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A Continuous Process for RO Concentrate Desupersaturation

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A Continuous Process for RO Concentrate Desupersaturation

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by

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ABSTRACT OF THE THESIS

A Continuous Process for RO Concentrate Desupersaturation

by

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Master of Science in Chemical Engineering

University of California, Los Angeles, 2016

Professor Yoram Cohen, Chair

Reverse osmosis (RO) desalination of inland brackish water can replenish dwindling water supplies in various regions around the world. However, successful implementation of RO technology requires high product water recovery (>85%) in order to minimize the volume of generated concentrate brine. Therefore, brine management is a critical aspect of inland water desalination. At high water recovery, dissolved mineral salts (e.g. $CaSO_4$, $CaCO_3$) may concentrate above their solubility limits and may crystallize, potentially blocking or damaging RO membrane surfaces, reduce water permeate flux, and shorten membrane life. Therefore, it is essential to reduce the propensity for mineral scaling in order to increase the potential for high product water recovery. Attaining high recovery for inland water desalination, while avoiding membrane mineral scaling, can be achieved via an intermediate concentrate demineralization (ICD) method that utilizes two-step chemically-enhanced seeded precipitation (CESP) process. In the CESP approach, primary RO concentrate is first treated via partial lime softening in which residual antiscalant in the

PRO concentrate is scavenged by precipitating calcium carbonate ($CaCO_3$). The filtered lime treated PRO concentrate is then treated in a seeded gypsum ($CaSO_4 \cdot 2H_2O$) precipitation step whereby, gypsum crystal seeds promote rapid crystal growth. As a consequence, the treated PRO stream is desupersaturated with respect to gypsum and upon filtration step; a secondary RO desalting step is carried out to increase the overall product water recovery.

Development of the ICD approach as a continuous process suitable for deployment in RO desalting is the focus of the present study. Accordingly, a novel system for continuous chemically enhanced seeded precipitation (CCESP) pilot was developed and constructed consisting of an alkaline chemical softening flocculation tank followed by a vertical static mixing bed reactor for seeded precipitation. The overall feasible feed slow rate for the pilot CCESP system was 0.026 – 0.25 gpm. Evaluation of the continuous ICD process performance was undertaken with a range of solutions that mimic PRO concentrate produced from desalination of San Joaquin Valley brackish water at a recovery of 63%. The major salts in the PRO concentrate feed to the CCESP included $CaCl_2$ (30.7 mM), Na_2SO_4 (145.4 mM), $MgSO_4$ (31.2 mM), $NaHCO_3$ (11.4 mM), and NaCl (20.3 mM). Antiscalant (Flocon 260, 5 mg/L) was introduced to the PRO concentrate in order to assess the feasibility for residual antiscalant (typically present in PRO concentrate) removal so as to avoid retardation of the subsequent gypsum desupersaturation step. The CCESP system enabled continuous gypsum desupersaturation by purging spent gypsum seeds and recycling a portion of the seeds or introducing fresh seeds to the fluidized bed. Various gypsum seeds were tested, with a focus on industrial sources for gypsum (e.g. mining, drywall, food, agriculture) due to their availability and low cost. The purity of the gypsum seeds was found to be a key factor, where gypsum seeds with >98% purity were found to

be most effective. Using the synthetic PRO concentrate, each of the two steps of the process were first evaluated individually to determine the optimal operating conditions and subsequently combined to evaluate the complete continuous operation. In the CCESP, lime softening occurs in a flocculation tank with recirculation, solids removal from the lime treated stream is via an inline centrifugal separator, and the gypsum seeded precipitation takes place in a fluidized bed. It was found that CCESP treatment of the PRO concentrate with 5.75 mM lime enabled up to 68% removal of the residual antiscalant. Subsequent gypsum seeded precipitation (initial seed loading of 240 g/L gypsum) reduced the PRO concentrate gypsum supersaturation index (SIg) level from 2.36 to nearly unity. The above level of gypsum desupersaturation was assessed to be sufficient for carrying out a secondary RO desalting that would enable increased recovery from 63% at the PRO step to an overall recovery of about 85% and possibly higher.

The present study successfully developed a continuous ICD process and demonstrated its technical feasibility. The present results are encouraging and support the merit of evaluating the process under field conditions. Overall, it is expected that deployment of the CCESP process will enable high recovery desalting of challenging inland water of high mineral scaling propensity.

The thesis of Jack Lei is approved.

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Nomenclature

α	gain for calcium ion activity calibration
α_{daily}	daily gain correction factor
AS	Antiscalant
β	offset for calcium ion activity calibration
β_{daily}	daily offset correction factor
CAD	Computer aided design
CESP	Chemically Enhanced Seeded Precipitation
CCESP	Continuous Chemically Enhanced Seeded Precipitation
C_b	bulk concentration
C_m	concentration at membrane surface
C_P	concentration of the permeate
CP	Concentration Polarization
D	solute diffusivity
DIW	de-ionized water
ΔE	potential difference
ΔE_{daily}	daily potential correction factor
gpm	gallons per minute
IAP	ion activity product
ICD	Intermediate Chemical Demineralization
J	permeate flux
k	solute feed-side mass transfer coefficient
K_{SP}	solubility product
L_P	permeability
π	osmotic pressure
PRO	Primary Reverse Osmosis
R_0	observed salt rejection
RO	Reverse Osmosis
RTD	Residence Time Distribution
SI	Saturation Index
SI_g	gypsum saturation index
SI_c	calcite saturation index
σ	salt reflection coefficient
SRO	Secondary Reverse Osmosis
t_d	response detection time
τ	reactor residence time
TOC	Total Organic Carbon
ξ	Extent of precipitation
Y	water recovery

Chapter 1

1. Introduction

1.1 Background

Water reclamation and reuse of wastewater and agricultural drainage water is a possible solution for water shortages in many inland locations around the world. Reverse osmosis (RO) membrane desalination is the primary technology for brackish water recovery, but the process generates a large volume of concentrate water (brine) if not operated at a high water recovery (>85%). RO membrane units operated in series can be utilized to obtain higher recoveries, but suffer from decreased lifetime due to mineral crystallization and membrane scaling.

As the recovery of permeate product is increased in RO processes, the concentration of mineral salts on the feed-side stream and on the membrane surface can increase to levels above their saturation limit leading to crystallization or deposition onto the membrane surface. The formation of mineral scale decreases the water permeate flux and may damage the membrane [6-8]. As a result of the possibility of mineral scaling, the achievable RO recovery is often operationally limited, leading to high volumes of concentrate waste.

Methods to increase water recovery of RO processes by treating RO concentrate have been proposed, including evaporation ponds, crystallizer tanks, membrane distillation, electrodialysis, and induced precipitation [8]. Such technologies have traditionally struggled with limitations based on volume (e.g. space required for evaporation ponds), energy cost (e.g. membrane distillation), and economic cost (e.g. high chemical dosage, capital) [10]. Emerging technologies for minimizing effluent discharge by maximizing water recovery have been proposed, which utilize stages of intermediate treatment on a RO tandem (primary RO and secondary RO) [10].

In previous work, the feasibility of intermediate concentration demineralization (ICD) of primary RO (PRO) concentrate was investigated as a means to enable secondary RO (SRO) operation [8]. A two-step, semi-batch chemically-enhanced seeded precipitation (CESP) process was developed to demonstrate the effectiveness of ICD for brackish water treatment, as summarized in **Fig. 1-1**. The study concluded that the CESP reduced the operational cost of RO by requiring less chemical and reaching higher recovery compared to conventional RO processes without ICD [8]. The CESP process was demonstrated in both laboratory and field settings, but was limited to a batch process. In this study, a continuous process was developed for demonstrating a continuous chemically-enhanced seeded precipitation (CCESP) process. This work forms a foundation for future CCESP demonstration in the field.

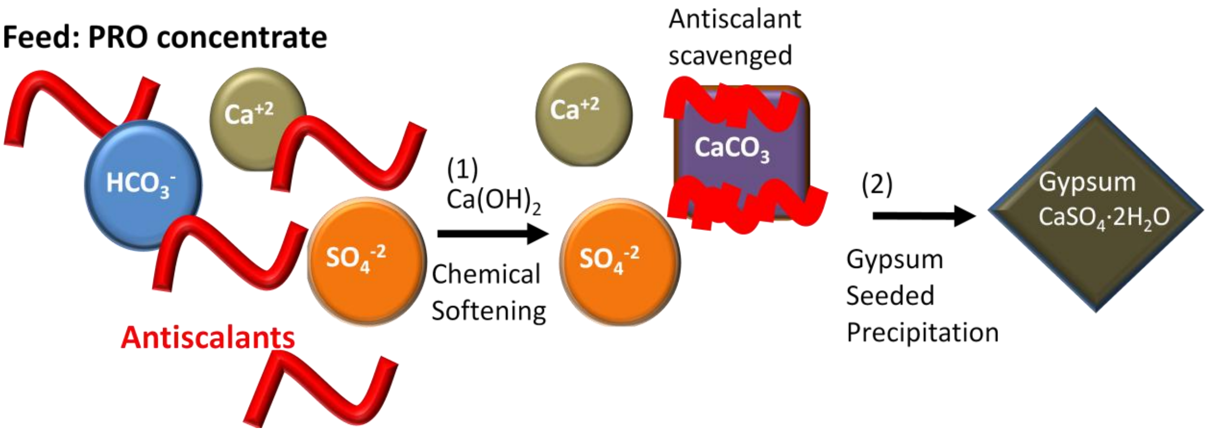


Figure 1-1. Two-step chemically enhanced seeded precipitation (CESP) process; Feed: antiscalant-stabilized supersaturated RO concentrate; (1): Addition of lime, $Ca(OH)_2$, to induce partial softening and antiscalant scavenging in precipitated $CaCO_3$ solid matrix; (2): Introduce gypsum crystal seeds for gypsum desupersaturation

1.2 Objectives of the thesis

The major goal of this thesis was to develop and demonstrate a continuous chemically enhanced seeded precipitation (CCESP) process. It was theorized that two discrete steps is feasible for continuous RO concentrate desupersaturation, where partial chemical softening is achieved through a solids flocculation reactor, and gypsum seeded precipitation occurs in a vertical fluidized bed. In order to demonstrate the CCESP process, a novel system with the potential capability of direct integration with primary RO (PRO) concentrate to enable subsequent secondary RO (SRO) desalting would be required. The antiscalant scavenging by partial chemical softening and gypsum seeded precipitation processes in the system may be evaluated and compared to previous batch CESP studies. Finally, the process requirements and operational range for the current system may be quantified. The main objectives of the research were to:

1. Design and construct a novel system for demonstrating a continuous CESP process and to determine the operational range for the system.
2. Demonstrate a continuous partial alkaline chemical softening for antiscalant scavenging in a solids contact flocculation tank.
3. Demonstrate continuous gypsum seeded precipitation in a vertical fluidized bed with seed purging and renewal.
4. Compare continuous CESP antiscalant scavenging and gypsum desupersaturation to batch CESP findings.

1.3 Approach

The thesis work followed the workflow presented in **Fig. 1-2**. In order to evaluate a process for continuous RO concentrate desupersaturation via chemical softening and seeded precipitation, a novel system was first developed and constructed. Initially, a series of experiments were carried out in batch mode, following the work of Rahardianto et al. [2], and these served to guide the subsequent evaluation of the CESP process in a continuous mode of operation. Simulation analysis of multi-electrolyte solubility was performed using

Stream Analyzer 3.1 (OLI Systems) software for the basis of experiment design. A model RO concentrate with known properties was generated for laboratory studies to allow for comparison with previous batch CESP studies. Due to the large volume of feed required to operate the system continuously, portions of the process (i.e. lime softening, antiscalant scavenging, and gypsum seeded precipitation) were evaluated individually. After system construction, the hydrodynamics and operation of the system were first evaluated using city tap water. Once the system control was evaluated and refined, the initial experiments focused on the chemical softening process. Lime softening enables antiscalant removal [8], which is essential in order to prevent gypsum seed poisoning that significantly lowers the precipitation effectiveness in the subsequent gypsum-seeded precipitation step. Various gypsum seeds were evaluated with respect to their effectiveness in promoting gypsum precipitation. Finally, the chemical softening and seeded precipitation processes were evaluated in series for a continuous CESP process experiment.

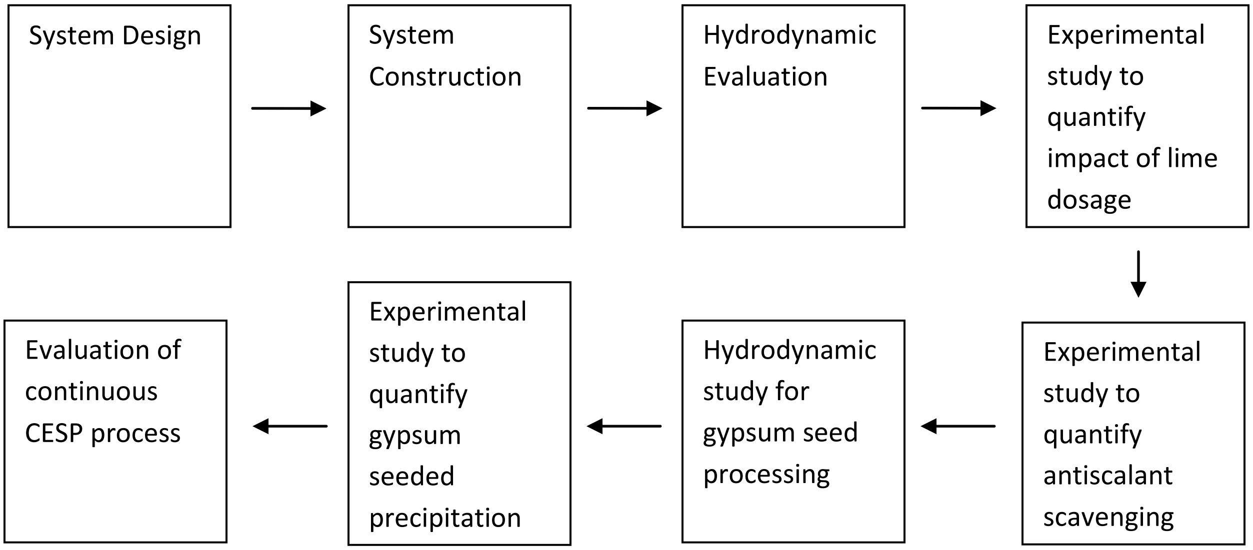


Figure 1-2. Research flowchart; CESP – chemically enhanced seeded precipitation

Chapter 2

2. Background and Literature Review

2.1 RO desalination

Reverse osmosis (RO) is a method for desalination by which pressure is applied to a feed solution across a semipermeable membrane which allows for separation of a solute lean stream (permeate or product) and a solute rich stream (retentate or concentrate) [1]. In order for separation to occur, the applied pressure must be greater than the osmotic pressure of the solution [1].

An RO membrane is characterized by its water permeability, L_P, and its salt rejection, R_0. Water permeability is a measure of the ease of water passage through the membrane. The flux through the membrane (L/m^2·h), J, is a function of permeability (L/m^2·h·psi), L_P, salt reflection coefficient, σ (~1 for RO membranes), applied pressure, ΔP, and osmotic pressure difference between the feed and permeate sides of the membrane, $\Delta\pi$.

$$J = L_P(\Delta P - \sigma\Delta\pi) \tag{2-1}$$

The osmotic pressure (psi), π, of saline water increases with solute concentration and for dilute solutions is a function of van't Hoff factor, i, solute concentration (mol/L), C, ideal gas constant (1.2059L·psi/mol·K), R, and temperature (K), T.

$$\pi = iCRT \tag{2-2}$$

Salt rejection is a measure of the membrane's ability to prevent salt passage through the membrane into the permeate stream. The observed salt rejection of an RO membrane, R_0, is defined as:

$$R_0 = 1 - \left(\frac{C_P}{C_B}\right) \tag{2-3}$$

where C_P and C_B are the concentrations of permeate and bulk streams, respectively. The bulk concentration is equal to the feed concentration, C_F, for low recovery RO operation. Recovery is a measure of permeate productivity and is defined as:

$$Y = \frac{Q_P}{Q_F} = 1 - \frac{Q_R}{Q_F} \tag{2-4}$$

where Q_P, Q_F, and Q_R are the permeate, feed, and retentate volumetric flow rates, respectively.

RO desalination is conventionally carried out in a cross-flow with a feed stream flowing tangentially across the membrane surface under high pressure shown in **Fig. 2-1**. The feed stream enters from one end and pressure drives a solute lean permeate stream through the membrane. The solute rich retentate stream is rejected by the membrane and exits the membrane channel.

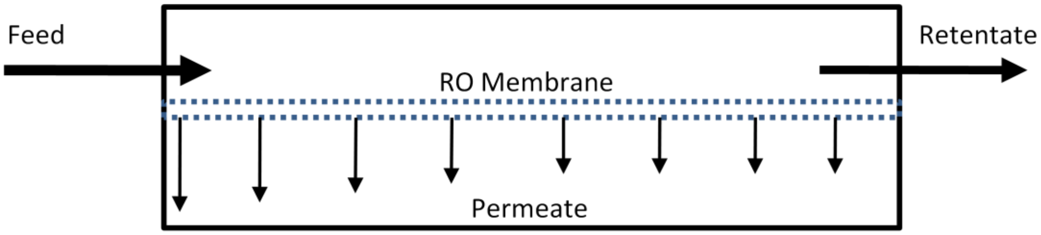


Figure 2-1.Simplified schematic of a cross flow RO membrane process.

Most large scale RO desalination facilities use spiral-wound membrane modules because they provide a large membrane surface area to volume ratio. Additionally, the membranes may be arranged in multistage units connected in series and in parallel as needed to produce the desired flow rate of permeate water. A module, shown in **Fig. 2-2**, consists of many layers of RO membranes separated by spacers which allow permeate to pass through to a perforated central tube for collection. As permeate is separated from the feed stream, the volume of retentate decreases, often requiring fewer membrane modules in parallel in the subsequent stages as shown in **Fig. 2-3**. Moreover, as most natural feed waters contain suspended particles, pretreatment is required to remove debris that could damage or plug the RO membranes.

