Membrane Mineral Scaling and its Mitigation in Reverse Osmosis Desalination of Brackish Water

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Membrane Mineral Scaling and its Mitigation
in Reverse Osmosis Desalination of Brackish Water

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requirements for the degree Doctor of Philosophy
in Chemical Engineering

by

John Francis Thompson

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ABSTRACT OF THE DISSERTATION

Membrane Mineral Scaling and its Mitigation in Reverse Osmosis Desalination of Brackish Water

by

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Doctor of Philosophy in Chemical Engineering
University of California, Los Angeles, 2017
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The treatment and desalination of inland water via reverse osmosis (RO) technology is gaining momentum for upgrading brackish groundwater and developing supplemental fresh water for various regions. In brackish RO plants, high water recovery is critical in order to minimize the volume of residual RO concentrate (brine), given the economic and environmental challenges of concentrate management. However, high recovery may be limited by mineral salt scaling resulting from supersaturation of sparingly soluble minerals (e.g., CaSO₄, BaSO₄, CaCO₃, SiO₂). Mineral scaling results in membrane surface blockage, reduction of permeate flux and shortening of membrane lifetime.

In order to control or prevent mineral scaling, effective mitigation methods must be developed and tested (i.e., the relationship between RO operating conditions and mineral scaling). To accomplish the above, early detection of mineral scaling is essential. To meet the above challenges, a novel high-pressure RO membrane monitoring system was developed to
allow direct membrane surface imaging. The membrane monitoring system (MMS) was interfaced with a slipstream from an RO plant, whereby captured membrane surface images were analyzed online. The present monitoring approach demonstrated, for the first time, early detection of silica scale formation and growth kinetics. Detailed silica scaling studies revealed that scaling consisted of discrete silica particles embedded in a silica “gel” layer. The membrane monitoring approach also served to evaluate the impact of a membrane biofilm on concentration polarization (CP) and mineral scaling kinetics. It was shown that biofilms enhanced CP within the biofilm and significantly exacerbated mineral scaling.

The membrane monitoring approach was subsequently deployed in a field study of desalination of brackish agricultural drainage (AD) water. In these studies, the membrane monitor was integrated with a mobile RO pilot plant, developed at UCLA, for real-time field optimization of RO operating conditions for averting mineral scaling. The above approach demonstrated that effective feed filtration for removal of suspended particles is critical for mitigating mineral scaling and reducing nucleation triggered by surface deposited particles. Moreover, antiscalant selection and dosage optimization was feasible under field conditions which also enabled determination of the maximum feasible water recovery level.
The dissertation of John Francis Thompson is approved.

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2017
Dedicated to my family and to my girlfriend April.

Thanks for your love and support.
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Chapter 1

Introduction

1.1 Background

Membrane-based separation processes for water purification and desalination are at the forefront of managing increasingly severe problems with fresh water scarcity, impaired groundwater quality, and other environmental issues [1-7]. By 2030, the world population is expected to surpass 8 billion, with nearly half of all people living in areas of medium or severe water stress [8]. In arid and semi-arid regions, such as the Western US, drought conditions, rising groundwater salinity, seawater intrusion, and accumulation of high-salinity agricultural drainage (AD) water all highlight the need for desalination of available saline water sources [9-11].

Although water desalination can be accomplished through a variety of approaches, including thermal processes such as multistage flash distillation (MSF) and multiple-effect distillation (MED), these are energy intensive [7, 11]. As a result, less energy intensive membrane processes, such as reverse osmosis (RO), have largely overtaken thermal methods [11]. Recently, there has also been increased interest in solar-powered desalination [12, 13], but this technology is in its early stages. For concentrated brine with salinity above that of seawater, membrane distillation could be a useful desalination approach, particularly when the source water is at elevated temperatures [14, 15].

RO remains the leading desalination technology due to its exceptional scalability and the evolution of considerable process and materials innovations over the past few decades. Promising developments include high-performance and fouling-resistant nanocomposite membranes [2, 16-27]. Indeed, 88% of desalinated water in the US is produced by RO, with the remainder produced by nanofiltration (NF), electrodialysis or electrodeionization [11]. Given
that about 73% of desalinated water is provided as potable drinking water (≤500 mg/L total dissolved solids, TDS) [11], RO is a logical choice, given its capability for achieving high rejection (>99.5%) of monovalent ions for producing low salinity water [2, 20, 21].

Desalination of seawater (~30,000-35,000 mg/L TDS) is currently the largest facet of RO desalination, facilitated by the incorporation of advanced pretreatment for fouling prevention and efficient energy recovery devices (ERD) to reduce energy consumption [28-31]. Seawater reverse osmosis (SWRO), accounting for over half of the world’s desalination capacity (i.e., > 70 × 10^6 m^3/day) [32], has become a popular choice for many regions with limited natural fresh water resources, including in the Middle East and Australia. In Israel, one of the world’s largest SWRO plants is the Sorek desalination plant, near Tel Aviv, with a capacity of 624,000 m^3/day (~165 million gal/day, MGD), beginning operation in 2013 [33, 34]. Saudi Arabia, a global leader in desalination, now produces a majority of its drinking water from seawater [35], while also employing desalination for reuse of reclaimed wastewater [36, 37]. In Australia, the arid climate and limited fresh water resources have spurred an expansion of desalination capacity, with planned or current construction of significant RO desalination projects in most of its major cities [38]. In Europe, Spain has also begun to develop significant RO desalination infrastructure [39]. In the US, RO is also expanding, with the over $1-billion, 50 MGD (~190,000 m^3/day) Carlsbad plant recently opening in San Diego County, California, providing ~10% of the water needs for a region previously forced to import 85% of its water supply [40]. Despite recent progress, SWRO plants are typically more expensive to build and operate than other (e.g., brackish) RO plants [11]. Also, the significant volumes of RO brine discharged into the ocean can impact the local marine environment, and this may require extensive environmental planning and permitting [41].
Desalination of inland brackish water (e.g., groundwater or agricultural drainage water) or municipal or industrial wastewater (WW), has certain advantages and challenges. Brackish water reverse osmosis (BWRO) has significant potential for expansion, given that brackish groundwater underlies a majority of the US [42]. Brackish water already accounts for 68% of the desalination capacity in the US, with only 4% from seawater, with coastal states such as California, Florida and Texas leading the way [11]. BWRO is an attractive desalination option since its source water is of lower salinity than seawater (~1,000-30,000 mg/L TDS [11, 43, 44]), implying higher feasible water recovery [19], and it generally has lower associated capital and energy costs [11]. Indeed, BWRO is seen as a promising solution for alleviating many inland water drought and salinity issues. For example, the Yuma Desalting Plant in Arizona, though not currently active, has a capacity of 73 MGD (~275,000 m³/day), and was designed for desalting brackish agricultural runoff, when the need arises, to mitigate increasingly severe drought and salinity problems in the Colorado River Basin, which supplies water to much of Nevada and California [9, 11, 45-47]. In the San Joaquin Valley of California, a bountiful agricultural region, brackish water reclamation with RO has the potential to ameliorate drainage issues causing the accumulation of high-salinity agricultural drainage water that contributes to rising groundwater salinity [10, 43, 48-52]. Additionally, large state-of-the-art RO facilities were built in Long Beach and Orange County for treating municipal wastewater effluent for mitigating seawater intrusion, via groundwater recharge, along the coast of Southern California [53, 54]. Lastly, there has also been extensive consideration of RO for the treatment of industrial wastewater, and particularly cooling tower blowdown water, in order to reduce water usage and waste [55-61].

In contrast to SWRO, inland disposal options for BWRO concentrate are more limited [10, 62-64]. Conventional methods of disposal or treatment such as surface disposal, deep well
injection, sewer disposal and solar evaporation ponds are not sustainable options [11], and can pose environmental hazards due to contaminants such as selenium [10, 65]. As such, they are poorly suited for treating or disposing of large volumes. As a result, high recovery RO has become a desirable option to minimize the volume of concentrated brine [41, 43, 64, 66-79].

