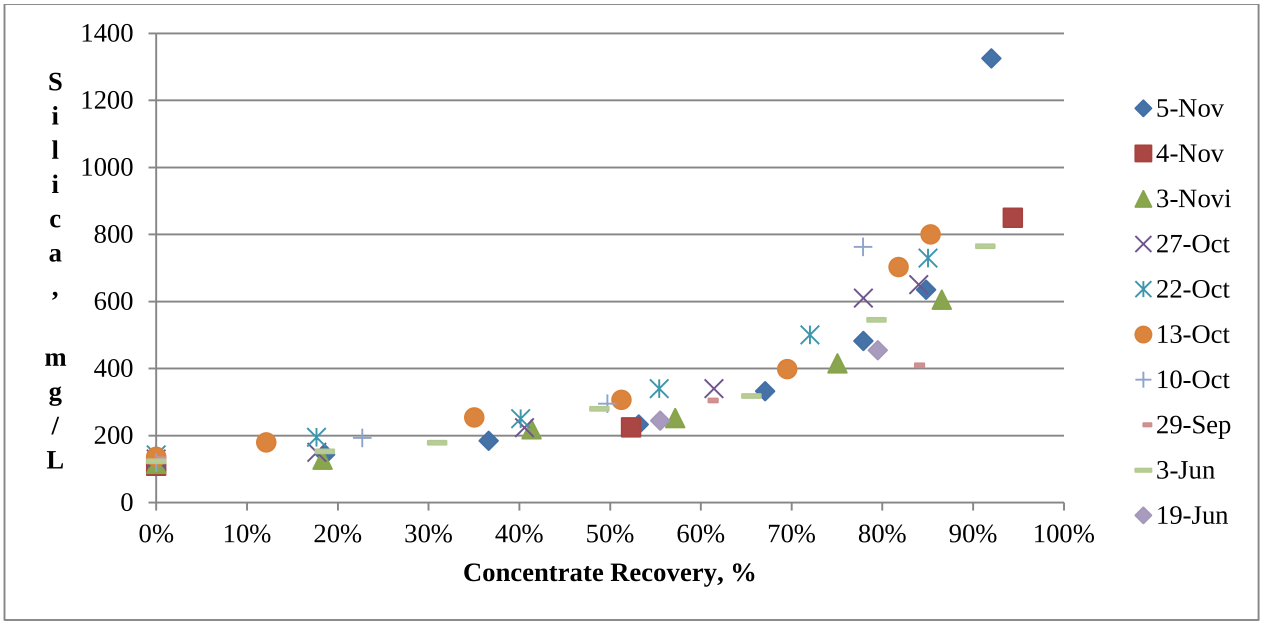

Figure 6: Silica Concentration versus Recovery from KBH Concentrate [15]

There was no scaling at batch treatment times as long as 130 minutes (at conductivities as high as 87,000 µS/cm), indicating that the induction time was longer than two hours. Other investigators have also shown that silica has a long induction time under various pH conditions [16,17,18]. Thus, the relatively long induction time of silica removed all concerns regarding silica scaling in the short batch-treatment-times of the CERRO process.

Studies conducted at the KBH desalting plant in El Paso, TX and at the BGNDRF site in Alamogordo, NM regarding seawater RO treatment of RO concentrate showed that calcium sulfate precipitation limited the recovery of water from the silica-saturated RO concentrate, not silica [15, 19]. Therefore, studies were undertaken to determine the effect of antiscalants on sulfate precipitation and to identify the best one [19]. The results are summarized here.

When no antiscalant was added (i.e., the control) to calcium sulfate-saturated well water from the BGNDRF site, precipitation occurred in less than 15 minutes at a simulated recovery of 50%.

Shih reported an induction period of 12.7 minutes [20]. The induction period increased from less than 15 minutes to over 330 minutes with increased dosages of Pretreat plus 0400 antiscalant at 60% recovery as shown in Figure 7.