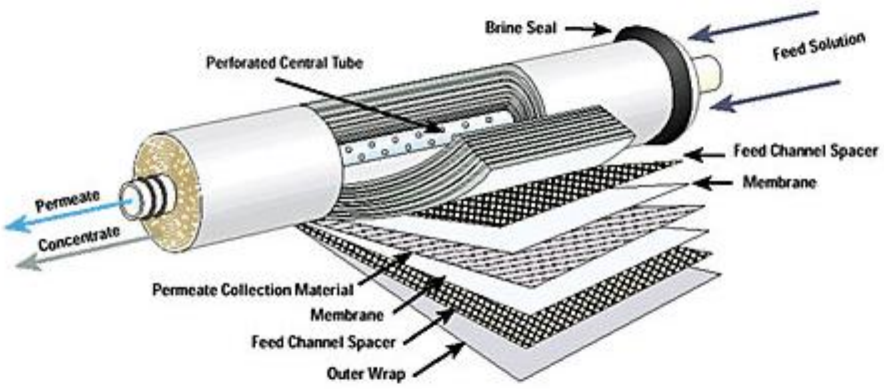


Figure 2-2.Schematic of a spiral-wound RO membrane element with internal structure cutout [8]

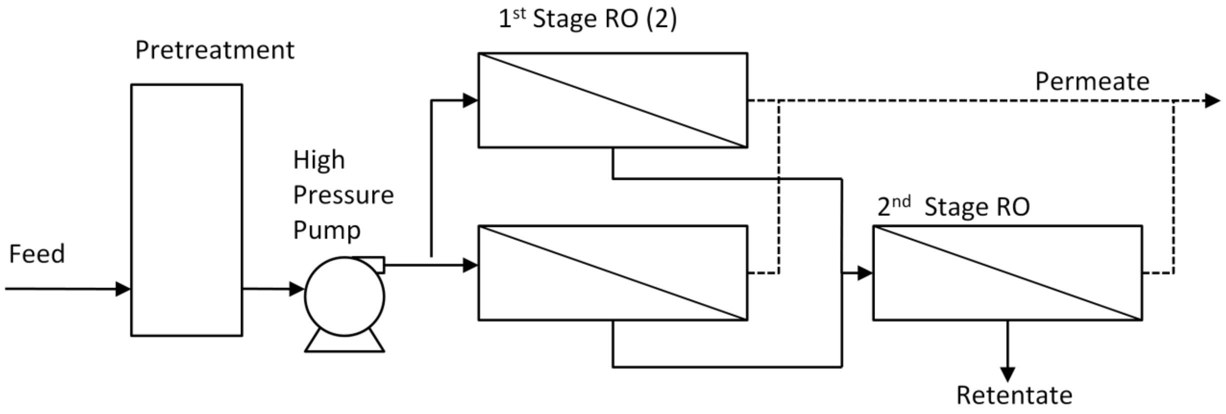


Figure 2-3. Example schematic of a multistage RO desalination process

2.1.2 Concentration Polarization

In RO processes, salt ions can accumulate near and at the membrane surface, resulting in local regions of increased concentration, commonly known as concentration polarization. The concentration polarization (CP) factor defines the concentration increase at the membrane surface relative to the bulk and can be approximated using the film model:

$$CP = \frac{C_M}{C_B} = 1 - R_0 + R_0 \exp\left(\frac{J}{k}\right) \quad (2\text{-}5)$$

whereC_M and C_B are the solute concentrations at the membrane surface and in the bulk, respectively, R_0 is the observed salt rejection, J is the permeate flux, and k is the solute feed-side mass transfer coefficient. The CP factor is important to quantify because salts in the bulk may be below their solubility limit, but may be supersaturated at the membrane surface and can potentially precipitate or crystallize onto the membrane, resulting in permeate flux decline [8]. The CP increases as the feed flows along the membrane channel and is greatest at the exit region as illustrated in **Fig. 2-4**.

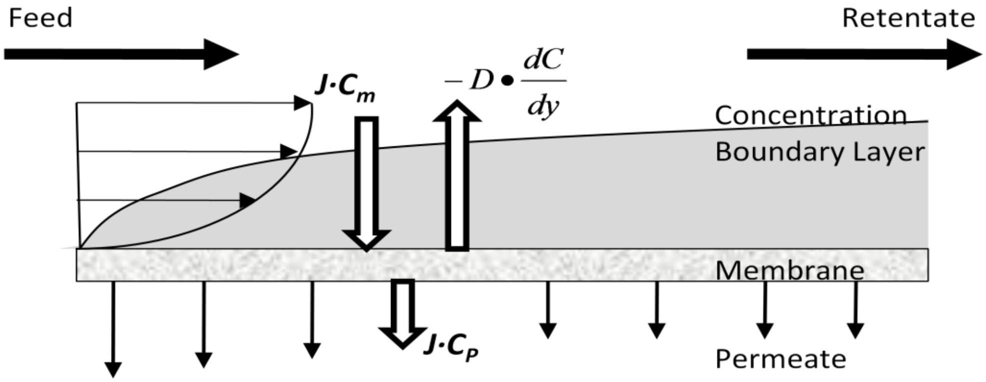


Figure 2-4. Schematic of the formation of a concentration boundary layer, where J is the water flux, $C_m$and C_P are solute concentrations at the membrane surface and in the permeate, D is solute diffusivity, and $\frac{dC}{dy}$ is the solute concentration gradient.

2.1.2 Recovery Limitation

Mineral salt scaling is the process by which sparingly soluble salts exceed their saturation concentrations and crystallize or precipitate in bulk or on RO membrane surfaces, blocking permeate flow through the membrane and reducing the productivity of product permeate [2-8]. Consequently, RO desalination processes must be operated at concentrations of salts below their scaling thresholds. The RO feed is often dosed with antiscalants (AS) which reduce crystallization kinetics and enable RO operation at or above saturation. Scaling thresholds of mineral salts of concern (e.g. gypsum, calcite) are typically expressed in terms of the saturation index (SI) which is the ratio of ion activity product (IAP) to the solubility product (K_{SP}).

$$SI = \frac{IAP}{K_{SP}} \tag{2-6}$$

For example, the SI for gypsum (SI_G) is defined as:

$$SI_G = \frac{(Ca^{2+})(SO_4^{2-})}{K_{SP,G}}, SI_C = \frac{(Ca^{2+})(CO_3^{2-})}{K_{SP,C}} \tag{2-7}$$

where (Ca^{2+}), (SO_4^{2-}), and (CO_3^{2-}) are calcium, sulfate, and carbonate ion activities, respectively, and $K_{SP,G}$, $K_{SG,C}$ are the gypsum and calcite solubility products, respectively. The recommended scaling threshold typically accounts for appropriate antiscalant usage and are above saturation (i.e. $SI \geq 1$). For example, the scaling threshold for gypsum is $SI_G = 2.3 - 4.0$ [3].

2.2 RO desalination via intermediate concentrate demineralization

In order to overcome the traditional RO desalination recovery limitation due to mineral scaling, a two-stage process integrating RO desalting with intermediate concentrate demineralization (ICD) has been shown to be a viable solution [8]. The ICD process reduces the concentration of scale precursor minerals (e.g. calcium, sulfate, and carbonate ions) in primary RO (PRO) concentrate to allow the treated concentrate to be further desalted in a subsequent secondary RO (SRO) process. Recent studies have shown that the staged RO with ICD process can enhance the overall recovery in brackish water desalination to >85%, minimizing the residual volume of generated RO concentrate [6-8]. Various methods for ICD incorporate induced precipitation of scale precursors such as alkaline induced calcium precipitation and seeded precipitation, as seen in **Fig. 2-5**.

2.3 Chemically-enhanced seeded precipitation

A two-step, chemically-enhanced seeded precipitation (CESP) process combining alkaline softening and seeded precipitation was developed and demonstrated to reduce saturation levels of gypsum. For example, it was shown to reduce SJV PRO water from 70-150% above saturation of gypsum to 10-15%, increasing the recovery from 52-62% to 93% [8].

Alkaline precipitation softening has been shown in various studies as an effective intermediate concentrate demineralization (ICD) method for calcium ion removal [7-8]. However, precipitation softening requires at least stoichiometric amounts of an alkaline chemical (e.g. sodium hydroxide, calcium hydroxide) to induce precipitation of calcium carbonate [4]. Therefore, ICD via softening can be costly relative to ICD via seeded precipitation. Chemical softening has also shown to be effective for demineralization in the presence of antiscalants (AS) which are normally present in PRO concentrate, with little impact on precipitation effectiveness [4]. Additionally, the precipitation of calcium carbonate has shown to scavenge AS into the solid matrix, enabling further precipitation via methods that may be inhibited by the presence of AS (e.g. seeded precipitation) [5].

Seeded precipitation is the process by which precipitation is induced by adding crystal seeds to provide sites for heterogeneous crystal growth. PRO concentrate is typically already supersaturated with respect to gypsum and stabilized by antiscalants.

Seeded precipitation is less chemically intensive than chemical precipitation softening. However, seeded precipitation processes have several limitations including poisoning by natural organics and antiscalants, and potential membrane damage in subsequent desalting processes [6-8].

Previous studies theorized that the CESP process could be carried out continuously [5,8]. Staged lime dosing (i.e. multiple lime additions) was shown to remove a higher degree of AS relative to an equivalent single lime dose [5]. A continuous process for ICD was desired for direct integration to a PRO process.

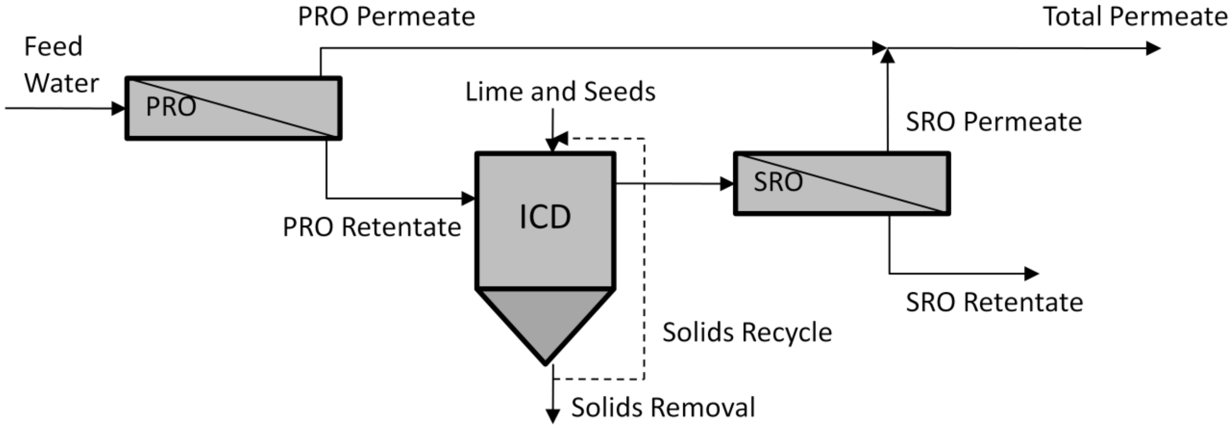


Figure 2-5. High recovery RO process utilizing intermediate concentrate demineralization (ICD) between primary RO (PRO) and secondary RO (SRO) stages

Chapter 3

3. Experimental

3.1 Materials

The scope of the study required that more economical sources of chemicals be used to justify a continuous operation mode. Five different gypsum seed crystals were tested: a “Ultra-fine” and a “Pulverized” gypsum was provided by US Gypsum, LLC (Denver, PA), “Terra Alba No.1” was acquired from USG (Chicago, IL), “Calcium sulfate dihydrate ACS Reagent Grade” was purchased from J.T. Baker (Avantor, Center Valley, PA), and “Calcium sulfate dihydrate ACS Reagent, 98%” was purchased from Sigma-Aldrich (St. Louis, MO). The lime slurry, “SLS 45”, was provided by Lhoist International and is 43-47 vol% $Ca(OH)_2$. All solutions were prepared by dissolving reagent-grade chemicals in de-ionized and distilled (DI) water. Synthetic model solutions were prepared using $CaCl_2 \cdot 2H_20$, $NaHCO_3$, $MgS0_4 \cdot 7H_20$, NaCl, and Na_2S0_4 reagents, all obtained from Fisher Scientific (Pittsburgh, PA) and McMaster-Carr (Santa Fe Springs, CA). Alkaline chemicals used were $Ca(OH)_2$ slurry obtained from Lhoist North America (Fort Worth, TX) and NaOH pellets (prepared as 1-M stock solution), which was obtained from Sigma Aldrich (St. Louis, MO). A proprietary PAA-based antiscalant, Flocon 260, was obtained from Biolab Water Additives (Lawrenceville, GA) as a solution with ~35%wt. total dissolved solids content.

3.2 Equipment

Materials and equipment were purchased from various vendors. A detailed parts list can be found in the Appendix.

3.3 System Design

The design of a continuous system for CESP was based on designs first proposed by McCool et al. [8].The current CCESP process diagram is shown in **Fig. 3-1**. Equipment capable of handling alkaline chemicals and solid slurries were selected. Based on the process diagram, a 3-D computer aided design (CAD) was developed as the blueprint for the construction as seen in **Fig. 3-2**. In order to process solid slurry, LLDPE tubing with 5/8" outer diameter (OD) was employed. For non-solid process flows, 3/8" to 1/2" OD tubing was used. The construction of the CCESP system began in August 2014 and completed in December 2014. The system measures 73" by 85" by 20" and is supported by a custom stainless steel strut channel frame (Unistrut, USA). The bed reactor can be disassembled by removing the flange bolts to decrease the height to 53". The system can be separated to form a three module system for transportation. The competed system can be viewed in **Fig. 3-3** and a breakdown of system components are listed in **Table 3-1**.

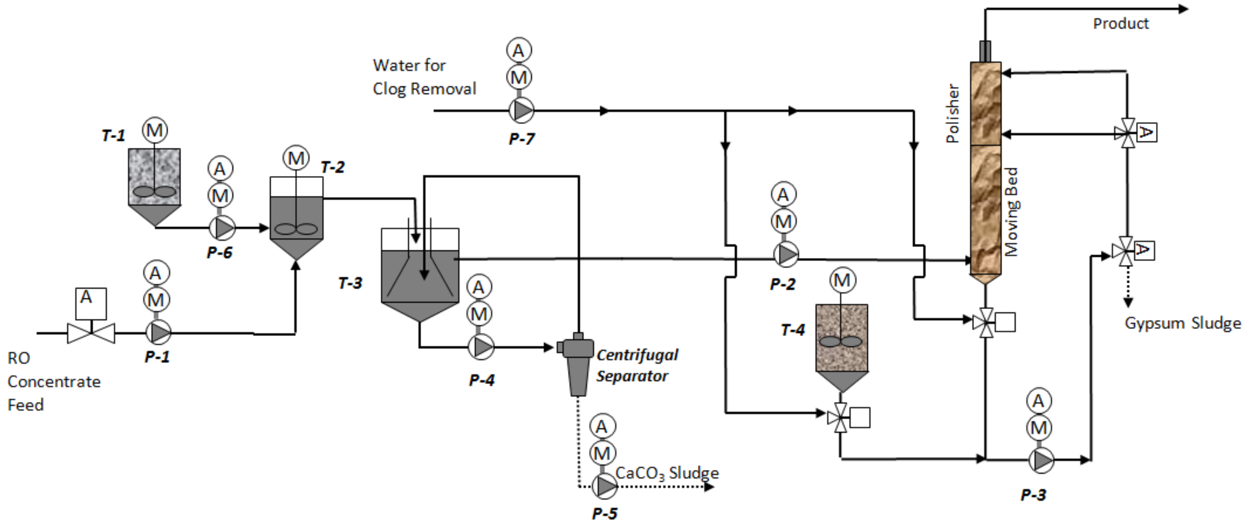


Figure 3-1. Process diagram of continuous CESP process

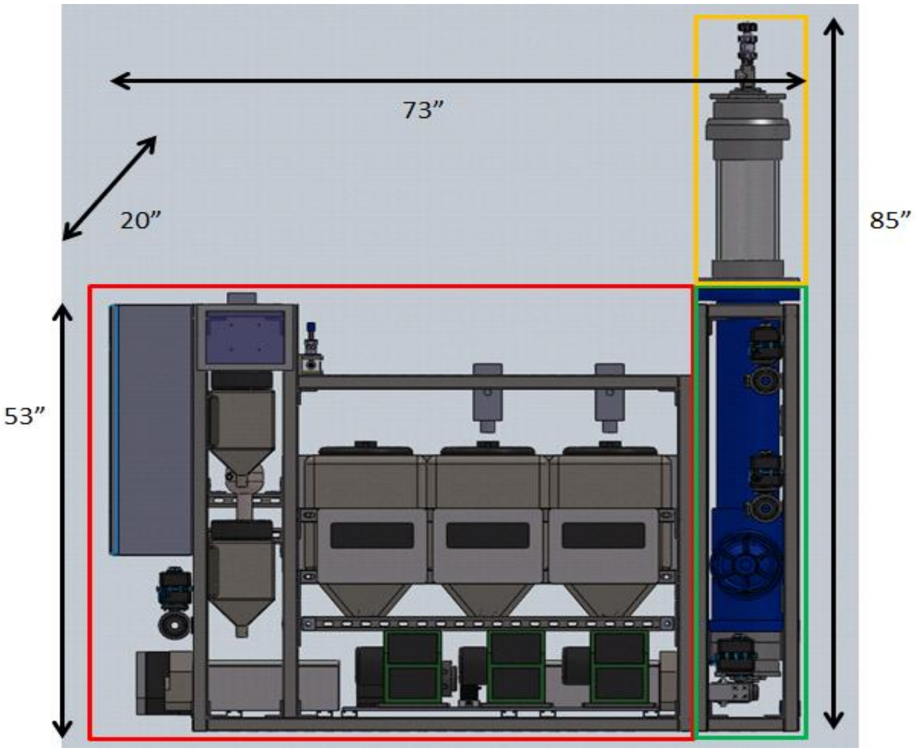


Figure 3-2.3D CAD model of initial CCESP system design with dimensions.