However, the attainable water recovery (i.e., the percentage of feed recovered as product water) is typically limited by mineral scaling propensity due to supersaturation of sparingly soluble mineral salts (e.g., CaSO₄, CaCO₃, SiO₂) [43, 72, 80, 81]. As the water recovery is increased, mineral scalants can exceed their saturation limits and precipitate in the bulk fluid or on the membrane surface, hampering water production and reducing the useful life of the membranes [82-87]. Concentration polarization (CP), whereby water permeation causes an elevation of salt concentrations near the membrane surface, is governed by hydrodynamics and mass transfer, and can also impact mineral scaling behavior [88-92].

In order to operate RO plants at high recovery, pretreatment schemes must prevent early fouling of the RO by removing suspended particulates and colloidal matter. This is typically done by coagulation or flocculation followed by prefiltering the RO feed using media filtration, microfiltration (MF) or ultrafiltration (UF) membranes [29, 59, 93-105]. To prevent mineral scaling, prefiltration is followed by the addition polymeric scale inhibitor, known as antiscalant (AS), to the RO feed stream [72, 78, 106-116]. Antiscalants are used to prevent or delay the onset of mineral scaling in desalination and heat exchange processes, and to retard the nucleation and growth of mineral scale crystals or particles [72, 78, 81, 87, 106-115, 117-122]. AS addition may also be accompanied by pH adjustment via acid or base addition [123]. Changes in pH can be effective for preventing scaling for certain scaling species whose solubility and speciation are sensitive to pH, such as calcium carbonate and silica [78, 123-126]. However, the increased cost
and chemical requirements of pH adjustment may limit its practice, particularly for naturally buffered water sources. Some tenacious yet commonly encountered mineral scalants may be relatively insensitive to changes in pH, such as calcium sulfate [43, 78, 113], necessitating antiscalant use.

Typically, RO desalination plants use a prescribed commercial antiscalant based on feed water composition, target water recovery, and thermodynamic solubility analysis (i.e., from water quality data) [72, 81, 108]. However, relying on such analyses may be insufficient for determining the so-called "optimal" antiscalant type and concentration (i.e., minimum dose for effective scale control) since they do not provide a prediction of the onset of mineral scaling, or the growth kinetics of mineral scaling [81]. Furthermore, it has been shown that AS effectiveness, while limited, is sensitive with respect to the AS selection and dose (and desired water recovery) [72, 78, 87, 106, 107, 110-113, 118, 119, 127-129]. Thus, the selection of appropriate antiscalant and dose (and desired water recovery) should be tested when possible. However, conventional pilot testing may require tedious and protracted studies [127, 130], due to current membrane monitoring methods.

In order to detect membrane fouling or mineral scaling, conventional RO plants typically rely on indirect salt passage or permeability decline measurements [130-133], the latter either as permeate flux decline or increased transmembrane pressure (TMP), where a ~10-15% decline is indicative of fouling or scaling [132]. Indeed, several membrane studies have also utilized such measurements as a means for studying the impact of fouling and mineral scaling [82-84, 109, 133-138]. In general, this approach is imprecise, given that measurable permeate flux decline may not be ascertained (e.g., beyond measurement uncertainty) until significant mineral scaling (e.g., as nuclei or small crystals) has occurred [85, 86, 139, 140]. Also, it is conceivable that
fluctuations in water quality or environmental conditions can also lead to flux decline. If scaling is late to be detected, the level of scaling may be severe to an extent that would make it infeasible to halt or reverse the mineral scaling process, necessitating membrane cleaning, which may require the RO system to be taken offline or have its membrane elements replaced. Using the above methods, there is no direct confirmation or characterization of fouling or mineral scaling that takes place until the membrane element is removed and analyzed via destructive autopsies [28, 76, 141-144], although this is still a useful tool for diagnosing fouling problems. It is emphasized that, in order to prevent the above scenario and associated interruptions of plant operation, early scaling and fouling detection (prior to performance decline) is necessary.

In the past decade, several alternative membrane monitoring approaches have been proposed, consisting mostly of indirect methods using either ultrasonic waves [136, 145-152] or electrical impedance measurements [153-155]. However, these approaches, which have limited spatial resolution, may be suited for detection of cake layer formation during colloidal or organic fouling, as opposed to detecting sparsely distributed and/or small crystals associated with the early onset of mineral scaling. While in some cases the sensitivity of such approaches may be sufficient for early detection of fouling relative to TMP rise [154] or permeate flux decline [153], these methods provide only an indirect indication of a buildup on the membrane.

In contrast with the above approaches to membrane fouling and scale detection, direct visual surface monitoring by optical means (along with image analysis) has been shown to provide for early scale detection as well as the quantification of nucleation and growth kinetics for gypsum crystals [78, 85, 86, 139, 156, 157]. The above direct surface imaging approach has enabled quantification of the extent of mineral scale coverage and its correlation with the observed level of permeate flux decline [113]. The success of previous studies suggests that there
is merit in using direct monitoring to evaluate other forms of fouling or scaling, and for real-time RO plant monitoring. Direct surface monitoring can also elucidate factors which can alter (i.e., mitigate or exacerbate) mineral scaling, as previously shown for gypsum scaling retardation with antiscalants [78, 112, 113], and exacerbation by coagulants used in RO pretreatment [128]. Clearly, understanding mineral scaling kinetics and the effect of RO operating conditions, as well as field conditions, are important in formulating effective scaling mitigation strategies. Thus, direct visual monitoring would have value as an experimental diagnostic tool for quantifying scaling kinetics, and as a smart membrane monitoring sensor integrated with a spiral-wound RO plant (e.g., on a slipstream of RO concentrate, where solute concentrations are highest) (Figure 1-1). The membrane monitor can provide real-time data, in tandem with other plant sensors, for plant optimization regarding fouling and scaling mitigation and membrane cleaning efficiency.

Figure 1-1. Illustration of integrated membrane monitoring as a direct fouling and mineral scaling sensor in a reverse osmosis plant.
1.2 Problem Statement

RO desalination of brackish water is challenging due to mineral scaling, which limits high recovery operation. When operating at high recovery, slipping into the operating regime where mineral scaling can occur must be avoided. Therefore, early detection of mineral scaling is essential, both in order to ensure that the RO membranes are protected and to optimize feed pretreatment strategies. Mineral scaling mitigation approaches must also be tested and optimized. The above requires sensitive membrane monitoring that would enable one to detect the onset of mineral scaling and also establish mineral scaling kinetics as impacted by environmental conditions, concentration polarization, as well as feed pretreatment methods. The present study addresses the above challenges by introducing a novel approach for fundamental quantification of mineral scaling kinetics under different operating conditions and various feed sources and for field optimization of RO process operation. A flow diagram describing the experimental dissertation work is provided in Figure 1-2.
1.3 Objectives of the Dissertation

The goal of this dissertation research was to evaluate and quantify mineral scaling kinetics required for developing effective mineral scaling mitigation strategies through direct monitoring of RO membranes. The experimental work focused on examining mineral scaling in
brackish water desalination, aimed at advancing the fundamental understanding of the operating conditions governing surface mineral scaling kinetics in field applications. Accordingly, the research objectives were as follows:

1. Elucidate mineral scaling kinetics, via direct membrane surface monitoring, of a challenging and previously poorly understood mineral scalant relevant to inland RO desalination, such as silica, for a wide range of supersaturation levels.

2. Investigate the local effects of an organic or biological fouling layer on concentration polarization and the resulting changes in mineral scaling kinetics and morphology.

3. Demonstrate direct membrane monitoring for assessing appropriate RO operating conditions (e.g., water recovery, feed filtration, antiscalant dose) for mitigating mineral scaling under field conditions and assess its applicability for use as a monitoring system for a spiral-wound RO pilot plant.

4. Evaluate and optimize the performance of proposed mineral scale mitigation and cleaning strategies in real-time using a membrane monitor integrated with a pilot or demonstration scale spiral-wound RO desalination plant with field water of high mineral scaling propensity.
1.4 Approach

The stated objectives were fulfilled via experimental laboratory and field studies. Prior to RO desalination experiments, feed water quality was analyzed in order to identify potential mineral scalants and calculate their saturation limits and thus mineral scaling propensity. Experimental testing utilized a custom plate-and-frame membrane cell developed for membrane surface monitoring, with appropriate lighting and optical sensors. Direct membrane surface monitoring and image analysis served to identify and quantify mineral scaling kinetics for the challenging mineral scalants of calcium sulfate (gypsum) and silica. Laboratory experiments involved synthetic solutions or a combination of synthetic solution and field water samples, whereas field experiments were conducted using field water pumped from the relevant source. Field studies enabled assessment of the RO plant operating conditions affecting mineral scaling. Subsequently the effectiveness of scaling mitigation was evaluated by integrating the membrane scaling/fouling monitor with a pilot RO plant in the field.