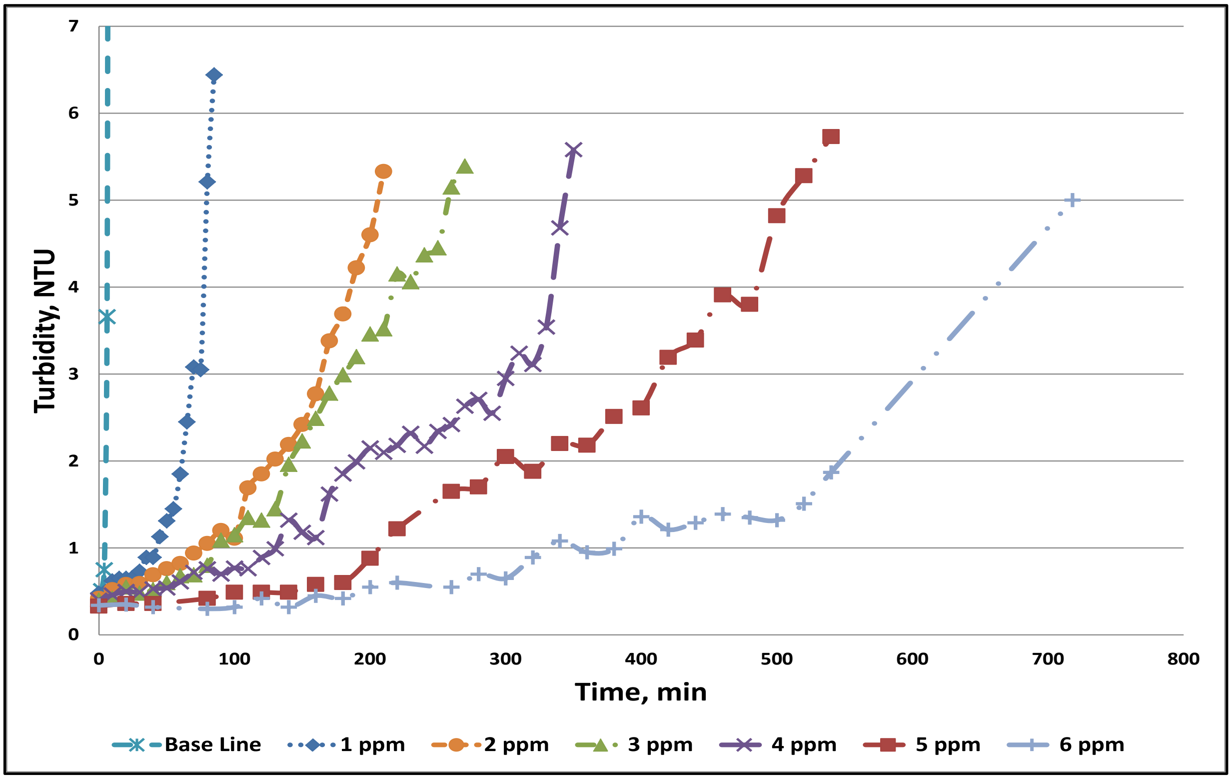

Figure 7: Effect of Antiscalant Concentration on Induction Time at 60% Recovery

The antiscalant concentration necessary to achieve a given recovery in a 60-minute batch processing time is shown in Figure 8.

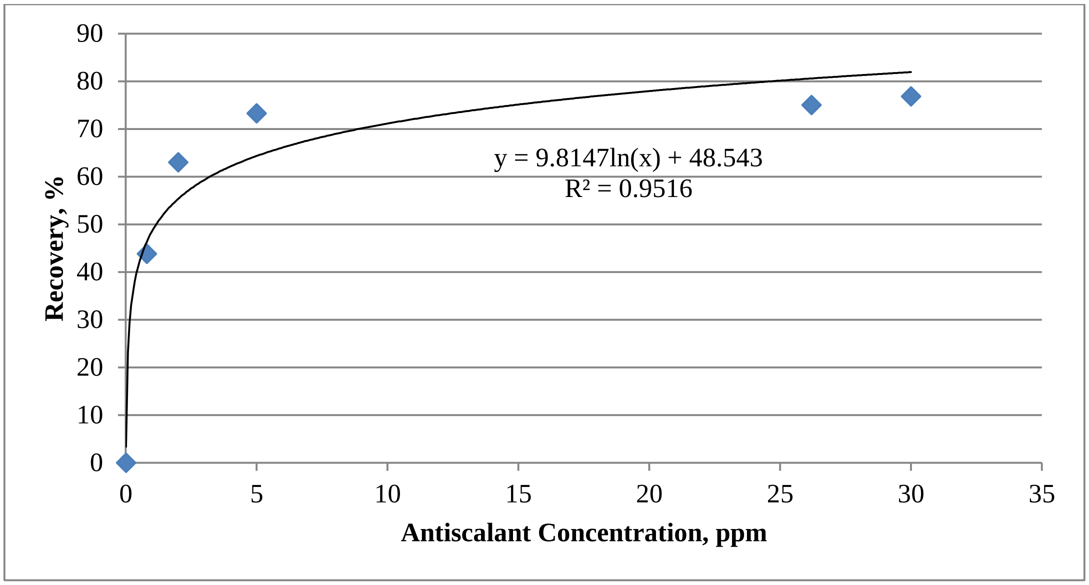

Figure 8: Predicted CERRO Recovery versus Antiscalant Concentration

The graph shows that a concentration of approximately 20 ppm would be required to reach a recovery of 75%. Since the antiscalant is concentrated (along with the other solutes) as permeate is removed for the feed solution, an initial dosage of 5 ppm would be required to have an antiscalant concentration of 20 ppm at a recovery of 75%.

4. Discussion of tunneling effect

Total disolved solids concentrations play a significant role in the prediction of scaling potentials. Calcium carbonate scaling potential has been extensively dealt with [24 - 26]. The complexities of dealing with TDS concentrations in scaling potentials are that one has to consider common ion effects , where each catión is common to pair with different anions, and each anions can pair with multiple cations. Further, ions in solution are not present as free species, but are solvated with water, and surrounded by ions with opposite charges. When concentrations increase , these interaction intensify, affecting scaling potentials [27] and extending the induction times for scaling to occur. As TDS concentration rises in the RO concentrate, we have the initial increase in scaling potential of salts with low solubilities. However, if TDS concentration can be rapidly increased to máximum levels possible with tándem RO, one will enter into a zone of operating conditions more favorable for máximum water extraction.

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5. Conclusions

The following conclusions can reasonably be made from the results obtained in this investigation:

1. A 60 % reduction in cross-flow velocity did not lead to fouling in the batch-treatment CERRO process.
2. There was no membrane fouling in the CERRO process even though the permeate flux exceeded the manufacturer's recommended value of 13 gal/ft^2-day by a factor of three at the beginning of the process and remained higher than the recommended value for over 80% of the batch processing time.
3. Even though the concentrate polarization factor indicated that the final concentrate was supersaturated in calcium sulfate, there was no precipitation during CERRO processing of KBH concentrate, even for batch processing times exceeding 2 hours.
4. The induction time of calcium sulfate can be significantly increased through addition of an appropriate antiscalant at the proper dosage. Our results indicated that a dosage of 5 ppm would allow for recoveries of at least 75%.

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