Figure 3-3. Completed CCESP system with labeled major components

Table 3-1. CCESP system components

Designation	Description
T-1	Lime tank with concentrated $Na(OH)_2 \sim 81$ mM
T-2	Mixing tank for chemical softening with lime
T-3	Flocculation tank for calcite crystal growth
T-4	Fresh gypsum seed tank with gypsum seed suspended in saturated gypsum solution (1kg/gal)
P-1	Feed pump
P-2	Fluidized bed inlet pump which draws from the top product of the flocculation tank and fluidizes the vertical seed bed
P-3	Gypsum seed transfer and recirculation pump which draws from the fresh seed tank or the bottom of the fluidized bed depending on the associated valve positions
P-4	Flocculation recycle pump which recirculates the contents of the flocculation tank through an in-line centrifugal separator, removing precipitated solids
P-5	Calcite purge pump which removes accumulated solids from the centrifugal separator
P-6	Lime dosing pump
P-7	Pump for solids clog removal
V-1	2-way actuated feed valve
V-2	3-way actuated seed inlet valve
V-3	3-way actuated seed purge valve
V-4	3-way manual ball valve for gypsum seed pump drawing selection and clog removal after fluidized bed bottom outlet
V-5	3-way manual ball valve for gypsum seed pump drawing selection and clog removal after gypsum seed tank

3.3.1 Alkaline treatment design

Design elements based on alkaline softening in industrial scale crystallizers were employed. Lime dosing occurs under rapid mixing in a small 2.5 gallon polyethylene tank (Plastic-mart, Austin, TX). The mixed product flows by gravity from the mixing tank to a large 10 gallon conical flocculation tank (Plastic-mart, Austin TX). A flocculation period is allowed for calcite nucleation and crystal growth. The flocculation tank employs a custom "sludge blanket", allowing separation of high velocity mixed inlets and calm settling region. **Fig. 3-4** illustrates the design of the flocculation tank. The bottom of the tank is connected to a high throughput centrifugal pump (United Pump PG-8000, City of Industry, CA) which draws the precipitated solids into a centrifugal separator (Lakos ILS-0037) where solids larger than 74 microns are removed from the stream prior to recycling back into the flocculation tank. The clarified top product is drawn into the gypsum seeded fluidized bed by the (P-2) peristaltic pump (Cole-Parmer, Vernon Hills, IL).

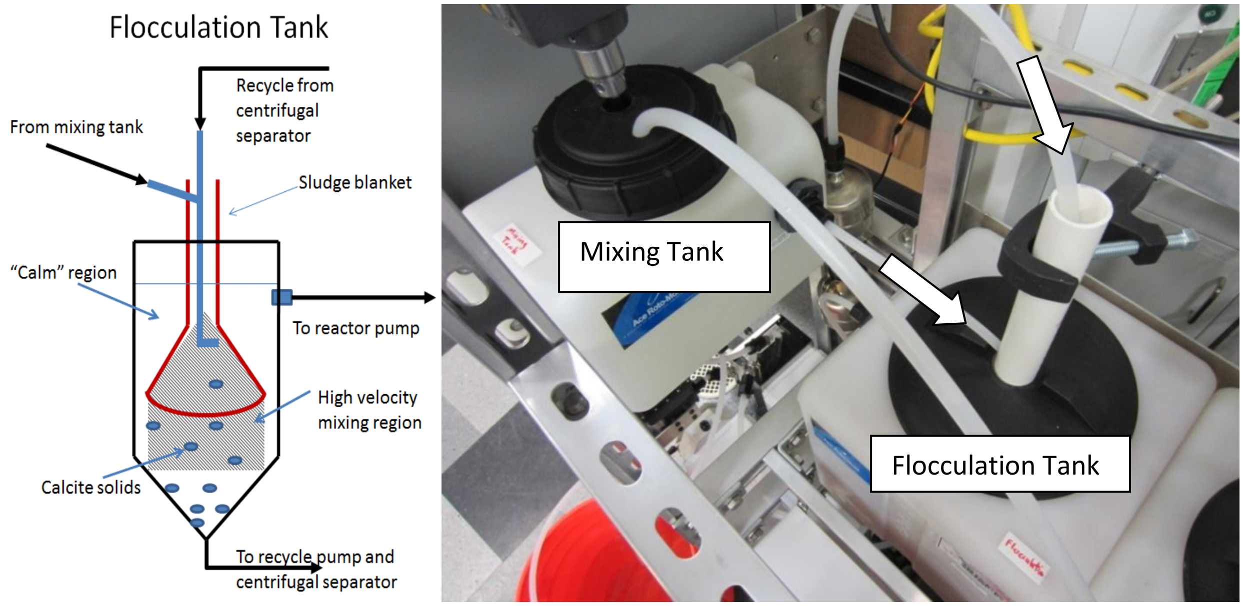


Figure 3-4. Diagram of flocculation tank with sludge blanket (left); Flocculation tank inlets (right).

3.3.2 Fluidized bed design

A 6" inner diameter (ID) Koflo 6-80-4-4-9I static mixer (Koflo Corp., Cary, IL) was used as the main component for the fluidized bed. A clear acrylic 6" ID pipe (McMaster-Carr, Santa Fe Springs, CA) was added as a "polisher" region for additional inlets. The bed stands roughly 8 feet tall and is topped with a Type 591 air release valve (Georg Fischer, UK) and product tube. The side inlet for the fluidizing flow originating from the flocculation tank is located near the bottom of the static mixer. A large peristaltic pump, P-3, (Cole-Parmer, Vernon Hills, IL) draws from the bottom of the static mixer and can recirculate the solids into one of two inlets at the “polisher” region via a set of actuated polypropylene valves (KZCO, Inc., Greenwood, NE). Within the “polisher” region is a ¼” thick polypropylene plate with ¼” holes and polyethylene mesh to distribute the flow from the static mixer and prevent channeling.

3.3.3 Sensor block design

A centralized sensor block was designed to house the sensors required for stream analysis. A clear acrylic block was machined to form a single flow channel with 5 sensor ports for the calcium ion probe, calcium ion reference, pH, pH reference, and temperature probes, as seen in **Fig 3-5.** The flow channel is connected to a set of actuated solenoid Type 0124 valves (BürkertVewaltung GmbH, Ingelfingen, Germany) and peristaltic metering pump (P-7) (Stenner Pump Company, Jacksonville, FL) which can retrieve in-line samples from various sampling points in the system.

Figure 3-5. Sensor block (left) connected to Orion VERSA Star meter (right)

3.3.4 Control software design

Equipment on the system are controlled via National Instruments cRIO controller connected to a dedicated PC. Software for the system was developed in National Instruments LabVIEW. A screenshot of the controlling software is shown in **Fig. 3-6**. Live pH and calcium ion data were acquired in .csv files using Star Com (Thermo Scientific, Waltham, MA).

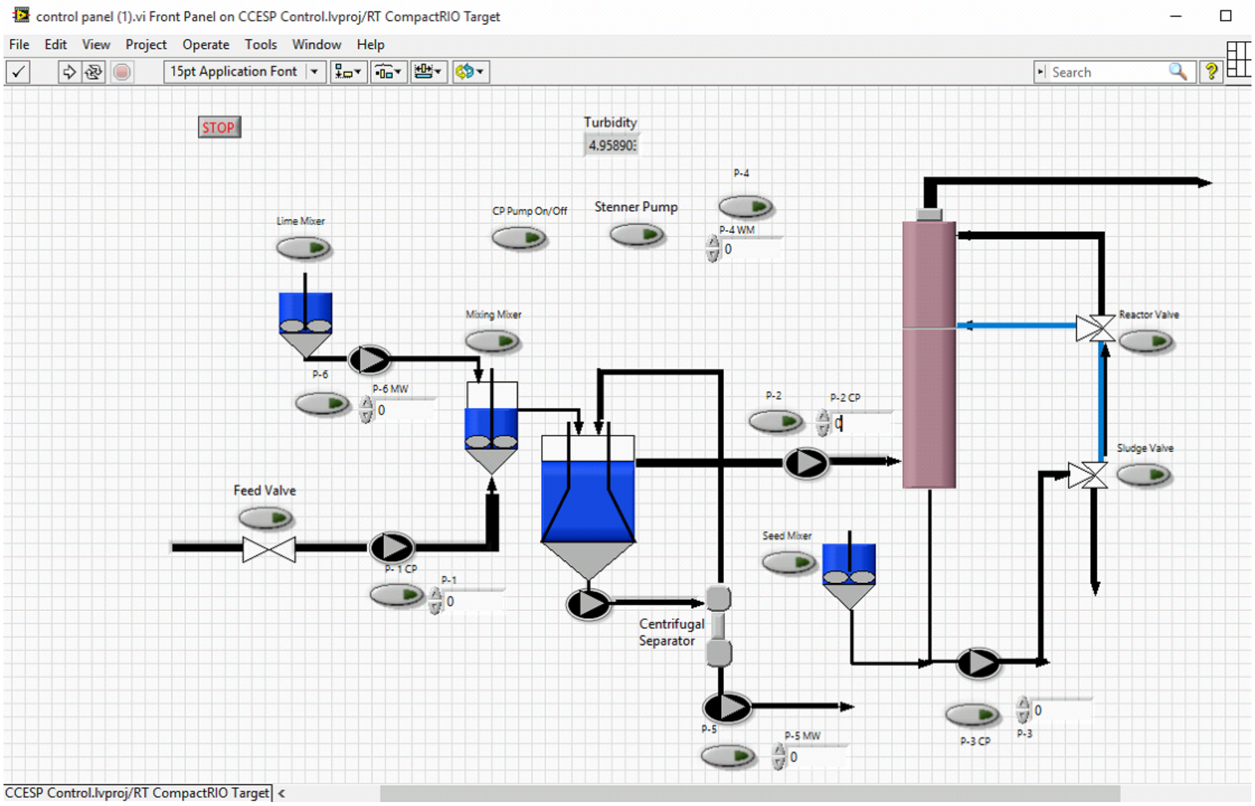


Figure 3-6. National Instruments LabVIEW custom software for CCESP system control based on process flow diagram; component designations are listed in detail in Table 3-1.

3.4 Analytical methods

The course of precipitation was followed via pH and calcium ion activity measurements. A calcium ion selective electrode (ISE25Ca-9) with a double junction reference electrode (REF251), a glass pH electrode (pHG211-8) with a single junction reference electrode (REF201), and a temperature probe were obtained from Radiometer Analytical (Lyon, France). The electrodes were connected to Orion VERSA STAR (Thermo Scientific, Waltham, MA) ion selective meters. Software was used (Orion Star Com, Thermo Scientific, Waltham, MA) to allow PC interfacing of ion selective meters and thus real-time data acquisition of calcium ion activity, pH, and temperature. The calcium ion selective electrode, as detailed in the Appendix, was calibrated using calibration solutions that mimic the composition of San Joaquin Valley agricultural drainage water.

PAA concentration in grab samples were measured via analysis of Total Organic Carbon (TOC) content, following US EPA Method 415.1 with an O·I·Analytical Aurora Model 1030 Total Organic Carbon Analyzer (College Station, TX).

Conductivity of salt for determining residence time distribution was measured using Oaklon CON 6+ Meter from McMaster-Carr (Santa Fe Springs, CA) which has a resolution from 0.01 µS to 200.0 mS.

3.4.1 Agricultural drainage concentrate model solutions

A synthetic RO-treated agricultural drainage concentrate was utilized as the RO concentrate feed water for the current study. The constituents of the Model RO concentrate solution are shown in **Table 3-2**.

Table 3-2. Composition and properties of model RO concentrate simulating 63% recovery of high-mineral brackish water[(a)]

Salt	Value	Units
$CaCl_2$	30.7	mM
Na_2SO_4	145.4	mM
$MgSO_4$	31.2	mM
$NaHCO_3$	11.4	mM
NaCl	20.3	mM
pH	7.8	
Gypsum SI	2.5	

(a) Brackish water composition based on data provided in [8].

3.4.2 Gypsum seed selection

In the current study, the precipitation kinetics for various gypsum seeds were tested. Specifically, industrial sources for gypsum were targeted for their economic value and larger seed size. **Table 3-3** summarizes the sources for the gypsum seeds and their cost. Calcium activity was measured by adding gypsum to a solution of Model RO concentrate and measuring the free calcium ion activity using calcium ion selective electrode (ISE25Ca-9)with a double junction reference electrode (REF251) (Radiometer Analytical, Lyon, France).

Table 3-3. Gypsum seed sources, size, and cost utilized in the current study.

Gypsum	Manufacturer	Purity	Particle Size (μm)	Price ($/kg)
1	J.T. Baker (Center Valley, PA)	>98%	42	220
2	Sigma-Aldrich (St. Louis, MO)	98%	19	150
3	USA Gypsum (Denver, PA)	~86%	317	0.30
4	USA Gypsum (Denver, PA)	~90%	117	0.30
5	USG (Chicago, IL)	98%	20	0.36

3.4.3 Hydrodynamic Characterization

The ability of the CCESP to operate was first qualified using city tap water. Equipment were calibrated manually with graduated cylinders. The residence time in each stage of the system is important to ensure adequate reaction and precipitation time. The residence time can be found by dosing a highly concentrated tracer and measuring the tracer response from the outlet. NaCl was used as the tracer and the concentration could be measured by correlation to conductivity using an Oakton CON 6+ Meter (Oakton Instruments, Vernon Hills, IL) which has resolution from 0.01 μS up to 200.0 mS.

3.4.4 Lime-dosing

The alkaline chemical softening step of CCESP was studied to determine the feasibility of steady-state operation. The solution pH was monitored via pH probes located after the flocculation tank. A simplified feed solution for lime softening experiments, shown in **Table 3-4** was used to decrease preparation time.

Table 3-4. Simplified Model RO concentrate solution[(a)] for lime softening experiments

Salt	Value	Units
$CaCl_2$	30.7	mM
$NaHCO_3$	11.4	mM
pH	7.8	
Calcite SI	20	

(a)Model solution without sulfate to avoid gypsum precipitation. Calcite SI is a factor of 20 above the brackish water feed solution

First, batch titrations were performed to correlate pH to lime concentration. Various concentrations of lime were selected for continuous operations measuring steady state pH response. Experiments were carried out in 1-L rectangular jars with square mixing paddle. After determining the corresponding lime dose with a pH response near pH 9.0, experiments using the CCESP system were carried out. pH was measured and grab samples were taken for TOC analysis.

3.4.5 Antiscalant Removal

Antiscalant removal was quantified by measuring TOC O·I·Analytical Aurora Model 1030 Total Organic Carbon Analyzer (College Station, TX). First, batch experiments were performed by taking 50 mL samples at various times after lime addition. For CCESP system experiments, grab samples from the flocculation clarified product were collected at various times after lime addition. A calibration curve was created relating TOC counts to concentration of Flocon 260 antiscalant. Detailed calibration and experimental procedures can be found in the Appendix.

3.4.6 Hydrodynamics of Fluidized Bed Crystallizer

The operational range of the peristaltic pump which recirculates the gypsum seed (P-3) was found by observing the flow characteristics of the seeded reactor. A minimum flow rate was found by sequentially decreasing the flow rate until clogging occurred. The minimum flow rate served as a baseline for the operational limits of the process and equipment. The maximum allowable flow rate was found by increasing the bed incipient fluidization was exceeded to the point where the seeds were carried out from the column (i.e. the top of the reactor).

The convective residence time of the bed reactor was determined by pumping a 100 – 150 mL pulse of saturated NaCl (>1.7 Molar) to a saturated gypsum stream ($SI_g \sim 1.1$). The Oaklon CON 6+ conductivity meter was used to measure the response at the bed outlet over time. The probe electrode was placed in a small 50 mL beaker with tubing connected to the top of the fluidized bed reactor. The product effluent from the fluidized bed reactor flowed into the beaker at 0.1 gpm set by the feed pump (P-2).

3.4.7 Gypsum seeded desupersaturation

A salt solution supersaturated with respect to gypsum was dosed into the fluidized bed to measure the desalting ability of the bed. The salt solution (SIg = 2.88), listed in **Table 3-5**, contained $CaCl_2$ (30.7 mM), $NaSO_4$ (145.4 mM), $MgSO_4$ (31.2 mM), NaCl (20.3 mM) dissolved in deionized water. The bed product stream was monitored online using a calcium ion probe. The calcium ion activity was correlated with the saturation index value (SIg) to determine the level of gypsum saturation in the stream.

Table 3-5. Simplified Model RO concentrate solution$^{(a)}$ for fluidized bed desalting experiments

Salt	Value	Units
$CaCl_2$	30.7	mM
Na_2SO_4	145.4	mM
$MgSO_4$	31.2	mM
NaCl	20.3	mM
pH	7.8	
Gypsum SI	2.88	

(a) Model solution without carbonate to avoid competing precipitation of calcium carbonate, $CaCO_3$, with gypsum, $CaSO_4{\cdot}H_2O$

3.4.8 Continuous chemically enhanced seeded precipitation

Using the model RO concentrate solution detailed in **Table 3-1**, lime softening followed by gypsum seeded precipitation. A complete bypass via a diverting line prior to the fluidized bed inlet was utilized for observing the lime treatment pH and calcium ion response prior to addition to the gypsum seeded bed. Flocculation tank clarified product was directly pumped through the sensor block during the bypass period. Grab samples were collected for TOC analysis for antiscalant removal. Afterward, the flocculation tank product bypass was closed (i.e. fluidized bed inlet reconnected to process pump, P-2) and the clarified product was pumped through the gypsum seeded fluidized bed reactor. The pH and calcium activity response from the fluidized bed product were monitored by allowing the top product from the fluidized bed to flow through the sensor block.