Chapter 3 describes the use of the direct membrane monitoring approach to assess the effect of silica supersaturation at the membrane surface on silica scaling kinetics and impact on permeate flux decline. The early development of silica scale particles was directly tracked in real-time and analyzed in terms of nucleation and growth rates, as well as membrane surface coverage and surface number density over time. The scaled membrane samples were subsequently analyzed to confirm the presence of silica using EDS, and the impact of local silica supersaturation on the scale morphology and surface roughness was also examined using SEM and AFM, respectively.

Chapter 4 details an investigation of the impact of a biofilm layer on membrane concentration polarization and resulting changes to mineral scaling kinetics. The biofilm layer
was formed by desalting actual samples of secondary municipal wastewater effluent (from a water treatment plant) in the membrane monitoring cell, during which the impact of biofouling on the membrane surface and permeate flux decline was monitored. Once the biofilm layer was established, a synthetic solution of calcium sulfate (gypsum) and trace nutrients to sustain the biofilm was desalted using the membrane monitor. Using a control experiment for gypsum mineral scaling without biofouling, the comparative impact of biofouling (and biofilm density) on concentration polarization and mineral scaling kinetics was quantified.

The application of direct membrane monitoring for rapidly evaluating the feasible operating conditions for RO desalination of brackish agricultural drainage (AD) water of high mineral scaling propensity is discussed in Chapter 5. The effectiveness of different levels of prefiltration for preventing particulate deposition and mineral scaling was evaluated. Subsequently, the appropriate antiscalant type and concentration were selected through a series of single-pass desalination experiments in which the mineral scale surface coverage was quantified in real-time. The feasible RO recovery limit imposed by mineral scaling was directly estimated through an extended run in which concentration polarization was periodically increased to simulate increasing water recovery conditions on mineral salt concentrations and mineral surface scaling. To verify the experimental results from the membrane monitor diagnostic tests, the membrane monitor was connected to a spiral-wound RO pilot plant concentrate stream while monitoring the membrane surface and the permeate flux in the membrane monitor for a slipstream from the RO plant’s tail membrane element.

Extension of the approach and operating strategies for mitigating scale formation for AD water desalination discussed in Chapter 5 is described in Chapter 6 for a long-term field optimization study. In the field study, the membrane monitor was fully integrated into a larger
RO demonstration plant for optimizing the feasible RO water recovery for a similar water source. Firstly, the impact of prefiltration on particulate deposition and mineral scale nucleation was quantified using direct mineral scale monitoring. Thereafter, the membrane monitor served to assess mineral scaling behavior for a slipstream of the RO plant concentrate. The water recovery level in the RO plant was periodically increased until mineral scaling was observed in the monitoring cell. During the study, the effectiveness of two commercial antiscalants was quantified for the degree of retardation for both crystal nucleation and growth. The antiscalant dose for the RO plant was changed in real-time, while monitoring changes in the mineral scaling kinetics, so as to determine the feasibly attainable maximum recovery. Finally, the effectiveness of a fresh water flushing scheme (using RO permeate) for scale removal was evaluated, as facilitated by direct surface scale detection.
Reverse osmosis (RO) desalination is a widely used pressure-driven separation process, whereby a solution is pressurized and passed through a semi-permeable membrane that allows passage of solvent, typically water, while largely rejecting solutes (typically dissolved salts) including divalent and monovalent ions, and suspended matter [19, 23, 158]. The feed solution is thereby separated into a low salinity permeate stream, usually the desired product, and a concentrated brine, also referred to as the retentate or concentrate stream. In order to obtain separation, the applied pressure must always overcome the osmotic pressure of the solution (i.e., the so-called thermodynamic restriction) [159]. The volumetric flux of permeate water through the RO membrane, $J_v$, as in Eqn. 2-1 [159-161], depends on the membrane permeability $L_p$ (inverse of the resistance to water flow), applied pressure difference between the feed and permeate $\Delta P$, osmotic pressure difference between the feed and permeate $\Delta \Pi$, and solute reflection coefficient, $\sigma$ [162]:

$$J_v = L_p (\Delta P - \sigma \cdot \Delta \Pi)$$

(2-1)

At dilute concentrations, the osmotic pressure is typically estimated using the van’t Hoff equation (Eqn. 2-2) [163]:

$$\Pi = iCRT$$

(2-2)

where $i$ is the dimensionless van't Hoff factor for a given solute, $C$ is the molar salt concentration (M), $R$ is the ideal gas constant (0.08206 L·atm/mol·K), and $T$ is absolute temperature (K).
However, in non-dilute systems, solute interactions must be taken into account using more complex functions or equations of state [164].

![Diagram of TFC RO membrane layers](image)

**Figure 2-1.** Illustration of the cross section of typical layers of a TFC RO membrane. Adapted from [20].

Although membrane materials continue to evolve, commercial RO membranes are typically composed of multiple polymer layers in an asymmetric thin-film composite or TFC (Fig. 2-1), with a thin barrier or “active” separation layer composed of aromatic polyamide, on top of a thicker porous support layer of polysulfone with a highly porous non-woven fabric underneath [2, 6, 20, 23, 165, 166]. Given that diffusion can still occur inside the membrane via solution-diffusion transport [160, 161, 163, 167], 100% membrane rejection is not strictly achieved for all dissolved salts. Solute flux in RO membranes is typically described with a concentration driving force as the first term of **Eqn. 2-3** (see also Fig. 2-5), whereas the second term is usually negligible since typically $\sigma \approx 1$ [168]:

\[
J_s = B(C_m - C_p) + \frac{J}{2}(C_m + C_p)(1 - \sigma)
\]  

(2-3)
where $J_s$ is the solute flux, $B$ is the solution-diffusion coefficient, and $C_m$ and $C_p$ are the solute concentration at the membrane feed surface and in the permeate, respectively. The intrinsic rejection, $R$, of a solute is quantified by:

$$R = 1 - \frac{C_p}{C_m}$$  \hspace{1cm} (2-4)

However, it is typical to report an “observed” rejection, $R_o$, or salt passage, $SP$, based on the more readily observable bulk concentrations in the feed and permeate streams (Eqns. 2-5, 2-6):

$$R_o = 1 - \frac{C_p}{C_f} ; \quad SP = 1 - R_o$$  \hspace{1cm} (2-5, 2-6)

where $C_f$ is the solute concentration in the feed stream.

RO modules typically use a crossflow configuration in which the feed solution flows parallel to the membrane while water flows tangentially through the membrane (Fig. 2-2).

**Figure 2-2.** Schematic of a cross-section of laminar crossflow RO operation with membranes on the top and bottom of the flow channel.
The fraction of water that is withdrawn and collected as product relative to the feed for continuous separation is defined as the fractional water recovery level, \( Y \) (Eqn. 2-7):

\[
Y = \frac{Q_p}{Q_f}
\]  

(2-7)

where \( Q_p \) and \( Q_f \) are the total volumetric permeate and feed flow rates, respectively. As the recovery is increased, the retentate salt concentration is elevated according to the concentration factor \((CF)\) which is related to the water recovery and observed salt rejection by an overall mass balance:

\[
CF = \frac{C_c}{C_f} = \frac{1 - Y(1-R_o)}{1 - Y}; \quad Y = \frac{CF - 1}{CF - (1-R_o)}
\]  

(2-8, 2-9)

where \( C_c \) is the salt concentration of the RO concentrate. The production of concentrated brine is undesirable and requires proper treatment or disposal, and thus achieving high recovery (>90%) brackish water RO to minimize the amount of brine byproduct is an essential goal for the foreseeable future [69, 71, 72]. Indeed, the reuse or treatment of residual brine produced from RO desalination has become a major research topic, with the main goal of reaching near 100% water recovery (so-called ZLD, zero liquid discharge), and typically a thermally-driven step such as evaporation is used to produce solid products [41, 43, 64, 66-72, 169].