Chapter 4

4. Results and Discussion

This chapter details operational modes of the CCESP system (**§4.1**), analysis of the residence time and hydrodynamics of various functional sections of the system (**§4.2**). The gypsum seed selection and gypsum bed characteristics are discussed in **Sections 4.3-4.5**, followed by the results of alkaline chemical softening and antiscalant scavenging (**§4.6**). Subsequently, the results for the complete CCESP process are discussed in **Section 4.7**.

4.1 CCESP Modes of operation

The continuous chemically seeded precipitation (CCESP) system was designed with the capability for continuous operation, as well as batch and semi-batch operation for alkaline softening due to modes of operation for purging and recirculation. A continuous operation is a single pass through the lime softening flocculation process followed by seeded precipitation in the vertical fluidized bed as shown by the blue highlighted flows in **Fig. 4-1**.

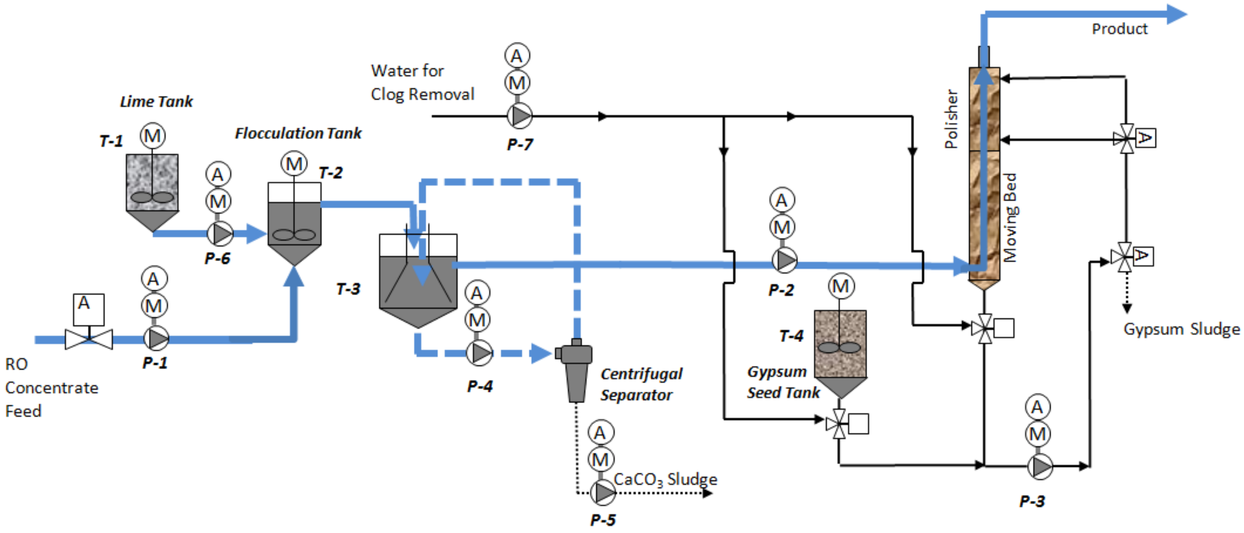


Figure 4-1. Single pass continuous operation with flows highlighted. The blue dotted line represents the recirculation in the lime softening section which removes particles >75 micron via the centrifugal separator.

As precipitation occurs in the lime softening flocculation tank, a purge valve and pump may be accessed to remove calcite-antiscalant solid matrix as shown in **Fig. 4-2.**

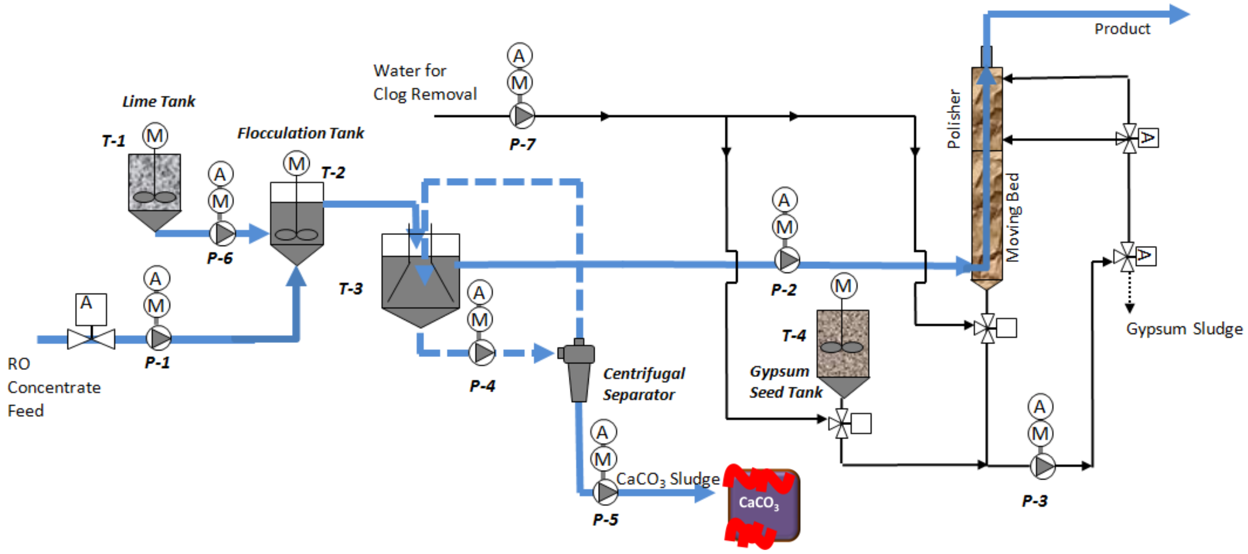


Figure 4-2. Calcite-antiscalant matrix solids purge by activating the centrifugal separator solids purge pump, P-5, during continuous operation

Crystal growth stagnation will decrease the precipitation kinetics of the gypsum seeds in the fluidized bed. After stagnation, fresh gypsum seed is desired to return the effectiveness of the seeded precipitation. A method to purge spent seeds from the fluidized bed is shown in **Fig. 4-3.** In order to replenish seeds, a valve below the gypsum seed tank (T-4) is opened and the stream is pumped into the fluidized bed through one of two inlets as shown in **Fig. 4-4.**

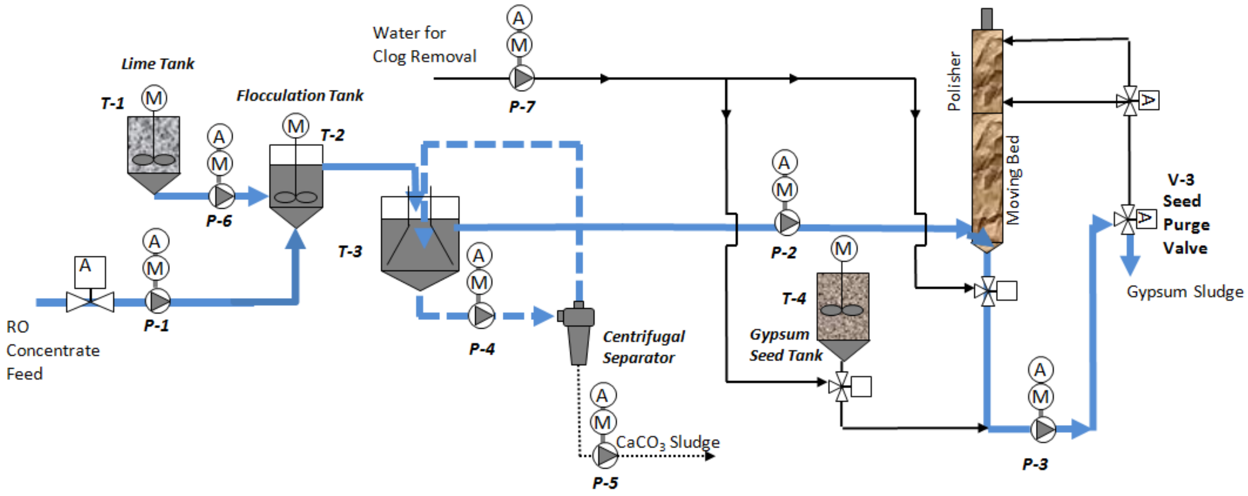


Figure 4-3. Mode for spent gypsum seed purge; The purge valve (V-3) is opened and the gypsum seed recirculation pump (P-3) draws from the bottom of the bed to the drain.

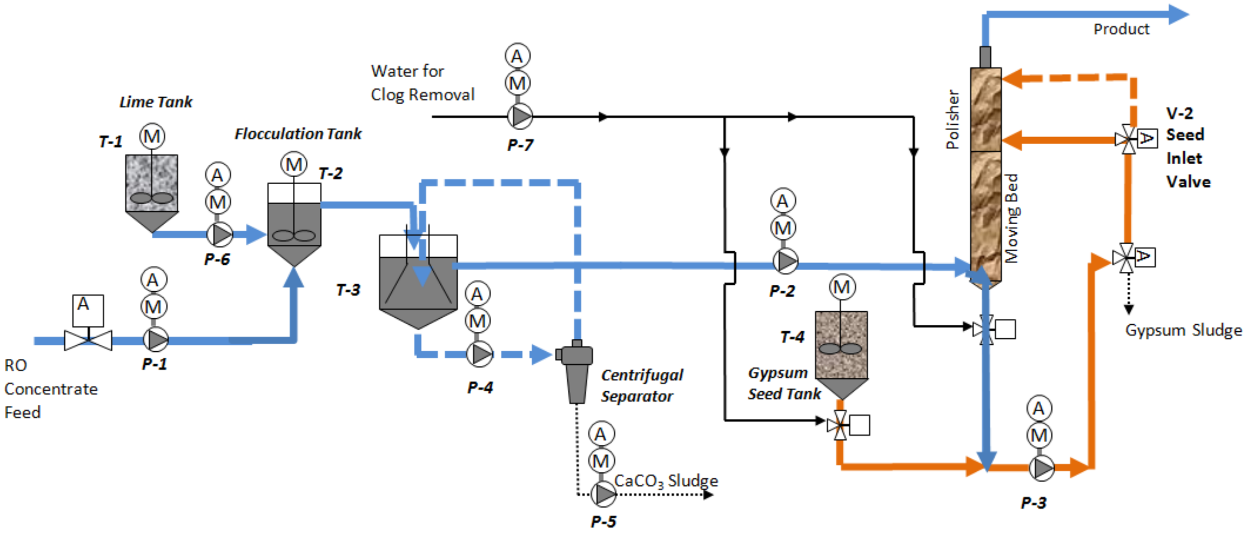


Figure 4-4. Mode for introduction of fresh gypsum seeds through two possible inlets (selected by actuating the seed inlet valve, V-2). Lines for seed introduction of new seeds are highlighted in orange.

At locations where flow rate may be constricted (i.e. turns, points of low elevation), gypsum seed settling occurs, which lead to the formation of clogs. A deionized water feed for dissolving gypsum was designed to flush locations where gypsum seed settling may accumulate into a clog (e.g. below the fluidized bed and below the gypsum seed tank), which has aided machine performance during startup and other low flow applications. A three way valve enables the water flush to effectively dissolve clogs between the tank and reactor outlets and the seed recirculation pump, P-3 as shown in **Fig. 4-5**.

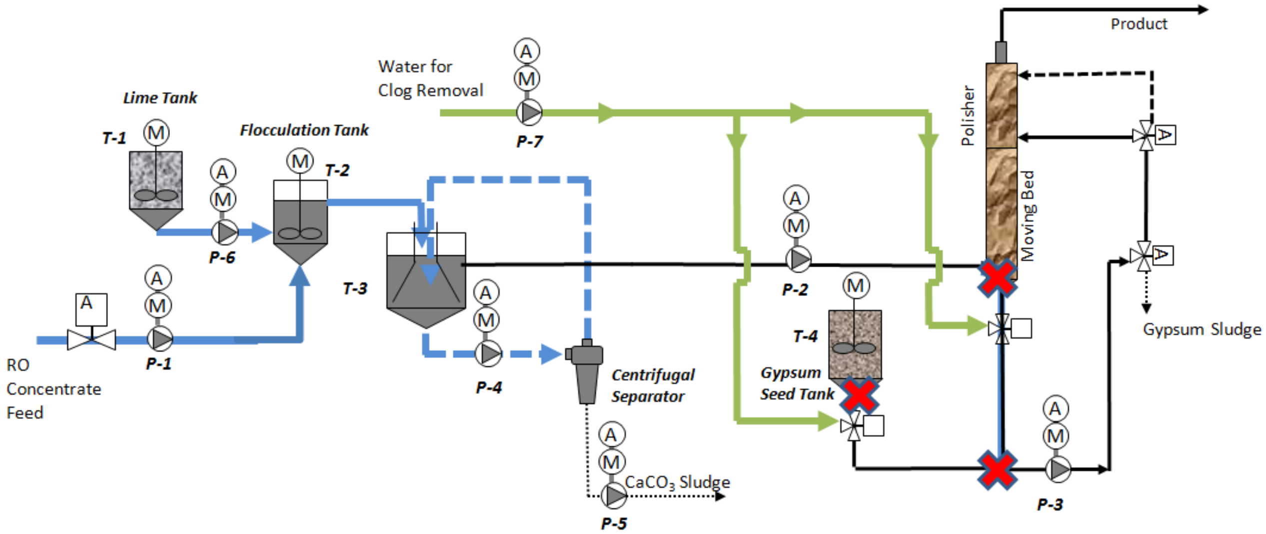


Figure 4-5. Deionized water is pumped from P-7 through the manual three way valves located directly below the gypsum seed tank and fluidized bed. Red X's represent areas where clogs have been observed (e.g. at the tank outlet, at the fluidized bed bottom outlet, and at the intersection of the solids recycle line). Clogs were cleared as needed via water steams (highlighted by the green lines) directed to the clogged areas.

4.2 Residence time characterization

The time allowed for the precipitation process to occur, which is essentially the hydraulic residence time, is critical in determining the efficiency of the overall CCESP process. For continuous processes, the ideal residence time, τ, is defined as V, volume of the system, divided by the flow rate, q. The actual residence time, however, is generally longer due to non-ideal mixing in various portions of the system.

The hydraulic residence time was determined for each section of the system using a pulse of a highly concentrated NaCl solution (>1.7 M). A pulse of 100 mL of the concentrated NaCl solution was pumped into the flocculation tank via the feed pump (P-1). Immediately after the volume was added, the inflow (i.e. to feed tank) to the pump was reconnected and operated normally (i.e., pump was started within one minute after contents of the tracer solution were introduced to the system). For the fluidized bed, a pulse of 150 mL of the concentrated NaCl solution was pumped via the fluidized bed inlet pump (P-2). After drawing the tracer solution, the fluidized inlet pump (P-2) was reconnected to the flocculation tank (T-3) and operated normally. Operating at 0.1 gpm, the mean residence time, τ, or the time at which 50% of the material has passed the system, of the lime softening section (i.e., P-1 to P-2) and the gypsum seeded bed (i.e., P-2 to bed top outlet) were found to be 52.37 minutes, and 55.45 minutes, respectively. The convective residence time distribution (RTD) for each section can be seen in **Fig. 4-6** and **Fig. 4-7**.

In previous batch CESP studies, 10 minutes reaction time after lime addition was found to be sufficient for the removal of up to 77% of the residual antiscalants (from the previous RO desalination step), up to 84% removal after 30 minutes [8]. Lime treatment was followed by addition of 10 g/L gypsum seeds for gypsum seeded precipitation (GSP). GSP was allowed for 60 minutes to desupersaturate the solution from SIg of 2.5 to levels slightly above saturation (SIg ~ 1.1) [8].

It is noted that in batch CESP, the convective residence time for the GSP process is ~ 8% higher than the convective residence time of the fluidized bed section of the current system. To overcome the impact of lower residence time, the gypsum bed can be loaded with higher ratio of seed (240 g/L for CCESP compared to 10 g/L in batch CESP), to increase the potential nucleation sites for gypsum growth, accelerating the desupersaturation process.

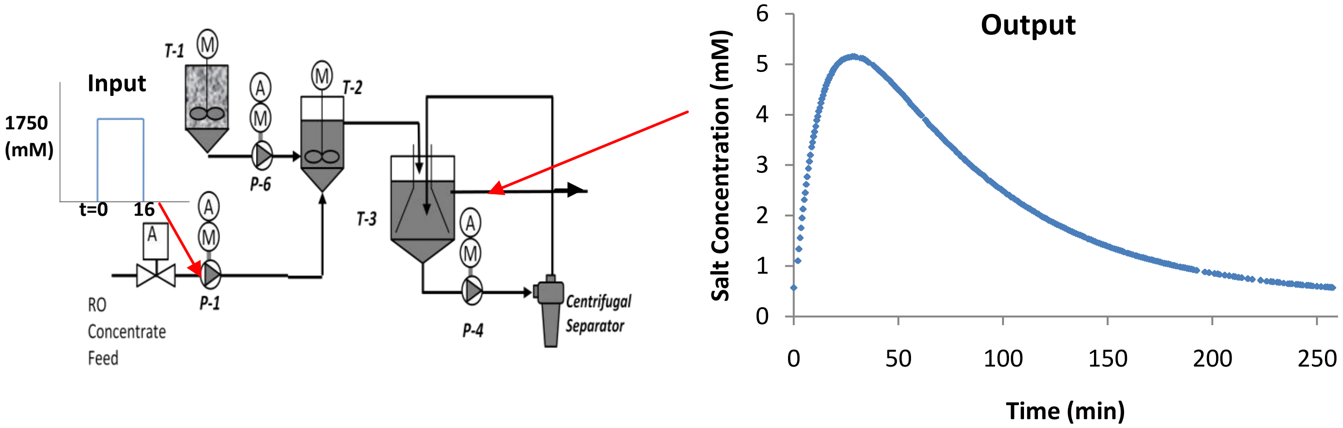


Figure 4-6. Left: Pulse input and measurement locations. Right: RTD of lime-softening section, which includes the feed pump, mixing tank, flocculation tank, recirculation pump, centrifugal separator, and all interconnecting tubing; first observation $t_d = 2$ min. Experimental conditions: square input of 1750 amplitude for 16 seconds directly fed to feed pump, measurement point at flocculation tank side outlet; feed flow rate = 0.1 gpm; 100 mL 1.75 M NaCl solution. Mean residence time: 52.37 min.