In order to maximize membrane surface area into a compact module, commercial RO membranes are typically manufactured in a spiral-wound configuration [90, 165], in which the permeate water spirals towards a central collection tube while the feed and concentrate streams flow axially along the membrane channels as depicted in **Fig. 2-3**. Feed and permeate channel gaps are provided by mesh spacers.
Large-scale desalination plants are typically configured as multi-stage systems for increased conversion (i.e., water recovery) [170] (Fig. 2-4), employing spiral-wound modules in series in order to meet water recovery specifications, while modules in parallel arrays accommodate flow capacity requirements. Plants typically have two stages, with the 1st stage being the largest to handle the greatest capacity. The 1st stage concentrate is fed as the 2nd stage feed to recover additional water. In addition to feed pump(s), there may be interstage booster pumps, depending on the system pressure demands and overall water recovery requirements. Typically there is a prefiltration system in order to remove suspended solids and chemical dosing step for fouling and scaling reduction using antiscalant addition or pH adjustment [104, 123].
2.1.2 Concentration polarization

At the membrane surface on the feed side, rejected solutes accumulate as water passes through the membrane, and this causes a local elevation of the solute concentration within the concentration boundary layer (i.e., concentration polarization). The degree of this accumulation is quantified by the concentration polarization (CP) modulus \( CP = \frac{C_m}{C_b} \), and frequently estimated by the stagnant film model [92] (Eqn. 2-10):

\[
CP = \frac{C_m}{C_b} = 1 - R_o + R_o \exp \left( \frac{J_v}{k_f} \right)
\]  

where \( C_m \) and \( C_b \) are the solute concentrations at the membrane surface and in the bulk solution, respectively, \( R_o \) is the observed salt rejection, \( J_v \) is the volumetric permeate flux, and \( k_f \) is the feed-side mass transfer coefficient, which describes the degree of solute diffusion along the concentration gradient from the membrane surface to the bulk solution (Fig. 2-5).

Figure 2-4. Simplified process diagram of a typical two-stage RO desalination plant.
Concentration polarization in a cross flow membrane channel such that $C_m > C_b$, where $C_m$ is the solute concentration at the membrane surface on the feed side, $C_b$ is the bulk solute concentration, $D$ is the solute diffusivity, and $dC/dy$ is the solute concentration driving force in the $y$-direction. Gray arrows represent solute flux while solid black arrows represent bulk flow.

Concentration polarization gradually increases axially along the membrane from inlet to outlet [89], as depicted in Figs. 2-5 & 2-6. As fluid flows along the membrane in crossflow mode, the bulk concentration increases as more water is removed; and the local osmotic pressure increases, thereby decreasing the net driving force for permeate water flux.

**Figure 2-5.** Concentration polarization in a crossflow membrane channel such that $C_m > C_b$, where $C_m$ is the solute concentration at the membrane surface on the feed side, $C_b$ is the bulk solute concentration, $D$ is the solute diffusivity, and $dC/dy$ is the solute concentration driving force in the $y$-direction. Gray arrows represent solute flux while solid black arrows represent bulk flow.

**Figure 2-6.** Concentration polarization modulus versus axial position in a rectangular RO membrane channel for different Reynolds numbers for a calcium chloride solution [89].
The quantification and prediction of the CP in relation to hydrodynamics and mass transfer is important because sparingly soluble minerals may exceed their solubility limit and precipitate within the boundary layer or at the surface. This may occur even when these minerals may be below saturation limits in the bulk fluid as predicted by water recovery and corresponding retentate concentrations. In order to determine the level of CP in a membrane module using Eqn. 2-10, the mass transfer coefficient, \( k_f \), must be estimated or determined, frequently from a Sherwood number correlation for a specific geometry and Reynolds and Schmidt numbers [89, 171-175].

There are a number of experimental approaches to estimate \( k_f \) or the CP level in a membrane channel [150, 172, 176]. However, one can use a model-based approach or computational fluid dynamics (CFD) simulations in order to account for spacer filaments in RO feed channels, geometry of membrane modules, as well as local variations in crossflow velocity and permeate flux [88, 89, 177-179]. CFD simulations coupled with mass transfer models of local CP have been used to predict crystal nucleation and growth rates and the resulting permeate flux decline with generally good agreement. Indeed, such is the case for experimental observations with a rectangular plate-and-frame RO flow cell, such as the one used in the present work [86, 88, 89]. More recently, a simple single-parameter model was used to predict surface area coverage of calcium sulfate scaling and resulting flux decline and frictional pressure drop for a tubular RO membrane [129]. In industrial RO membrane systems, operating guidelines limit the level of CP (typically, \( CP \leq 1.2 \) [43]) by limiting the allowable water recovery level per membrane element (\( \leq 18\% \) for standard 40” long elements) [180].

In experimental systems with low membrane area and low recovery (e.g., <1%), one can induce supersaturation within a CP layer rather than using supersaturated feed. Such systems can
be correlated to conditions expected in the tail element of RO plants by defining an equivalent recovery level, $Y_{eq}$ \textbf{(Eqn. 2-11)}, according to the CP modulus in the experimental system by modifying \textbf{Eqn. 2-9}. Conversely, a CP allowance factor, $\alpha \geq 1$, may be added to \textbf{Eqn. 2-9} to account for CP that may be encountered in a RO plant \textbf{(Eqn. 2-12)} [43].

$$Y_{eq} = \frac{CP - 1}{CP - (1 - R_o)}; \quad Y = \frac{(CF / \alpha) - 1}{(CF / \alpha) - (1 - R_o)}$$ \quad (2-11; 2-12)

\textbf{2.1.3 Membrane fouling}

Membrane fouling is the accumulation of foreign material onto membrane surfaces or inside membrane pores that is detrimental to membrane performance or the overall performance of the membrane system. Aside from mineral scaling, membrane fouling typically refers to the deposition of inorganic colloidal matter (including silica) [181-183], natural organic matter (NOM) [184-193] or bacterial microorganisms [25, 194-200]. The buildup of a fouling layer is described as a “cake” layer [135, 136, 176, 183, 201-204], or in the case of bacterial adhesion (i.e., biofouling), a “biofilm” layer [198, 205, 206]. Fouling layers (\textbf{Fig. 2-7}) impede water permeation through the membrane, and foulant material can also contribute to axial pressure drop in RO modules by adhering to feed channel spacers [196, 207-209]. Not only does fouling decrease productivity, but it can also impair product water quality by intensifying the membrane salt passage [182, 191, 198, 206] \textbf{(Fig. 2-8)}. One difference between membrane fouling and mineral scaling is that colloidal and biological fouling are typically expected to impact the lead membrane elements in RO plants, while mineral scaling and polymeric silica fouling are usually expected in the tail RO elements [132, 210] \textbf{(Fig. 2-9)}. Cleaning and removal of membrane fouling layers is a formidable task, and often requires the use of large volumes of harsh
chemicals (e.g., NaOH) and biocides for biofilm removal, often using heated solutions paired with pH adjustment [132, 211].

Figure 2-7. SEM micrographs depicting biofouling (*P. aeruginosa*) (A) and a cracked silica fouling layer (B) on membrane surfaces, adapted from [198] and [212], respectively.

Figure 2-8. The impact of biofouling on RO permeate flux and salt passage for different wastewaters (Left) from [198]; and (Right): the impact of organic fouling on TMP at various constant permeate flux levels from [135].
Figure 2-9. RO membrane fouling of lead element by iron oxides (left) and gypsum mineral scaling of tail element (right) from [210].

The rate of membrane fouling depends on membrane and feed spacer properties, operating conditions (e.g., permeate flux, crossflow velocity) and feed water characteristics (e.g., total suspended solids, bacteria levels, salinity, pH, turbidity, total organic carbon (TOC), silica concentration, etc.) [93, 101, 124, 184, 213-219]. The types and extent of membrane fouling also vary with the water source type (e.g., seawater, brackish groundwater, wastewater effluent, etc.). Recent work has suggested the concept of a “critical” permeate flux value for a given RO feed quality, below which fouling is avoided or is negligible [135-137, 220, 221]. However, most current fouling prevention or mitigation approaches involve the removal of potential foulants from RO feed waters.