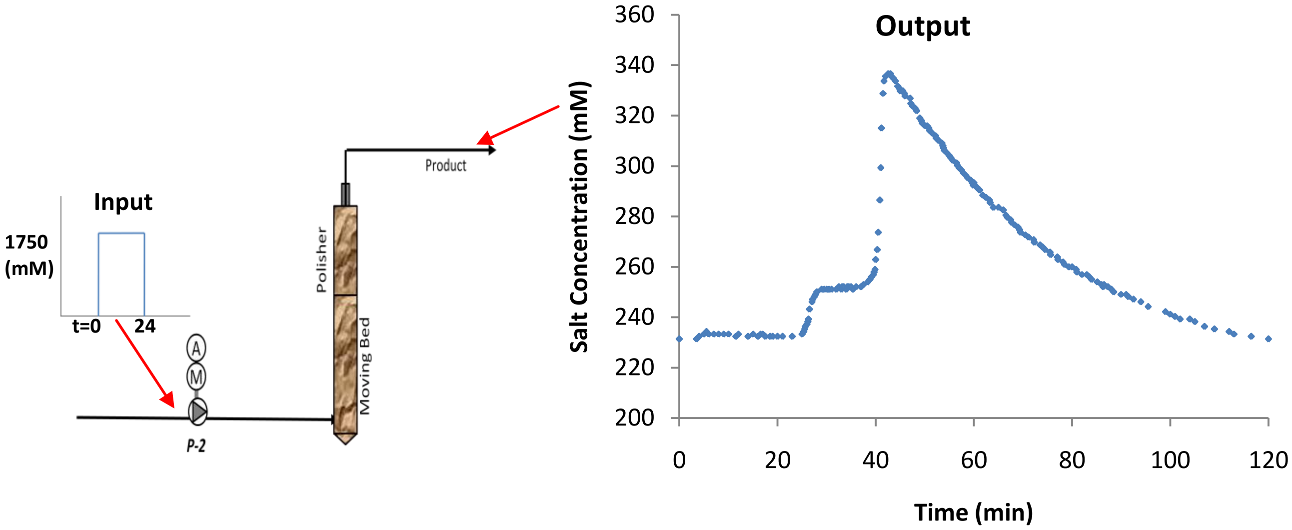


Figure 4-7. Left: Pulse input and measurement locations. Right: RTD of gypsum seed bed with direct injection and no recirculation; first observation $t_d = 25$ min. Experimental conditions: square input of 1750 mM amplitude for 24 seconds; feed flow rate = 0.1 gpm; 150 mL 1.75 M NaCl solution. Mean residence time: 55.45 min.

4.3 Gypsum seed selection

In the current study, the precipitation kinetics for various gypsum seeds were tested. Specifically, industrial sources for gypsum were targeted for their economic value and larger seed size. **Table 3-3** in **Section 3.4.2** and **Fig. 4-8** summarize the various sources of gypsum tested for calcium ion activity during precipitation in a 1-L batch container of Model RO solution. All gypsum seeds enabled about 45% removal of free calcium ion with varying kinetics. Gypsum seeds types 2, 4, and 5 (**Table 3-3**), exhibited the fastest precipitation kinetics as shown in **Fig. 4-8**.

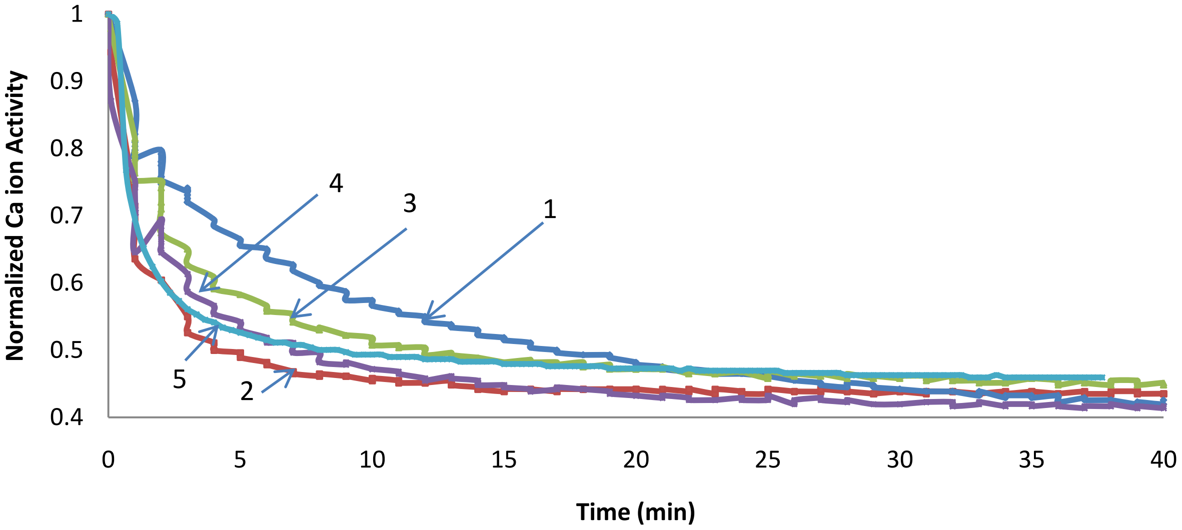


Figure 4-8.Calcium ion activity measurement of five gypsum samples. 1-J.T. Baker, 2-Sigma-Aldrich, 3-USA Gypsum (0.3mm), 4-USA Gypsum (0.1mm), 5-USG. The solution composition was as provided in Table 3-2 with initial gypsum seed loading of 10 g/L.

Gypsum #4 (USA Gypsum 0.1 mm, Denver, PA) and Gypsum #5 (USG, Chicago, IL) were selected for testing system operation, as detailed in **Section 4.4,** due to their rapid precipitation kinetics and economical cost. However, when suspended in water as gypsum slurry, Gypsum #4 exhibited characteristics suggesting the presence of impurities (e.g., high optical opaqueness and foul-odor, **Fig.4-9)**. Impurities also appeared in the USA

Gypsum sample (Gypsum #4) when viewed under optical microscope, shown in **Fig. 4-10.** Subsequent filtrations of the impurities suspended along with Gypsum #4 in saturated gypsum solution using 5 micron cartridge filters were ineffective in removing the impurities. As the effect of the impurities in Gypsum #4 could not be decoupled from the gypsum seed impact on precipitation kinetics, Gypsum #5, USG Terra Alba, was selected for subsequent CCESP operations.

Figure 4-9. Impact of impurities in gypsum on appearance of seed slurry in Gypsum 4, USA Gypsum (left) compared to high-purity Gypsum #5, USG (right)

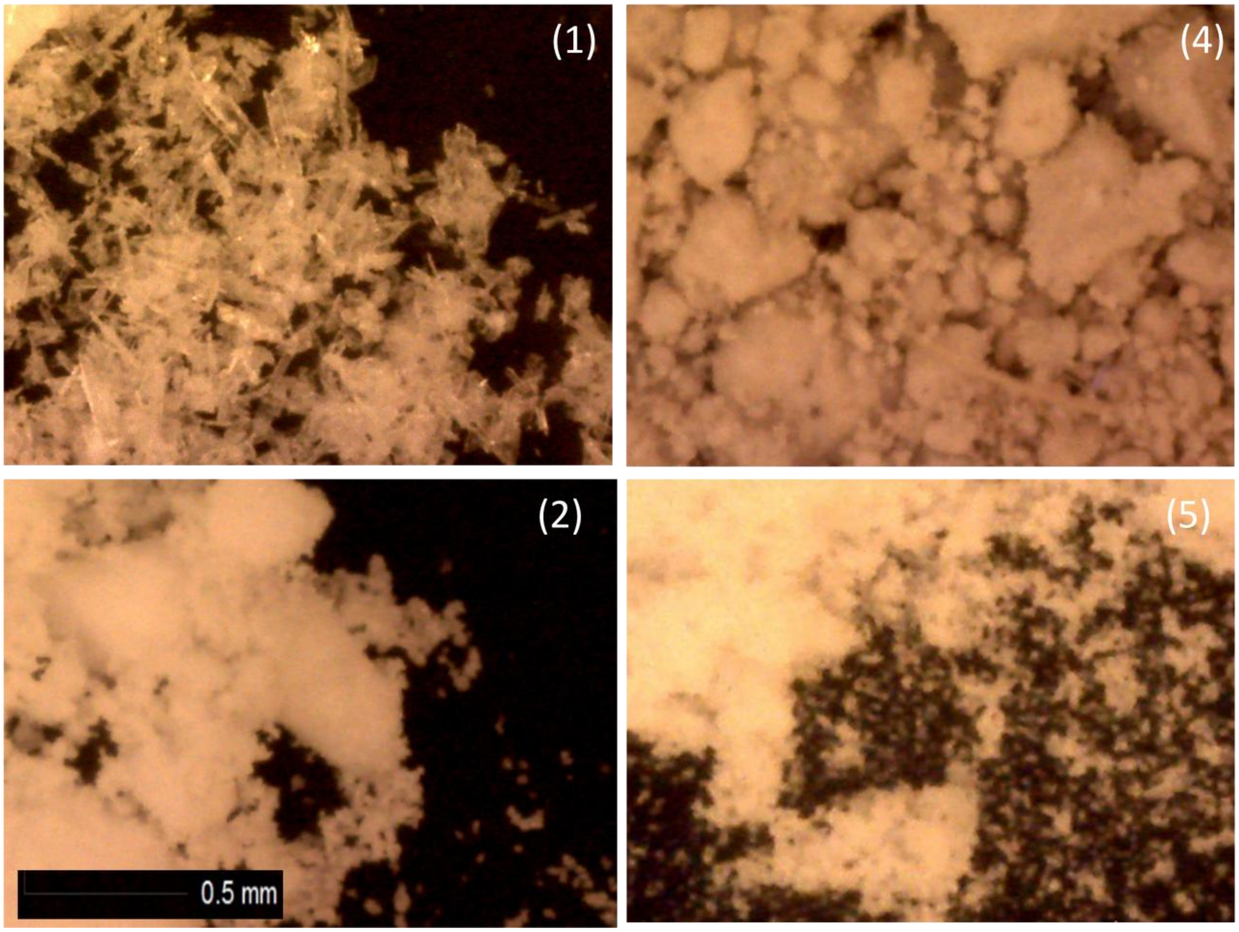


Figure 4-10. Optical microscope images of gypsum; 1 – J.T. Baker, 2 – Sigma Aldrich, 4 – USA Gypsum (0.1 mm), 5 – USG Terra Alba

4.4 Gypsum seeded fluidized bed hydrodynamics

The hydrodynamics of the gypsum seeded fluidized bed were investigated in order to determine the operational range of the seeded precipitation process. The pump's ability to process and transport gypsum seeds was assessed as the limiting factor for a given gypsum seed concentration. It was determined that 10 kg gypsum seeds in saturated gypsum solution described in **Section 3.4.7** was the limit of the pump to operate without physical clogging, 24 times the concentration used in batch experiments. Higher volume fraction for gypsum seeds corresponded to increased number of sites for gypsum crystal growth, and therefore, more rapid precipitation kinetics.

The effect of the flow rate (controlled by feed pump, P-1) on the settling of seed particles in the fluidized bed was observed through the clear acrylic "polisher" region of the fluidized bed. The bed height, which is the level at which a solid-liquid interface can be observed, can be manipulated using the fluidizing pump, or fluidized bed inlet pump, (P-2) and the gypsum seed recirculation pump (P-3). Increasing the flow rate from the fluidizing pump (P-2) will cause the bed height to rise. Turbulence is observed when both recirculation (P-2) and fluidizing pumps (P-3) are operating, resulting in persistent resuspended particles and increasing bed height, as shown in **Fig. 4-11** and **Fig. 4-12**. Once the suspended solids top interface is at a height near the top of the precipitation reactor, if the fluidizing inlet flow rate ceases, the solids will sediment at various recirculating flow rates. As the recirculating flow rate increases, settling rate also increases as shown in **Fig.4-13**.

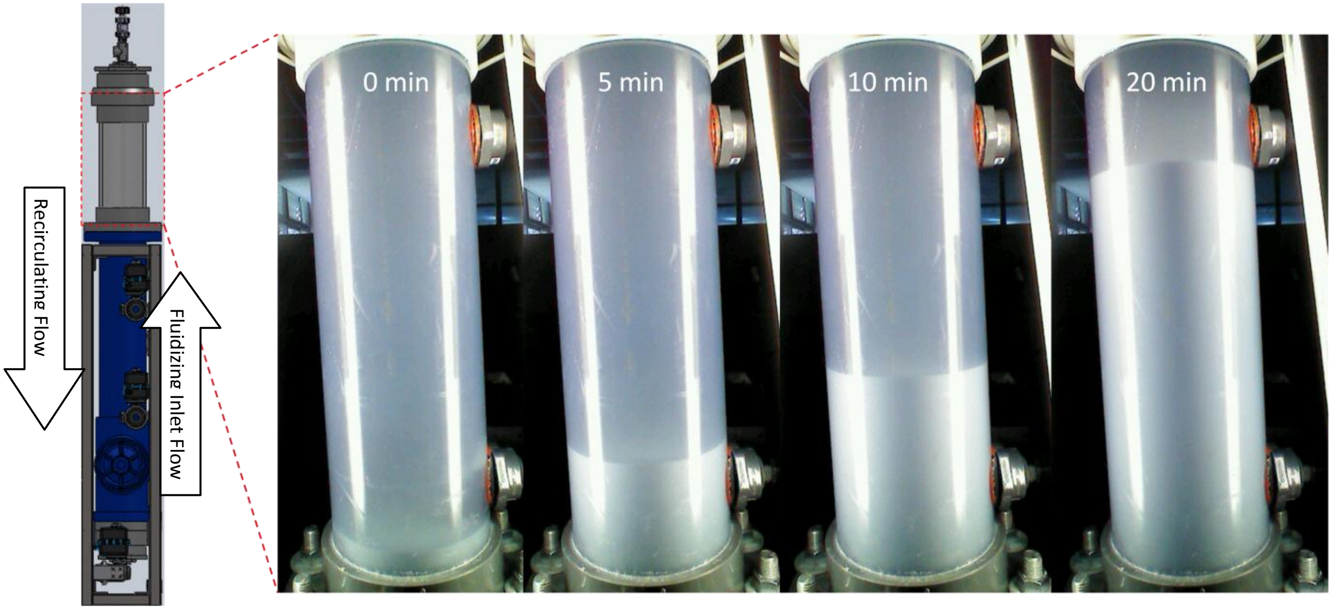


Figure 4-11. Unsteady state fluidized bed clear "polisher" region. Experiment conditions: Recirculating flow rate (P-3): 1 gpm; fluidizing inlet flow rate (P-2): 0.18 gpm; 240 g/L USG Terra-Alba gypsum. Height of the clear polished region is approximately 19 inches. The feed solution to the CCESP system is detailed in Table 3-5.

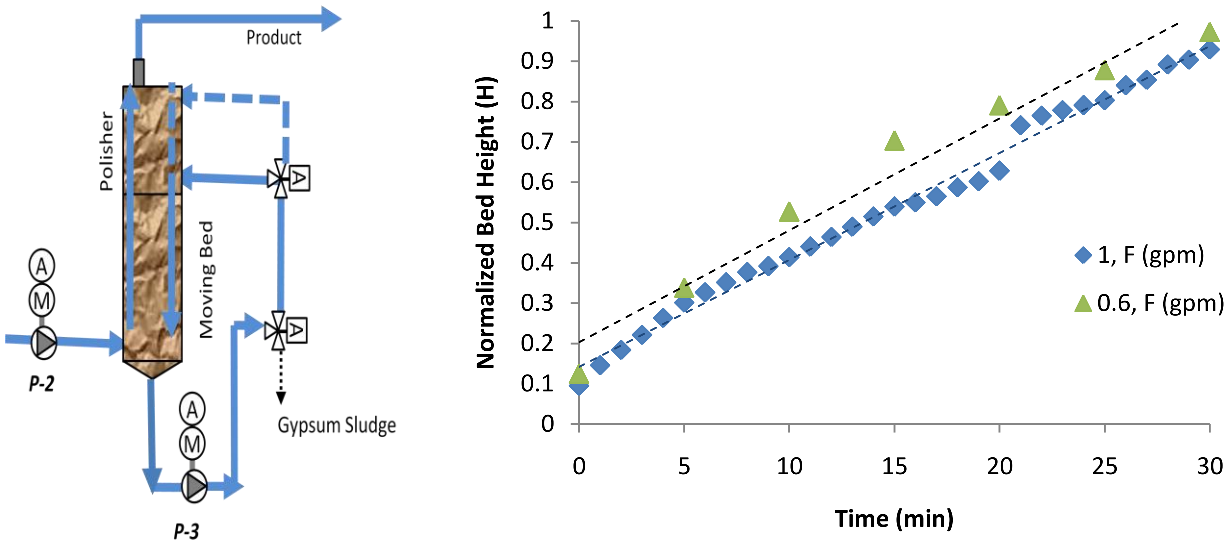


Figure 4-12. Bed height function while fluidizing and recirculating flows are occurring, where F is the fluidizing flow rate. F is held constant at 0.18 gpm at different recirculating flow rates. $H = h/h_0$, where h is the recorded height of the bed and h_0 is the height of the polisher region, 18.9 inches. The feed solution to the CCESP system is detailed in Table 3-5.