In order to prevent fouling and associated problems and improve permeate flux, conventional pretreatment typically utilizes coagulation or flocculation, whereby particles are aggregated for easier removal, followed by a combination of media filters, cartridge filters, or backwashable MF or UF hollow fiber membranes [59, 94, 95, 97-105, 222-224] (Figs. 2-10, 2-11). While chlorination may additionally be used to disinfect RO feed and prevent biofouling, this requires dechlorination of the RO feed. It is noted, however, that free chlorine oxidizes and
can permanently damage polymeric membranes thereby leading to decreased salt rejection [123, 132, 166, 168, 225].

**Figure 2-10.** Example of RO pretreatment using inline coagulation following by UF membrane treatment, adapted from [94]. (PAC = polyaluminum chloride)

![Diagram of RO pretreatment using inline coagulation following by UF membrane treatment]

**Figure 2-11.** Improvement of permeate flux decline levels in RO desalination using membrane prefiltration, from [59].

![Graph showing permeate flux decline levels over time for different treatments]

In addition to conventional pretreatment techniques, several alternative pretreatment methods have been proposed for fouling (and scaling) prevention (particularly aimed at silica
removal), including activated carbon (BAC) addition [103], ion exchange [226], electrocoagulation [189, 212], adsorption [227], and ozonation [103]. When the above pretreatment schemes are unsuccessful or not feasible, RO plants may utilize dispersants, organic polymeric additives that impede the agglomeration of foulant particles and their subsequent deposition, and these may also retard mineral scaling to some degree [104, 123, 132]. For silica, specific inhibitors may also be employed to impede polymeric or colloidal silica formation [110, 123, 124, 214, 215, 228].

Common indicators of membrane fouling potential include turbidity, a measure of back-scattered light or “cloudiness” of a solution when exposed to a light source. Another metric is silt density index (SDI) [229], which is a measure of the extent of fouling by particulate matter on a 0.45 μm microfilter where a higher SDI value indicates a greater extent of particulate fouling. To prevent RO membrane fouling, it is recommended that RO feed water should have a SDI of 4.0 or less, with a recommended long-term average of 2.5 and a maximum turbidity of 1 NTU (nephelometric turbidity units) or less, with a recommended long-term average of 0.5 NTU [104].

While SDI requires a test kit and offline test procedure, turbidity can be monitored with online sensors, and is thus more convenient. One limitation of SDI is that it does not consider particles smaller than 0.45 μm, while the drawback of turbidity is that it is an aggregate metric of particle concentration and size and may not account for particles that do not exhibit light back-scattering, as has been demonstrated for small gypsum crystals formed in solution [140]. Therefore, some plants utilize particle counters to monitor the RO feed water [101, 132]. It should also be noted that the presence of particles in RO feed water can promote heterogeneous nucleation of mineral scale crystals and reduce the induction time for mineral precipitation,
thereby accelerating mineral scaling [230]. It follows that it may be useful to explore the merit of reducing mineral scaling by implementing effective RO feed prefiltration.

Lastly, an important impact of fouling to consider is that the local concentration polarization and osmotic pressure at the membrane surface may be enhanced by biofilms [198, 206, 231] and cake layers [201, 232]. Therefore, the coupled effect of membrane fouling layers on mineral scaling should be investigated [233]. Although studies of combined membrane fouling and mineral scaling are rare, studies have suggested that macromolecular foulants can both retard mineral crystal growth [234], and as is the case with biofoulants, may increase the CP level within the foulant layer [198, 206, 231].

### 2.2 Membrane Mineral Scaling

#### 2.2.1 Mineral scaling fundamentals

While conventional pretreatment is largely effective for fouling mitigation, it still does not remove sparingly soluble salts, thus mineral scaling still remains a significant hurdle for high recovery brackish RO and nanofiltration (NF) desalination [43, 72, 75, 81, 204]. Major mineral scalants of concern, naturally present in brackish water, include gypsum (CaSO$_4$·2H$_2$O) [43, 78, 82, 84-87, 113, 129, 140, 235, 236], calcium carbonate (CaCO$_3$) [78, 119, 125, 237, 238], and silica (SiO$_2$) [58, 68, 124, 138, 212, 239-243]. Typically of lesser concern are calcium phosphate [116, 244, 245], strontium sulfate (SrSO$_4$) [43] and barite (BaSO$_4$) [116, 246]. As the water recovery is increased, these minerals may become supersaturated in the retentate stream and either precipitate in the bulk stream and deposit on the membrane, or crystallize directly on membrane surfaces (Fig. 2-12) [81].
The prediction of mineral scaling tendency and RO recovery limits imposed by mineral scaling commonly utilizes thermodynamic calculations of supersaturation of a mineral salt's constituent ions, known as the saturation index, $SI$ [43, 247]:

$$SI_x = \frac{IAP_x}{K_{sp,x}} \tag{2-13}$$

where $IAP_x$ is the ion activity product, and $K_{sp,x}$ is the equilibrium solubility product constant for a given mineral denoted by $x$. For example, calcium sulfate (gypsum) saturation index is calculated from:

$$SI_g = \frac{[Ca^{2+}][SO_4^{2-}]}{K_{sp,g}} \tag{2-14}$$

where the activity of constituent ions is calculated from the product of the ion concentration and its activity coefficient. For example, calcium activity is calculated from: $[Ca^{2+}] = [Ca^{2+}] \cdot \gamma_{Ca^{2+}}$, where $[Ca^{2+}]$ is the molar concentration of calcium ions and $\gamma_{Ca^{2+}}$ is the activity coefficient for calcium. When the saturation index is above unity, then the solution is supersaturated with...
respect to a given mineral (i.e., $SI_x > 1$). In order to predict scaling tendency and corresponding RO recovery limits, the concentrations used in Eqn. 2-13 are typically the RO retentate concentrations based on the concentration factor, $CF$ corresponding to a specific RO recovery level (Eqn. 2-8). A thermodynamic software package for simulating solute and electrolyte interactions in aqueous solutions is commonly used for determining the values of $K_{sp,x}$, activity coefficients $\gamma_i$, and resulting $SI_x$ values [248].

In order to estimate saturation indices at the membrane surface, $SI_{x,m}$, the bulk solute concentrations must be multiplied by the CP factor (for each ion, $i$) before determining its chemical activity (Eqn. 2-15). The other calculated parameters ($K_{sp,x}$, $\gamma_i$) should also be recalculated under conditions at the membrane surface.

$$SI_{x,m} = \frac{IAP_{x,m}}{K_{sp,x}} = \frac{1}{K_{sp,x}} \prod_i CP_i C_{b,i} \gamma_i$$

Since calcium carbonate solubility is sensitive to solution pH, a commonly used metric for estimating its scaling tendency is the Langelier saturation index, LSI [249]:

$$LSI = pH - pH_s$$

which is the difference in the measured pH value and the pH at which calcium carbonate is saturated for a given feed solution. Therefore, a negative LSI indicates that a solution can dissolve CaCO$_3$ and a positive LSI indicates a supersaturated solution where scaling can occur.

It should be noted that the prediction of scaling tendency, while useful for determining whether or not scaling can thermodynamically occur, does not provide information on mineral scaling kinetic rates for nucleation and growth; and thus by itself is not sufficient for predicting mineral scaling, particularly under field conditions [81].
Mineral scale nucleation is commonly described by the classical nucleation theory [109, 112, 230]:

\[ J_n = A_N \exp \left( - \frac{a_N}{(\ln(SI))^2} \right) \]  

where \( A_N \) is a nucleation rate constant or “frequency” constant, \( SI \) is the saturation index of the mineral of interest (Eqn. 2-13) and \( a_N \) is a lumped parameter defined as:

\[ a_N = \frac{16\pi\gamma^3v^2f(\theta)}{3k_B^3T^3} \]  

where \( \gamma \) is the crystal surface energy, \( v \) is the molar crystal volume, \( f(\theta) \) is a heterogeneous nucleation factor, \( k_B \) is Boltzmann’s constant (1.38 \times 10^{-23} \text{ J/K}), and \( T \) is absolute temperature (K). The parameter \( f(\theta) \) is equal to unity for homogeneous nucleation (i.e., in pure bulk solutions) and \( f(\theta)<1 \) for heterogeneous nucleation, in which crystal nucleation takes place on a foreign surface (e.g., suspended particles or membrane surfaces). The determination of nucleation rates, \( J_n \), as a function of \( SI \) is important for understanding mineral scaling kinetics. However, for certain ranges of \( SI \), it is possible to observe an “induction” period, \( t_{\text{ind}} \), defined as the period to detect the first observable crystals. Typically, this period has been estimated by either changes in bulk turbidity for bulk precipitation [111, 118], or the onset of observable permeate flux decline associated with mineral scaling [109, 129, 246, 250-252]. However, these approaches have been challenged in recent years as microscopic measurements have suggested that significant nucleation can take place before it is suggested by changes in permeate flux [85, 125, 140, 238]. Indeed, previous work with silica precipitation hypothesized that the majority of silica particle nuclei are formed during the induction period [253].

As mineral scale crystals grow laterally, more membrane surface area is steadily blocked, reducing water permeation and shortening the useful membrane life [82-87, 132]. The growth of
individual scale particles or crystals is typically described by a simple rate model with a concentration driving force [83, 84, 86, 112]:

\[
\frac{dm}{dt} = k_c A_e (C_m - C_s)^n
\]  

(2-19)

where \( m \) is the mass of the crystal, \( k_c \) is a mass transfer coefficient for crystal growth, \( A_e \) is the crystal surface area, \( C_m \) is the mineral salt concentration at the solution-crystal interface, \( C_s \) is the saturation concentration and \( n \) is a power valued between 1 (diffusion-controlled growth) and 2 (surface-reaction controlled). The approximation \( n=1 \) is used for typical conditions under which mineral scale crystals are observed [112]. Assuming a hemispherical geometry for the mineral crystals, then \( A_e = \pi \cdot d_{eq}^2 / 2 \) and \( m = \rho \cdot \pi \cdot d_{eq}^3 / 12 \), the change in crystal diameter can then be described by:

\[
\frac{d(d_{eq})}{dt} = \frac{2k_c}{\rho} (C_m - C_s)
\]  

(2-20)

where \( d_{eq} \) is the equivalent diameter of the crystal and \( \rho \) is the crystal mass density. The development of crystal growth has been estimated by flux decline models [83, 84, 129], as well as by direct microscopic observation on a membrane surface [85, 86, 112].

Mineral scales can have drastically different morphologies, depending on water chemistry and presence of growth retardants (i.e., antiscalants, Sec. 2.2.2), ranging from mineral crystals such as rhombohedral calcite or spherical vaterite (CaCO₃), gypsum (CaSO₄·2H₂O) rods and rosettes, and amorphous silica particles (Fig. 2-13). Silica chemistry is quite complex; and in water, aqueous silica exists as silicic acid or silicate ions, and depending on water chemistry, may form polymeric silica, colloidal silica, or metal silicates [124]. Silica deposits are amorphous rather than crystalline [253, 254]. In all cases, mineral scale is difficult to remove once established, and often requires high or low pH cleaning (e.g., with citric acid or NaOH),
with chelating agents such as EDTA or surfactants such as SDS [116, 132, 146, 242, 255, 256]  
(Fig. 2-14). Therefore, early detection of mineral scaling is critical to enable efficient cleaning 
and minimal usage of chemicals and thus reduction in plant downtime.

Figure 2-13. Examples of mineral scaling morphologies: Top Row: calcium sulfate (gypsum) 
rods and rosettes [236]; Middle Row: spherical and rhombohedral calcium carbonate crystals [257], Bottom Row: amorphous silica [138].
Figure 2-14. Example of chemical cleaning and removal of severe calcium sulfate mineral scaling using a combination of chemicals for complete recovery of permeate flux from [255].

2.2.2 Mineral scaling mitigation

While mineral scaling can be reduced to a degree by effective fouling mitigation schemes, more targeted approaches are necessary for mitigating mineral scaling. Clearly, operating at conservatively low or “safe” water recovery levels can avoid supersaturation and mineral scaling. However, this approach reduces productivity, increases brine production and thus is not recommended for brackish water RO. There have been other proposals for mitigating scaling, such as the continuous rotation of the membrane modules, thereby introducing shear at the membrane surface to periodically disrupt concentration polarization [258]. The application of this cumbersome approach has not been validated under field conditions. Another alternative approach is the application of ultrasound waves to mitigate scaling [259], but this would likely be difficult to employ in full scale applications. Indeed, most mitigation techniques have focused on either the removal of scale precursors, chemical pretreatment for scale suppression, or adjusting plant operating conditions.
Mineral scaling mitigation methods that minimize the use of chemicals and plant downtime are clearly desirable. Over the past decade or so, the concept of feed flow reversal (FFR) (Fig. 2-15) has been demonstrated as an approach to mitigate scale crystal formation by alternating the crossflow direction such that the tail membrane becomes the lead membrane. In such an approach, the axial CP profile is periodically reversed in order to reset the induction period for mineral scaling [260]. If the bulk solution is undersaturated with respect to the primary mineral scalants, FFR enables the periodic dissolution of mineral scale crystals previously formed near the exit or tail element of RO trains [139, 261].

Figure 2-15. Concept of feed-flow reversal (FFR) operation for mineral scaling mitigation in brackish water RO [139].

Another technique proposed for mitigating mineral scaling and removing fouling layers is by inducing permeate back-flow via forward osmosis by temporarily introducing a high salinity feed solution [262, 263]. This is thought to dislodge foulant particles on the membrane surface and clean the surface.
In addition to direct scale removal, several processes for RO pretreatment or scale precursor removal have been proposed as additional process units. These include nanofiltration [264-266], CO₂ stripping [267], and chemical softening and/or induced precipitation [75, 226, 268-275]. While nanofiltration is less energy intensive, NF membranes can experience mineral scaling and other fouling problems similar to RO [49, 141, 191, 235]. While such pretreatment schemes can be effective, hybrid processes are inherently more complex, limiting their application.

Given that mineral salts may be near/at or above saturation in brackish water RO concentrate, demineralization (i.e., induced precipitation) processes have been proposed for RO concentrate treatment aimed at high recovery operation, usually implemented as interstage processes with secondary RO desalting (Fig. 2-16) [74, 76, 77, 276, 277]. The demineralization of BWRO concentrate has been successfully demonstrated for removing significant mineral salts (e.g., CaCO₃ and CaSO₄), while reducing brine disposal requirements. Economic analysis for desalination of brackish AD water (salinity of ~14,810 mg/L TDS, feed SI₉≈0.85–0.97) revealed that a conventional RO system operating at only 62% water recovery can still be competitive with a two-stage RO system with interstage demineralization operating at 93% overall recovery, even with a higher percentage of associated brine disposal costs [74]. Therefore, it follows that if RO desalination can be safely operated at increased recovery levels with effective scaling mitigation (e.g., >75%), a conventional RO system may be more economical, while also being simpler to operate and requiring less chemicals. Such an RO process, when integrated for high recovery or concentrate treatment, could also improve the performance of the demineralization process by providing greater concentration driving force for precipitation. One should also note
that an integrated system with RO concentrate treatment becomes more competitive as both brine disposal costs and product water value increase.

Figure 2-16. Two-stage RO process with intermediate concentrate demineralization (ICD). (PRO: primary RO; SRO: secondary RO) from [278].

A conventional technique for preventing CaCO₃ mineral scale formation is by the adjustment RO feed pH. It is common to accomplish the above by the addition of sulfuric or hydrochloric acid to reduce the pH and LSI (Eqn. 2-16) of the RO feed and shift the bicarbonate equilibrium in favor of dissolved ions [78, 123]. On the other hand, operation at high pH has been recommended for preventing silica scaling in RO, though this should be coupled with hardness removal to prevent metal silicate scaling [124]. For example, the so-called High Efficiency RO (HERO) process operates at high pH to avoid silica scaling and uses ion exchange pretreatment to remove hardness cations [124]. However, adjustment of pH is costly for buffered waters and is not effective for all scale-forming species [43]. Additionally, it is usually recommended to operate RO membranes within a specified safe pH range to increase the useful life of the membranes [132, 166].