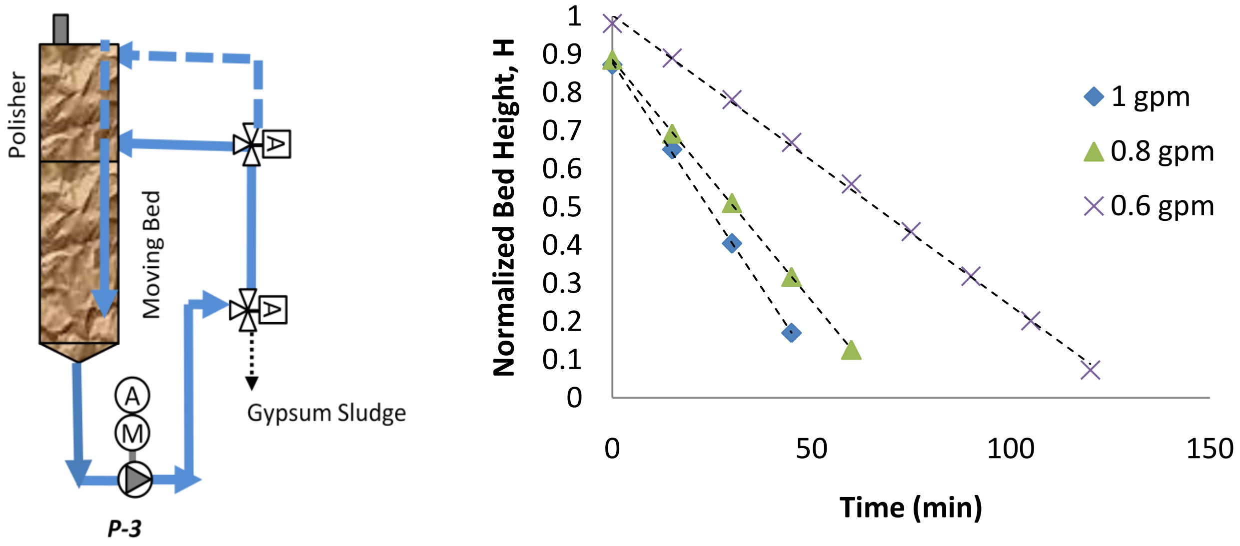


Figure 4-13. Unsteady state bed height during single flow, recirculating operation. Bed height brought to steady state at non-zero height and the response to 1, 0.8, and 0.6 gpm recirculating flow rate was recorded. $H = h/h_0$, where h is the recorded height of the bed and h_0 is the height of the polisher region, 18.9 inches. The feed solution to the CCESP system is detailed in Table 3-5.

In order to determine the feasible operational range for the fluidized bed, various inlet fluidizing flow rates were evaluated with respect to the resulting bed height. As shown in **Fig. 4-14** the fluidizing bed height varied linearly over the range of feasible inlet feed pump flow rate. Stable bed heights could only be sustained at low inlet flow rates between 0.026-0.25 gpm. As the flow rate increases above the incipient fluidization limit, seed crystals are carried out of the bed with the product stream. Therefore, one has to operate below the incipient fluidization flow rate. Operation of the fluidized bed with recycle (i.e., particle recirculation) increased mixing within the fluidized bed, re-suspending the mineral salt particles and this resulted in expansion of the fluidized bed. As a consequence, new gypsum seed may not be introduced while the system is operating continuously. In the above case, intermittent introduction of fresh seed and seed recirculation or purging may be necessary to maintain gypsum seed mass and precipitation rate.

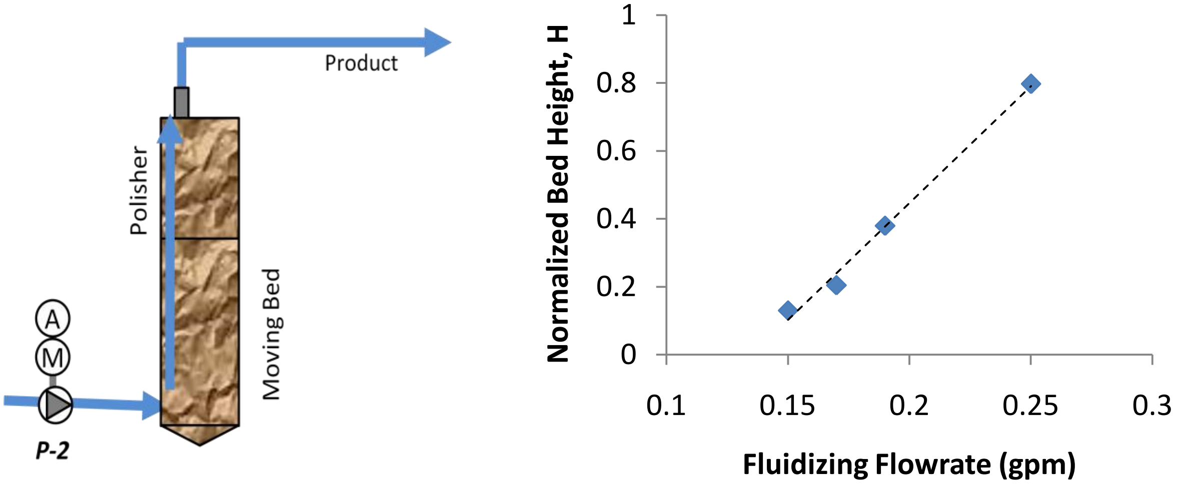


Figure 4-14. Steady state bed height within the polisher region at various fluidizing flow rates, recirculating flow rate is 0. $H = h/h_0$, where h is the recorded height of the bed and h_0 is the height of the polisher region, 18.9 inches. The feed solution to the CCESP system is detailed in Table 3-5.

4.5 Gypsum seeded desupersaturation

The effectiveness of the fluidized column for gypsum desupersaturation was examined by measuring the calcium ion activity of the product stream. Starting with a feed supersaturated with respect to gypsum (SIg 2.88), the fluidized bed was able to reduce the gypsum saturation index to 1.3 as shown in **Fig. 4-15**.

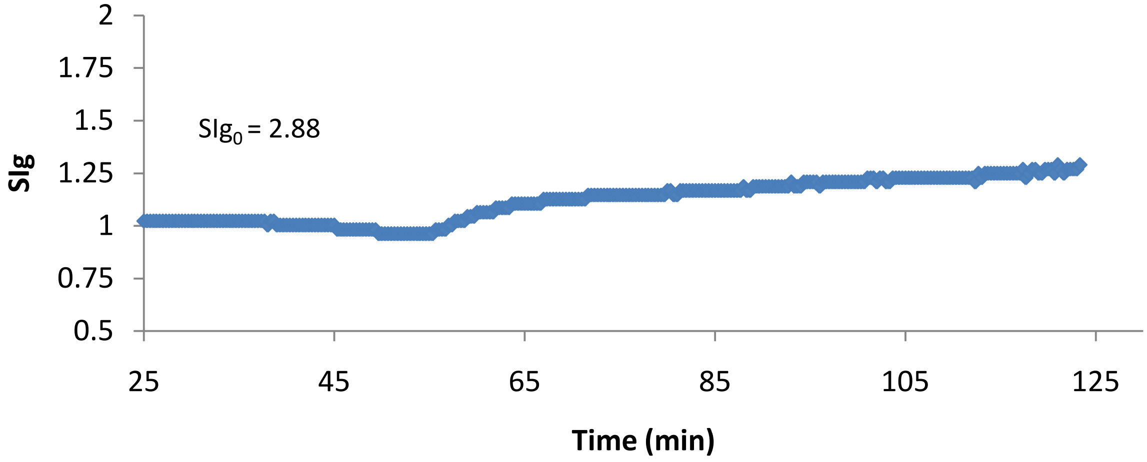


Figure 4-15. Gypsum seeded desupersaturation from Sig_0 2.88 at t = 0 to Sig = 1.3. t_d = 25min; Flow rate is 0.1 gpm. The feed solution to the CCESP system is detailed in Table 3-5.

4.6 Antiscalant removal via continuous lime softening

Antiscalants that are added to the RO feed increase the stability of supersaturated solutions, limiting precipitation and scaling of the RO membranes. However, the presence of antiscalants in the primary RO concentrate inhibits gypsum crystal growth and thus retards the progress toward desupersaturation of the solution with respect to this mineral scalant [7-8]. In order to combat the negative impact of residual antiscalants in the primary RO concentrate, partial lime softening can be used so as to remove the residual antiscalant from the primary RO concentrate [8]. It should be recognized that conventional alkaline softening requires stoichiometric amounts of alkaline chemical in order to precipitate calcite. Thus, only partial softening is used primarily for antiscalants removal prior to the subsequent step of seeded gypsum precipitation in the fluidized bed reactor.

Assessment of the lime step of the CCESP process was carried out through a series of experiments with model RO concentrate prepared at a composition of 11.4 mM sodium bicarbonate and 30.7 mM calcium chloride. Stream Analyzer 3.1 (OLI Systems, Morris Plains, NJ) thermodynamic software was used to determine the lime dose correlation to pH. Several lime dose concentrations were tested in continuous softening experiments (**Fig. 4-16).** The results demonstrate a sharp transition to higher pH at lime dose of about 10 mM, which is indicative of the lime neutralizing the bicarbonate and forming calcite at stoichiometric amounts. Partial lime softening at lower pH (i.e., pH 9) was shown to be effective in inducing calcite precipitation for antiscalant scavenging to enable subsequent gypsum seed precipitation [8].

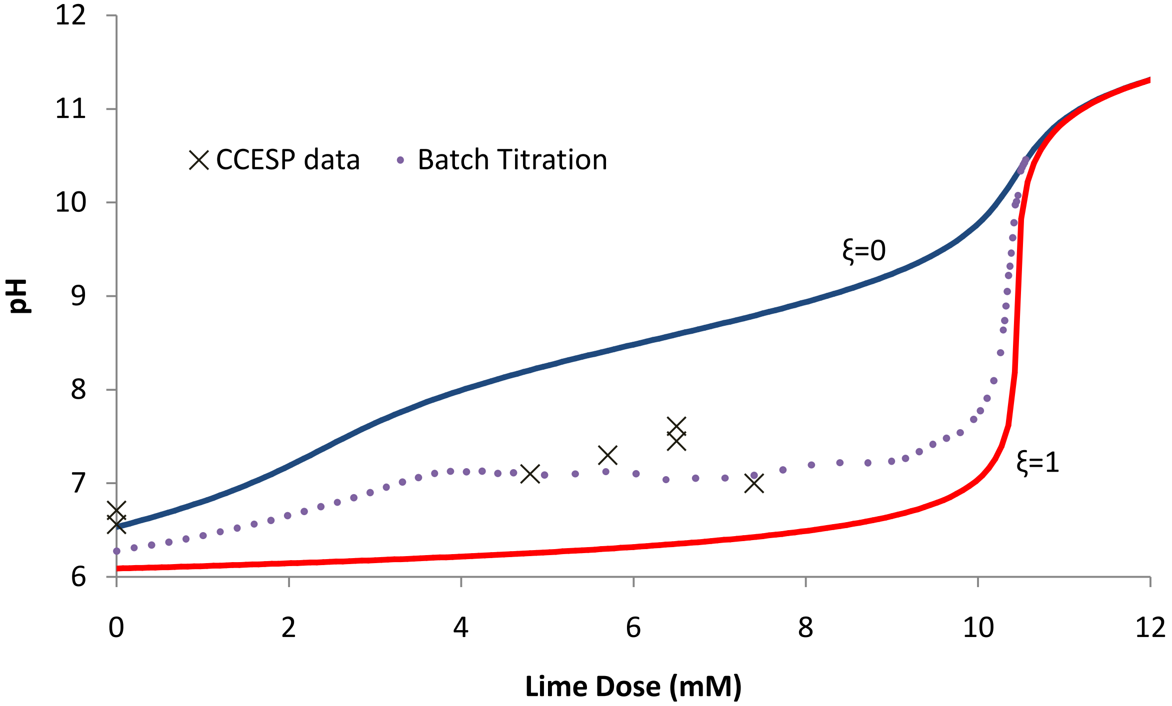


Figure 4-16. Stream Analyzer simulations (solid lines) of the simplified model RO concentrate detailed in Table 3-4 (without antiscalant) where ξ is the extent of precipitation of calcite, where ξ = 0 is for the supersaturated solution prior to precipitation, and ξ = 1 is for the saturated solution after complete precipitation. Experimental results are for steady state batch titrations and CCESP lime softening are overlaid on the graph. CCESP pH was sampled in real time using the sensor block

diagram immediately after the flocculation tank outlet pump, P-2; Simplified model RO solution with no antiscalant detailed in Table 3-4 used throughout.

As expected, experimental results for the continuous CCESP are between the two simulated batch titration curves representing the cases of complete calcite precipitation and no calcite precipitation, indicating that precipitation is taking place in the CCESP process. It is estimated that the extent of reaction for the CCESP process was ξ ~ 0.4 which is what would be expected for initial feed of pH~6.8. For both the batch and CCESP experiments, grab samples for TOC analysis to determine the degree of antiscalant removal. As shown in **Fig. 4-17** and **Fig. 4-18**, antiscalant removal rate was faster in batch relative to CCESP. A removal rate in the batch lime treatment was comparable to previous studies which reported 77% antiscalants removal after 10 minutes, and 84% removal after 20 minutes for a solution of $CaCl_2$ (30.7 mM), Na_2SO_4 (145.4 mM), $MgSO_4$ (31.2 mM), $NaHCO_3$ (11.4 mM), and NaCl (20.3 mM) with addition of 0.6 g/L lime. The lime setup in the CCESP process resulted in significantly lower rate of antiscalants removal reaching 77% removal over a period of 60 minutes.

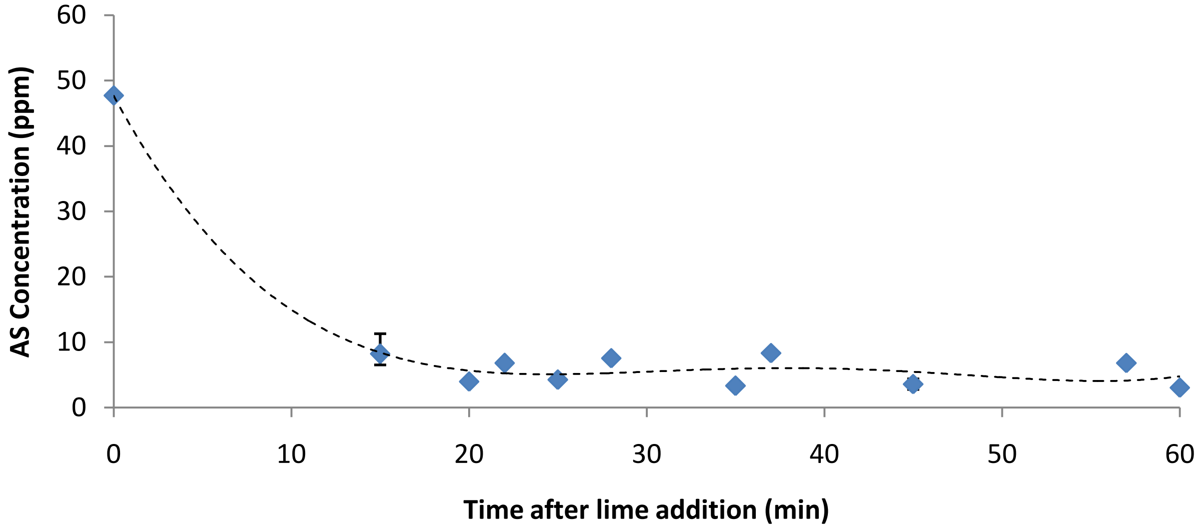


Figure 4-17. Batch CESP antiscalant removal from a solution of the composition provided in Table 3-4 demonstrating 77-87% AS removal after 15 minutes; lime dose: 5.4 mM

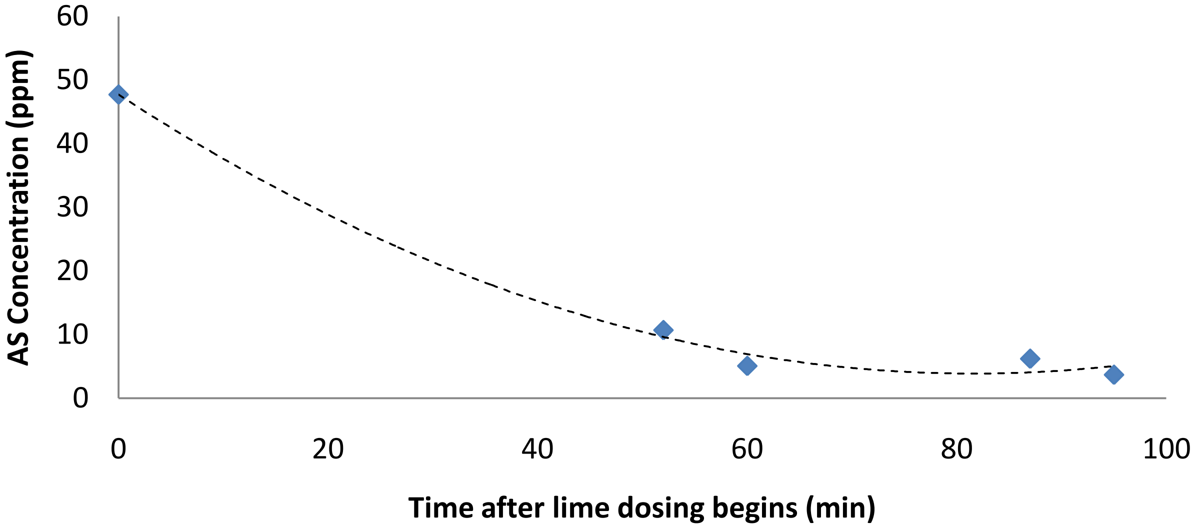


Figure 4-18. CCESP system antiscalant removal from a solution of the composition provided in Table 3-2, achieved with continuous lime dose of 5.75, demonstrating 78% AS removed after 50 minutes.