Despite the above efforts, the most widely practiced approach for mitigation of pH insensitive mineral scalants (e.g., gypsum) is the addition of scale inhibitors (i.e., antiscalants,
Antiscalants are typically polyelectrolytes or other polymeric acids of many varieties including polyphosphates (e.g., sodium hexametaphosphate, SHMP), polyphosphonic acids, polycarboxylic acids or polyacrylic acids, though most antiscalants are provided as proprietary blends [81]. Antiscalants sequester or scavenge mineral scale precursors and can adsorb onto mineral crystal surfaces (e.g. gypsum crystals), thus retarding both the nucleation and growth of scale crystals [22, 72, 81, 107, 112, 113, 236, 279]. While antiscalants do not remove mineral scalants from the feed stream, they can significantly delay the onset of mineral precipitation at supersaturated conditions and reduce the severity of permeate flux decline [78, 81, 87, 106, 108, 109, 112, 113, 117, 280]. Antiscalants can also lead to alteration of crystal morphologies of mineral crystals [81, 117, 234, 236].

Antiscalant selection for RO processes currently relies primarily on feed water quality analyses revealing sparingly soluble mineral salts [72, 81, 104, 108, 123, 132] and the evolution of their supersaturation as water recovery is elevated [43]. Industry guidelines also provide maximum recommended mineral supersaturation levels for effective antiscalant use [43, 123]. For effective antiscalant use, antiscalants must also be compatible with the type of membranes being used. Selection of the appropriate antiscalant feed dose for mineral scale control is particularly important, since higher concentrations of AS are typically more effective [72, 78, 87, 106, 107, 110-113, 118, 119, 127, 128]. However, the AS dose should be optimized in order to limit chemical costs. Overdosing also risks promoting biofouling or antiscalant fouling [72, 281-283]. Additionally, residual antiscalants in the RO concentrate must often be removed for effective brine treatment [276, 284].
2.2.3 RO membrane mineral scaling and fouling detection techniques

2.2.3.1 Conventional membrane performance monitoring

In conventional RO plants, testing of antiscalants and other operating conditions (i.e., water recovery) for scaling and fouling mitigation usually involves tedious long-term pilot studies. One shortcoming of such studies is that they typically rely on long-term trends of RO membrane permeability or other indirect indicators of fouling and mineral scaling (e.g., Fig. 2-17, Fig. 2-18) [109, 127, 130, 131, 280].

**Figure 2-17.** RO permeate flux decline due to silica scaling (Left) as a function of water recovery with different antiscalant types [280]; and (Right) flux decline at different gypsum saturation indices, with and without antiscalant addition [113].
Figure 2-18. Permeate flux decline (predicted and measured) during gypsum scaling of a RO membrane at different saturation index (SI) values, from [129].

Another approach for early mineral scaling detection in RO plants proposes the use of a small surrogate RO system for use with a portion of the RO concentrate from a larger plant. This above approach serves to provide more sensitive measurement of the normalized permeate flux [133] (Fig. 2-19). However, with such monitoring approaches, there is no direct confirmation of fouling or scaling until a membrane autopsy is performed [28, 76, 141, 142]. While autopsies can reveal the elemental composition of mineral scales, early detection and prevention are clearly preferable.

Figure 2-19. Schematic showing placement of a small surrogate RO system (scaling monitor) for monitoring flux decline due to scaling from RO concentrate slipstream [133].
Commonly monitored indicators of mineral scaling include normalized permeate flux (for constant pressure), transmembrane pressure (TMP) (for constant permeate flow), axial pressure drop, or salt passage [82-84]. Typically, a 10-15% change is diagnosed as a fouling or scaling problem [132]. However, quantifying the onset of mineral scaling via such performance indicators is imprecise. As discussed previously, nucleation of mineral crystals can occur much earlier than the detection of its influence on flux decline. Secondly, flux decline may also be a result of other types of fouling (e.g., particulate matter, biofouling). Salt passage increase may be due to a membrane integrity breach that can have various causes [168]. Lastly, changes in environmental conditions (e.g., water temperature or salinity) can result in changes to osmotic pressure and permeate flux (Eqns. 2-1 & 2-2). However, when fouling or scaling has already caused a 10-15% change in performance, it may be well-established and difficult to clean [81]. Clearly, early detection of incipient membrane mineral scaling is necessary to prevent the occurrence of performance decline and enable corrective operating adjustments before it becomes infeasible to take such actions.

2.2.3.2 Indirect membrane monitoring methods

The state of the art in RO membrane monitoring and fouling detection has evolved over recent years with several “non-invasive” monitoring techniques emerging as alternatives to conventional performance monitoring. These include ultrasonic time domain reflectometry (UTDR) and electrical impedance spectroscopy (EIS).

The UTDR approach involves pulsing ultrasonic waves into a membrane cell fitted with ultrasonic transducers that indicate the time required for the ultrasonic waves to pass through
different materials in the membrane cell, including fouling layers. The waves are reflected back to the transducer and the wave amplitude is measured in real-time (Fig. 2-20).

\[ t = t_{\text{fouling}} = t_B - t_C \]

**Figure 2-20.** Concept of UTDR fouling detection in a parallel plate flow cell (Left) and representation of typical UTDR detection results (Right) from [150].

The thickness of a reflected layer (e.g., fouling layer) can be estimated by calculating the travel distance ($\Delta d$) from the measured arrival time ($t$) if the wave velocity ($c$) through the medium is known, using the following equation (Fig. 2-20):

\[ t = \frac{2\Delta d}{c} \]  

(2-21)

The UTDR method has been demonstrated for both colloidal fouling and mineral scale detection [136, 145-150]. However, mineral scale detection usually requires the use of multiple transducers spaced along the length of the cell (Fig. 2-21). Indeed, mineral scaling nucleates stochastically in localized areas as opposed to a widespread (biological, organic, or colloidal) fouling layer. However, even with multiple transducers, mineral scaling may not first occur (i.e., as sparsely distributed small crystals or crystal nuclei) on transducer locations. This shortcoming
is further highlighted by the fact that the presence of an internal transducer can disrupt the local concentration polarization by blocking permeation in the local membrane region [145].

Figure 2-21. UTDR setup with multiple ultrasonic transducers on a RO cell for mineral scaling detection, from [147].

Figure 2-22. UTDR detection of colloidal silica fouling indicating changes in ultrasonic amplitude over time, from [150].
While UTDR measurements could in principle provide early detection of colloidal fouling, indicated as a change in amplitude (Fig. 2-22), and also estimate fouling layer thickness (for layers ≥0.5 µm), there are clear limitations when it comes to incipient mineral scaling detection. Comparisons of UTDR and flux decline measurements have shown that in this approach the level of accuracy is essentially similar to that obtained with flux decline measurements. Nonetheless, with the proper signal calibration, UTDR monitoring was demonstrated as a sensor to control feed flow reversal operation for effective scaling mitigation [151, 152].

![Electrical impedance spectroscopy setup for RO membrane fouling detection](image)

**Figure 2-23.** Electrical impedance spectroscopy setup for RO membrane fouling detection, from [154].

Electrical impedance spectroscopy (EIS) monitoring has also been proposed for mineral scale detection, as well as detection of biofouling and colloidal fouling [153-155, 285, 286]. In EIS, a sinusoidal AC current is applied at various frequencies using electrodes in a membrane cell (Fig. 2-23) and the electrical properties (conductance, impedance, etc.) of the membrane are
measured. However, it is emphasized that the membrane electrical properties can change due to fouling or mineral scaling on the membrane surface and distinguishing the above is complex and may be infeasible.

**Figure 2-24.** EIS detection of calcium sulfate scaling on RO membrane compared with permeate flux decline data, at various frequencies, from [153].