4.7 Continuous chemically enhanced seeded precipitation

The variation of pH with lime dose was first modeled using Stream Analyzer 3.1 (OLI Systems) to determine feasible lime doses necessary for operation near pH 9 for partial lime softening (**Fig.4-19**).

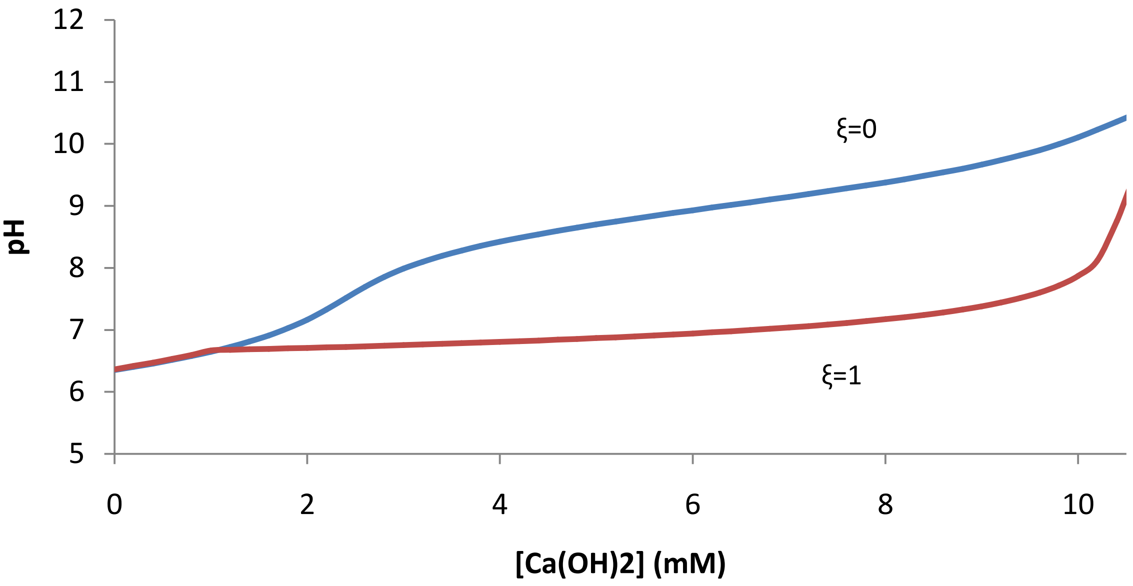


Figure 4-19. Stream Analyzer 3.1 simulation of the pH versus lime dose for model RO concentrate solution with no antiscalants (Table 3-2)

where ξ is the extent of precipitation of calcite, where ξ = 0 is the case of no calcite precipitation, and ξ = 1 indicates complete calcite precipitation. It is noted that in batch CESP experiments conducted by McCool et al., lime dosages were in the range of 3.37-4.72 mM for RO concentrate solution of similar composition (i.e., $CaCl_2$ (30.7 mM), Na_2SO_4 (145.4 mM), $MgSO_4$ (31.2 mM), $NaHCO_3$ (11.4 mM), NaCl (20.3 mM)) [8]. However, based on the simulation results shown in **Fig. 4-19**, 5.75 mM lime was selected for proximity to pH of 9, which shows favorable precipitation kinetics during lime softening. The pH variation with lime dose in the CCESP experiments is shown in **Fig.4-20**. After 70 minutes of startup, real-time measurement of pH were taken along with calculations of SIg at the flocculation tank (T-3) product outlet leading to the fluidized bed inlet pump (P-2). The flocculation tank pH reached steady state after 150 minutes at pH 8.65. SIg decreased from 2.36 in the initial feed to 1.6 after lime softening. Samples were also taken for TOC analysis to determine antiscalant concentration. Antiscalant concentration was reduced from 6.15 ppm to 2 ppm, a 68% decrease, after lime softening.

Once the lime softening section reached steady state, the flocculation product bypass was closed and lime-softened product flowed into the gypsum seeded bed. **Fig. 4-21** shows the pH and SIg from the gypsum bed product after gypsum seeded precipitation. The gypsum seeded bed reactor reduced the lime softened product water from SIg 1.6 to 1. pH also decreased from pH 8.64 to pH 8.5. Steady state was observed after roughly 150 minutes of startup time.

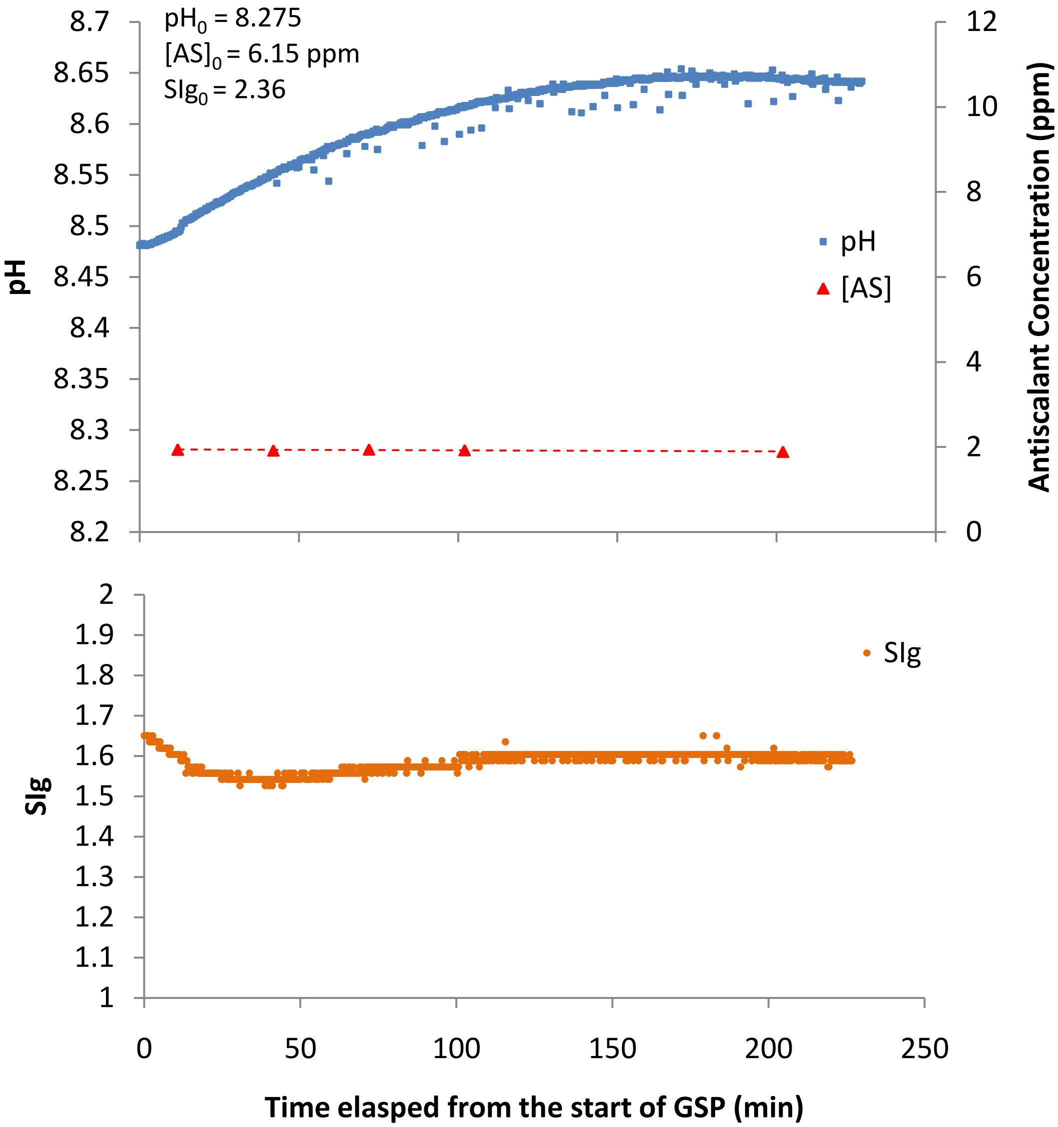


Figure 4-20. CCESP lime softening data: pH, Sig, and antiscalant removal from a solution of the composition reported in Table 3-2 with initial antiscalant concentration of 6.15 ppm. Experimental conditions: 5.75 mM lime, 0.1 gpm overall flow rate.

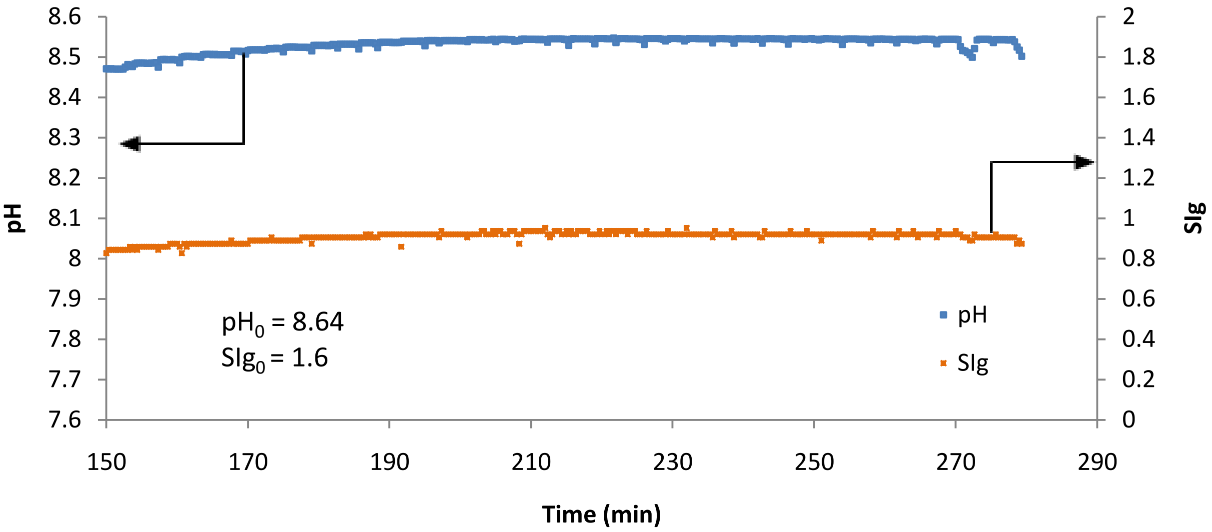


Figure 4-21. CCESP continuous gypsum bed pH and SIg at reactor outlet for CCESP of a solution composition as reported in Table 3-2 with initial antiscalant composition of 6.15 ppm in the feed stream to the CCESP system. Desupersaturation is shown from an antiscalant scavenged feed with SIg = 1.6 to SIg = 1. Steady state was achieved 150 minutes after the start of continuous pumping of lime-treated gypsum supersaturated solution through the fluidized gypsum bed. Experimental conditions: 240 g/L gypsum seed, 0.1 gpm overall flow rate.

The lime softening process of the current CCESP system successfully removed 68% of the residual antiscalant (present at a level of 6.15 ppm in the model RO concentrate) with negligible removal after the first 70 minutes of startup. Additionally, the current system successfully continuously desupersaturated the concentrate feed solution. The feed solution SIg decreased from 2.4 to 1.5 after lime treatment, and decreased to 1 after gypsum seeded precipitation. Both continuous processes displayed time-invariant conditions after start up, which suggests sustainable continuous operation.

Chapter 5

5. Summary and Conclusions

A process and system was developed and demonstrated for continuous chemically enhanced seeded precipitation (CCESP) process for desupersaturation of primary RO concentrate. CCESP operation relies on initial removal of antiscalants via partial lime softening which in present process enabled up to 87% antiscalants removal from the RO concentrate feed stream.

1. Investigations of system performance with various types of gypsum seeds revealed that seeds of size range 19-300 microns were most appropriate for maintaining proper fluidization and settling of large crystals formed in the crystallization step. For the present system, gypsum mass loading of ~0.24 kg/L was most effective for fluidized bed precipitation reaction and avoidance of clogging of intermediate transfer tubing.
2. The present pilot system was determined to be able to handle a feed flow rate in the range of 0.026-0.25 with the upper limit established so as to avoid vertical carryover of gypsum particles from the fluidized bed.
3. Continuous desupersaturation of high-salinity model RO concentrate via gypsum seeded precipitation was demonstrated utilizing a fluidized bed, reducing a solution of $CaCl_2$ (30.7 mM), Na_2SO_4 (145.4 mM), $MgSO_4$ (31.2 mM), and NaCl (20.3 mM) from SIg 2.88 to 1.3.
4. A continuous chemically enhanced seeded precipitation (CCESP) process of a synthetic RO concentrate solution with $CaCl_2$ (30.7 mM), Na_2SO_4 (145.4 mM),

$MgSO_4$ (31.2 mM), $NaHCO_3$ (11.4 mM), and NaCl (20.3 mM), Flocon 260 antiscalant (6.15 ppm) was successfully demonstrated in the continuous system, resulting in SIg reduction from 2.36 to 0.9 and 68% removal of residual antiscalant.

In order to optimize the CCESP system operation is critical to be able to monitor the rate of calcium removal via gypsum precipitation. In this regard, the use of optical sensors could be considered for real time monitoring of particle size distribution. In addition, real time determination of the height of the fluidized section of the precipitation reactor could be useful in ensuring effective operation of the fluidized bed reactor. Finally, investigation of the CCESP process under field conditions would contribute to further optimization of the overall process and its integration in high recovery RO desalination.

Appendix

Detailed experimental procedures

A. Pump calibration procedure**(§3.4.3)**

1. Open “NI Measurement” software and locate analog output module controlling specific pump, labeled AI. Wiring documentation or LabVIEW block diagram can be referenced for the specific AI and module for each pump.
2. Right click and select “Probe” to open a new window with a histogram and user inputted value. The value represents the analog signal, or in the case of the pumps, the current.
3. Changing the value of the current between 0.004-0.02 controls the speed of the pumps.
4. Use a volumetric cylinder and stop watch to manually calibrate pump volumetric flow rate and current. The calibration curve equation can be inputted to the LabVIEW program to convert a user inputted flow rate to a current input for the pumps.

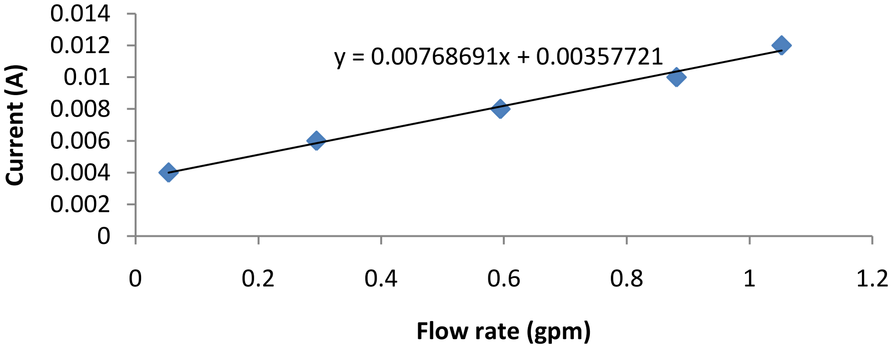


Figure A-1. Calibration curve for the feed pump, P-1 (Cole-Parmer, Vernon Hills, IL)

B. Calcium ion selective electrode (ISE) calibration

Six standards of known calcium concentration and activity were prepared for calibration of the calcium ISE prior to each use. The details of the calibration method are provided below (A. Rahardianto, UCLA, 2009)

1. Prepare six calibration standard solutions mimicking the composition of the RO concentrate model solution excluding sodium bicarbonate.
2. The six calibration standards should mimic the compositions expected throughout the CCESP experiences covering the range of Sig (e.g., ~1.0-2.5) expected over the course of the demineralization process as shown in Table A-1.
3. The master calibration curve for the calcium ISE is found by plotting the measured potential difference (ΔE) versus the logarithm of the known calcium activities (mol/kg-water) as shown in **Fig. A-2**. A fitted line will yield a gain (α) and offset (β) unique to the calcium ISE (see item (5) below) which, in the present system, had the values -15.067 mV/p(Ca^{2+}) and 147.24 mV, respectively.
4. Perform daily calibration prior to using the calcium electrodes using standards 2, 4, and 5 to calculate the daily gain and offset values (α_{daily} and β_{daily}).
5. The daily gain and offset values should be used to correct the measured potential (ΔE_{daily}) using the following linear equation: $\Delta E = \frac{\alpha}{\alpha_{daily}} \cdot \Delta E_{daily} + \beta - \beta_{daily} \left(\frac{\alpha}{\alpha_{daily}}\right)$.

Table A-1. Solution composition and calcium ion activity index for standard calibration solutions

Composition of calibrated standard solutions (mM)						
	STD1	STD2	STD3	STD4	STD5	STD6
CaCl2	36.5	30.7	22.2	16.5	11.7	8.7
Na2SO4	145.4	145.4	136.8	131.1	126.4	123.3
MgSO4	31.2	31.2	31.2	31.2	31.2	31.2
NaCl	20.3	31.6	48.8	60.2	69.7	75.8
SIg	2.95	2.52	1.85	1.39	1.00	0.74
Calibration Standard	2.30	2.37	2.49	2.61	2.75	2.88

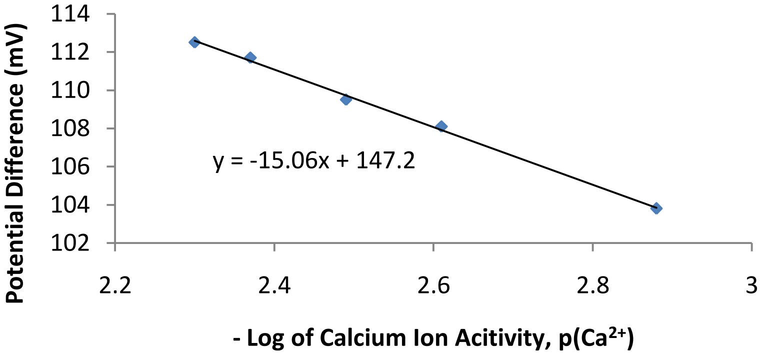


Figure A-2. Calcium ISE master calibration curve based on standard calibration solutions. STD 5 removed as an outlier.

C. TOC Analyzer Operation **(§ 3.4.5)**

A manual for the O·I·Analytical Aurora Model 1030 Total Organic Carbon Analyzer (College Station, TX) is available on the dedicated PC where more detailed instructions can be found. The essential steps for operating the TOC analyzer are provided below.

1. Ensure that there is a sufficient supply of the needed chemicals in the containers. Empty the waste container. Only use ultra-pure DI water. Check persulfate and phosphoric acid concentrations as prescribed in the system manual.

2. Prepare samples using glass vials and order them from low to high concentrations in the circular loading tray. Samples should be surrounded by “blanks” filled with DIW (e.g. Blank 1, Sample 1, Sample 2, Blank 2)
3. Click on “Wet Chemistry” under the Aurora 1030W program where access is provided through the appropriate user name and password.
4. Turn on N_2 gas and activate “Automated Start/Stop” under the “Maintenance” tab. Select “Wake up now” and allow for system to activate. Ensure that pressure shows “20 psi” indicating sufficient N_2.
5. Once the system is ready, select “Syringe” and “Prime All” to rid lines of air bubbles.
6. A “Method” is required for each measurement consisting of a calibration curve which the system references to convert carbon counts to concentration. Details for the set up method are provided in the instrument manual.
7. A “Sequence” must be created for each measurement which is the instruction list for the TOC Analyzer. Under “Editor”, a new sequence can be created for measuring sample sets. “Load” past sequences for reference.
8. “Auto-zero” the “NDIR detector” prior to starting runs.
9. Once the system completes a sequence, it will automatically turn off to “Gas-Saver Mode”. However, N_2 gas should be manually turned off to limit gas loss.
10. In order to view the results, open the “Reporter” software. Select “Wet Chemistry” and results can be viewed in chronological order. Data can be exported into a .csv file.

D. Preparation of Model RO Concentrate solution **(§ 3.4.1)**

1. Model RO concentrate constituents are: 145.4 mMNa_2SO_4, 31.2 mM$MgSO_4 \cdot 7H_2O$, 11.4 mM$NaHCO_3$, 20.3 mM NaCl, 30.7 mM$CaCl_2$
2. Divide salts into smaller portions to aid dissolution rate (e.g. 1 kg split into four 250 g additions).
3. Weighed salts should be first dissolved in separate containers prior to being added to the system feed tank.
4. Prepare 40 gallons of feed at a time to prevent precipitation at local areas of high concentration caused when adding salts. Mix using the attached mixer (Model A-1.0 Neptune Mixer Company, Lansdale, PA).
5. Salts should be added in the following order: Na_2SO_4, $MgSO_4$, $NaHCO_3$, NaCl, $CaCl_2$. Precipitation in the feed tank should be avoided.

E. Lime softening experiment procedure **(§ 3.4.4)**

1. A simplified solution for lime softening experiments containing 11.4 mM $NaHCO_3$ and 30.7 mM $CaCl_2$ was prepared for preliminary testing.
2. The fluidizing pump (P-2) should be redirected to the sensor block for live pH and calcium ion activity measurements.
3. Determine lime dosage using Stream Analyzer 3.1 (OLI Systems, Morris Plains, NJ) thermodynamic simulation.
4. Pump feed (P-1) and lime (P-6) into the mixing tank while mixing at 1200 rpm. Allow the flocculation tank to fill to the level of 4 gallons before turning on the recirculation pump (P-4).

5. Once the flocculation tank reaches 8 gallons, turn on the fluidizing flow pump (P-2) and record pH and calcium ion activity measurements using Star Com software (Thermo Scientific, Waltham, MA) and a calcium ion selective electrode (ISE25Ca-9) with a double junction reference electrode (REF251), a glass pH electrode (pHG211-8) with a single junction reference electrode (REF201), and a temperature (Radiometer Analytical; Lyon, France).
6. Grab samples may be collected at various times to measure TOC for indication of the removal of antiscalants.

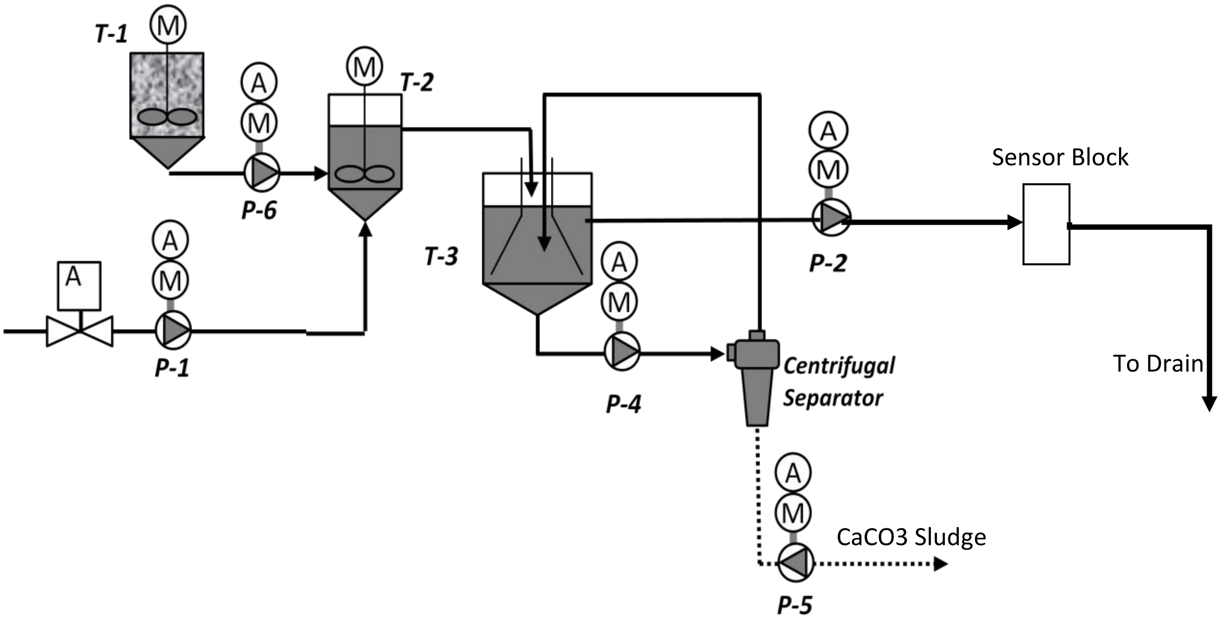


Figure A-3. CCESP set up for lime softening experiments; P-2 bypasses the fluidized bed reactor to the sensor block.

F. Gypsum seed preparation **(§3.4.6)**

1. Prepare saturated gypsum solution with Sig>1. For example: 18.63 g/L Na_2SO_4, 7.68 g/L $MgSO_4 \cdot 7H_2O$, and 3.52 g/L NaCl (Sig=1.39). Roughly 1 gallon/ kg of seed required. Na_2SO_4 is nearly at solubility limit and should be dissolved first.
2. Add gypsum seeds to the saturated gypsum solution and mix thoroughly.
3. Add gypsum seed solution mixture to gypsum seed tank. Turn on seed tank mixer to 750 rpm. If mixer begins to gallop due to increased fluid viscosity, lower the rpm.
4. Turn on seed pump (P-3) and set flow rate to < 1 gpm to pump contents of seed tank into bed reactor. Bed capacity is roughly 11 gallons and seed tank capacity is 10 gallons.
5. Allow solids in the bed to settle prior to fluidizing flow operation. Time to settle: 20-60 minutes.

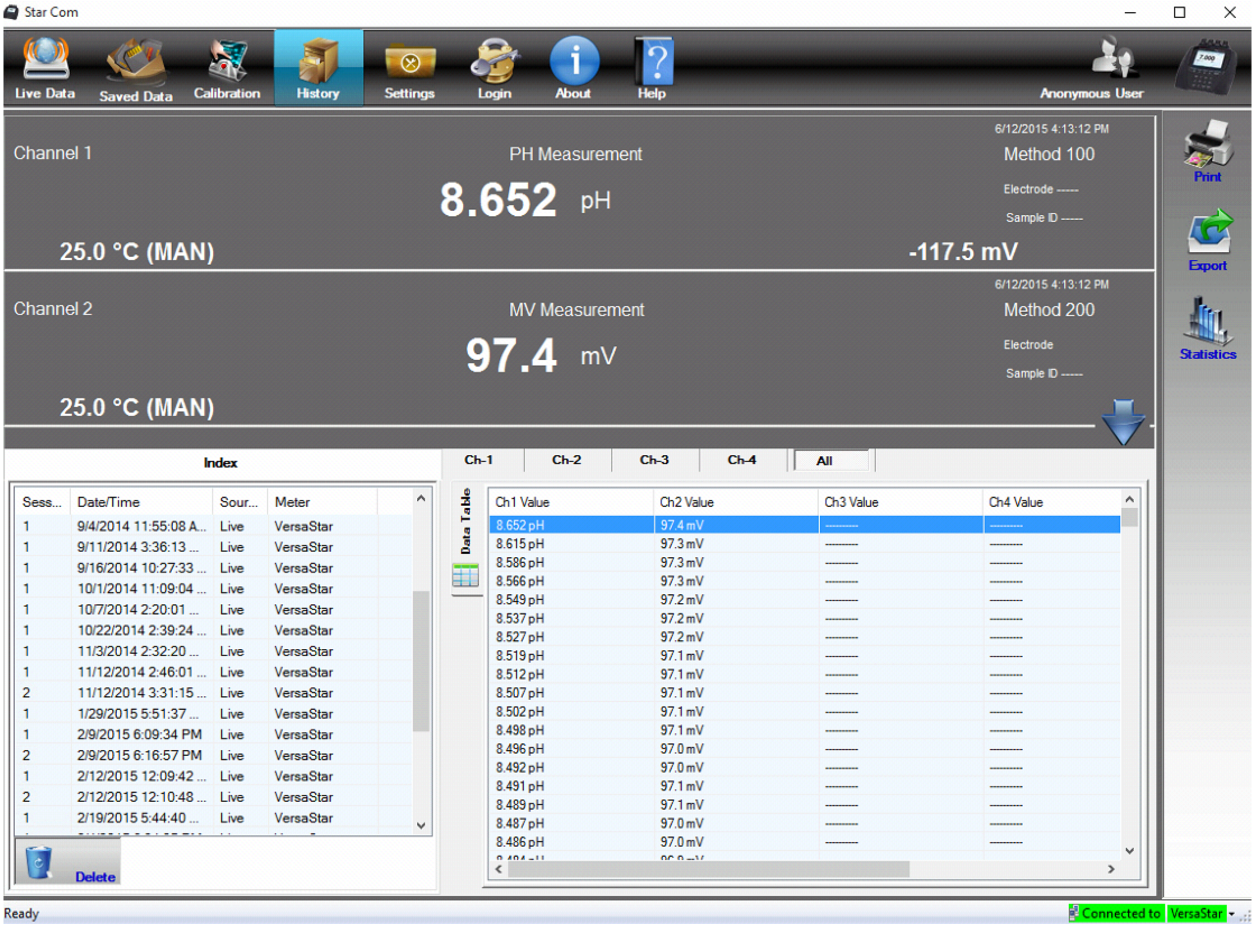
G. Gypsum bed height experiment procedure **(§ 3.4.6)**

1. Gypsum seed is loaded into the bed reactor as shown in Appendix F.
2. A time lapse camera should be set up to record bed height fluctuations in the clear "polished" region of the reactor. Photographs should be taken at 5-30 minute intervals.
3. Bed height should be measured using image analysis comparing the known height of the clear "polisher" region to the height of the solid-liquid interface.
4. Two pumps, the seed recycle pump (P-3), and the fluidizing flow pump (P-2) may be used to control the fluidized bed height.

H. CCESP Procedure **(§ 3.4.8)**

1. Prepare a batch of Model RO feed water with total volume of at least 20 gallons.
2. Access the connected PC and initiate LabVIEW file: “CCESP Interface”
3. Open feed valve (V-1). Ensure that water level from feed is reaching the valve.
4. Initiate and prime pumps by enabling “Cole-Parmer Pumps”. The pumps should all be running at “15” rpm, which can be confirmed on the controller boxes.
5. Check the controller boxes for pump connectivity and correct orientation. Controllers showing “0” may be experiencing a loose connection. Orientation for forward flow is shown by the markings on the controller.
6. Increase the flow rate for the feed pump (P-1) gradually. Do not exceed 2 GPM or 600 rpm. The feed will begin to fill the mixing tank.
7. Turn on the mixing tank mixer manually. The mixer aids in the flow of the feed from the mixing tank to the flocculation tank. Do not exceed 1300 rpm.
8. Increase the flow rate for the recycle pump (P-3) gradually once the flocculation tank begins to fill. The recycle pump should be operated at > 3 gpm to enable separation using the centrifugal separator. Do not exceed 600 rpm or ~ 5 gpm
9. Once the flocculation fills to 8 gallons, Turn on the bed feed pump (P-2) and set to the same flow rate as P-1. Flocculation clarified product water will begin entering the fluidized bed for gypsum seeded precipitation.
10. Limit overall flow rate (P-1 and P-2) to <0.25 gpm to prevent the fluidizing velocity from exceeding the settling velocity of the seeds. Seed crystals will be carried out of the bed with the product at higher flow rates.

11. Measurements of streams properties can be acquired using the sensor block system to draw a side stream using the sensor pump (P-7) or via stream redirection.
12. Live pH and calcium ion activity should be recorded using Star Com 1.0 (Thermo Scientific, Waltham, MA) as seen in **Fig. A-3**. Data may be exported in .csv file for analysis.



Channel 1
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Method 100
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Electrode -----
Sample ID -----
25.0 °C (MAN)
-117.5 mV

Channel 2
MV Measurement
6/12/2015 4:13:12 PM
Method 200
97.4 mV
Electrode
Sample ID -----
25.0 °C (MAN)

Sess...	Date/Time	Sour...	Meter
1	9/4/2014 11:55:08 A...	Live	VersaStar
1	9/11/2014 3:36:13 ...	Live	VersaStar
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1	10/1/2014 11:09:04 ...	Live	VersaStar
1	10/7/2014 2:20:01 ...	Live	VersaStar
1	10/22/2014 2:39:24 ...	Live	VersaStar
1	11/3/2014 2:32:20 ...	Live	VersaStar
1	11/12/2014 2:46:01 ...	Live	VersaStar
2	11/12/2014 3:31:15 ...	Live	VersaStar
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1	2/9/2015 6:09:34 PM	Live	VersaStar
2	2/9/2015 6:16:57 PM	Live	VersaStar
1	2/12/2015 12:09:42 ...	Live	VersaStar
2	2/12/2015 12:10:48 ...	Live	VersaStar
1	2/19/2015 5:44:40 ...	Live	VersaStar

Ch1 Value	Ch2 Value	Ch3 Value	Ch4 Value
8.652 pH	97.4 mV	---------	---------
8.615 pH	97.3 mV	---------	---------
8.586 pH	97.3 mV	---------	---------
8.566 pH	97.3 mV	---------	---------
8.549 pH	97.2 mV	---------	---------
8.537 pH	97.2 mV	---------	---------
8.527 pH	97.2 mV	---------	---------
8.519 pH	97.1 mV	---------	---------
8.512 pH	97.1 mV	---------	---------
8.507 pH	97.1 mV	---------	---------
8.502 pH	97.1 mV	---------	---------
8.498 pH	97.1 mV	---------	---------
8.496 pH	97.0 mV	---------	---------
8.492 pH	97.0 mV	---------	---------
8.491 pH	97.1 mV	---------	---------
8.489 pH	97.1 mV	---------	---------
8.487 pH	97.0 mV	---------	---------
8.486 pH	97.0 mV	---------	---------

Figure A-4. Star Com (Thermo Scientific, Waltham, MA) software for live pH and calcium ion activity measurement and acquisition

I. System Shutdown and Maintenance

1. Decrease the pumps flow rate setting to "0" gal/min.

2. Drain remaining feed water and rinse tank with DI water. Prepare container with 20 gallons of DI water for system wash.
3. Change orientation of feed pump and open valve to drain the mixing tank. Increase feed pump (P-1) to 1 gpm and drain all mixing tank contents. Pump the remaining lime using P-6 into mixing tank for draining.
4. Turn valve after recycle pump, located underneath the mixing tank to drain to waste. Increase recycle pump to 2 gpm until flocculation tank is empty.
5. Increase separator metering pump (P-4) to 500 mL/min and drain separator.
6. Return valves to forward operation mode and fill system with DI water. Repeat steps 3 and 5 to drain DI water.
7. The flocculation tank has a bypass valve for draining. Turn on the flocculation pump (P-2) in the forward direction and the tank will drain. Fill tank with DI water and drain to rinse tank.
8. To drain the bed reactor, open the sludge valve (V-3) and turn on the seed pump (P-3). A slower flow rate (< 1 gpm) is recommended to prevent clogging and damage to the pump tubing.
9. A more thorough cleaning of the reactor bed is recommended after every complete seed replacement to prevent bacterial growth. Open the reactor at the coupling union above the polisher region and flush DIW into the reactor. Disassemble the reactor if comprehensive cleaning is required.
10. Tubing for the peristaltic pumps should be replaced every 2 months for preventative maintenance.

11. Clogs may be dislodged by connecting P-7 to a series of side inlets and pumping DI water to dissolve the seeds. Turn off seed pump (P-3) once a clog occurs to prevent damage to the pump tubing.

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