Similar to UTDR, EIS studies have proven sensitive to colloidal fouling, and capable of the detection of fouling buildup prior to significant flux decline or TMP increase, where a clear shift in the membrane conductance was observed while ≤10% increase in the TMP was observed [154]. For mineral scaling (CaSO₄) detection, EIS was capable of detecting changes in electrical conductance that occurred more rapidly than changes in permeate flux decline (Fig. 2-24) [153].

However, both EIS and UTDR only provide an indirect indication of a foulant buildup on the membrane surface, without direct visual confirmation. Therefore, it may be advantageous to employ a more direct monitoring approach, which can also help elucidate mineral scaling kinetics and evaluate mineral scaling mitigation methods (Secs. 2.2.1 & 2.2.2).
2.2.3.3 Direct visual membrane monitoring

Unlike indirect approaches, direct monitoring of membrane surfaces by visual means (e.g., microscopy) can provide unambiguous detection and characterization of membrane fouling and mineral scaling. Direct visual monitoring of membrane fouling and mineral scaling is a non-invasive method, pioneered by Cohen and Uchymiak [85, 157] specifically for high pressure RO system monitoring (Fig. 2-25). Such direct membrane surface monitoring has been demonstrated as a particularly effective approach for detecting the early onset of mineral scaling [85]. The approach was utilized to investigate gypsum scaling kinetics (Figs. 2-27, 2-28) through real-time surface image analysis. Mineral scaling kinetics were thus quantified and scale morphology was also be ascertained visually [78, 85-87, 91, 113, 139]. Using this approach, one can evaluate the evolution of crystal nucleation and the growth rate of individual crystals over time (Fig. 2-29). At different SI values, the diffusive crystal growth model (Eqns. 2-19, 2-20) can be applied and fit to experimental data to determine the dependence of supersaturation on growth rates.

![Figure 2-25. Membrane monitoring cell for direct detection and monitoring of mineral scaling, left image adapted from [156].](image)
Figure 2-26. Experimental setup for optical RO cell for mineral scaling detection in total recycle mode [85].

Figure 2-27. Demonstration of visual detection of incipient mineral scaling prior to significant flux decline using the Ex-situ Scale Observation Detector (EXSOD) [85].
Direct visual monitoring of mineral scaling development can also been used to validate or confirm theoretical models of mineral scaling nucleation (Sec. 2.2.1). For example, the visually observed nucleation rate of mineral scale crystals is given as [112]:

\[
J_N = \frac{1}{1 - \phi} \frac{dN}{dt} = \frac{\dot{J}_N}{(1 - \phi)}
\]  
\begin{equation} \tag{2-22} \end{equation}

where \(J_N\) is the nucleation rate (Eqn. 2-17), \(dN/dt\) or \(\dot{J}_N\) is the observed time rate of change for the number of mineral scale crystals, and \(\phi\) is the fractional surface scale coverage on the membrane. Direct observation of gypsum crystal nucleation can also reveal valuable insights into the change in crystal nucleation rates and associated parameters by the addition of antiscalant (Fig. 2-30). Additionally, direct monitoring can also verify the predicted scaling behavior from the local distribution of saturation indices resulting from CFD simulations [88] (Fig. 2-31).

**Figure 2-28.** Tracking of mineral crystal growth (Top) and quantification of the time progression of membrane surface area coverage by mineral scale at different SI values (Bottom Left) and individual crystal growth tracking (Bottom Right) [86].
Figure 2-29. Change in gypsum crystal nucleation rates as a function of saturation index with and without antiscalant [112]. Note: AS = antiscalant.

Figure 2-30. Observed gypsum mineral scaling on membrane sample (a) and model-predicted saturation index of gypsum at the membrane surface in a plate-and-frame membrane module (b) [88].

Direct membrane monitoring useful for laboratory studies of mineral scaling kinetics and can also be used for online RO plant monitoring. For example, in a recent study, an optically transparent membrane monitoring system was integrated with a spiral-wound RO pilot plant’s
concentrate stream in order to enable triggering of flow reversal for scale mitigation [139]. In the study, mineral scaling was detected prior to observable permeate flux decline in the monitoring cell and in the RO plant’s tail membrane element (Fig. 2-32).

![Membrane Monitor Permeate Flow Rate](image)

**Figure 2-31.** (A) Detected mineral scale surface coverage detected using membrane monitoring cell for direct observation, and associated permeate flux decline in the scale monitoring cell, tail element, and overall plant permeate during spiral-wound RO pilot plant monitoring and (B) optical surface images of mineral scale development, adapted from [139].

Given the promise of the above membrane monitoring approach for detection of mineral scaling and evaluation of operating conditions (e.g., $SI$, antiscalant), such a method would be helpful for evaluating mineral scale mitigation strategies. Here it is noted that direct visual monitoring of mineral scaling under field conditions or other mineral scales of interest (e.g., silica) has not been reported, in part due to the challenge of performing real-time image analysis.
Chapter 3

Real-time Direct Detection of Silica Scaling on RO Membranes

3.1 Overview

Silica scaling or fouling can be particularly problematic in brackish and industrial waste water RO, even when hardness is removed from the source water [74-77, 124, 226]. The range of encountered silica concentration is typically ~12–60 mg/L [43, 75, 87, 138, 212, 287] for brackish water and ~28–200 mg/L [58, 100, 102] for certain industrial wastewater streams (e.g., cooling tower blowdown (CTBD) water). Upon RO desalination of such water sources, silica can precipitate on the membrane surface when its concentration exceeds its solubility which, for example, is only ~115 mg/L at pH=7 and 25°C [288-290]. Indeed, silica has one of the most confined recommended upper limits of supersaturation (i.e., SI=1) for effective antiscalant use, according to industry guidelines [123]. Unlike some mineral salt scalants, silica chemistry is quite complex. Under supersaturated conditions, silica in solution can form “polymeric silica” and spherical colloidal particles in the nano-size range that may further agglomerate to form particles in the submicron size range [124, 138, 253, 291-294].

Silica polymerization initially involves silanol groups reacting to form dimers. In neutral or acidic conditions (pH < 7.5) silicic acid dimerizes according to the condensation reaction [124, 253, 254, 289, 295]:

\[ 2\text{Si(OH)}_4 \rightarrow (\text{OH})_3\text{SiOSi(OH)}_3 + \text{H}_2\text{O} \quad (3-1) \]

and under alkaline conditions (pH > 7.5), silicic acid reportedly dimerizes with silicate ion according to [253, 296]:

\[ \text{Si(OH)}_4 + \text{SiO(OH)}_3^- \rightarrow (\text{OH})_3\text{SiOSi(OH)}_3 + (\text{OH})^- \quad (3-2) \]
Silica dimers can then polymerize further with large formed oligomers that grow to larger particles, which can then agglomerate into rearrangeable networks or “gel” that makes up amorphous silica scale. It is noted that while silica solubility increases with temperature [124, 288, 290, 297, 298], the rate of silica polymerization is higher at elevated pH and temperature [291-294].

Previously, the study of the kinetics or inhibition of silica precipitation has almost exclusively taken place in bulk solutions [228, 253, 254, 295, 296, 299-302], and only rarely extended to membrane studies [138, 243, 280, 287]. While prior studies have suggested an induction period for silica precipitation [124, 296, 299, 300, 303-305], it is not yet clear whether such an induction period would impact the onset of silica scaling and associated permeate flux decline for membrane systems. Additionally, in many RO membrane studies, silica fouling is induced by introducing pre-made colloidal silica particles (usually 20 nm nominal size) [135, 136, 148, 150, 154]. In practical operation, RO retentate silica concentrations may realistically contain dissolved silica and be closer to the saturation limit, according to standard guidelines [126].

In order to mitigate silica scaling in RO operations, chemical antiscalants, dispersants or polymerization inhibitors may be utilized to prevent silica polymerization or agglomeration, often with mixed results [58, 110, 228, 243, 280, 287, 306], in addition to operation at high pH when feasible [124, 126, 214, 215]. Success with antiscalants has been limited, spawning efforts to formulate silica-specific inhibitors [110, 124, 228] as well as silica removal as RO pretreatment [94, 212, 226, 227, 271, 306, 307], which can be effective, though this requires additional process units. Operating at high pH further requires effective hardness and metals removal, with recommended levels of Fe$^{3+}$ and Al$^{3+}$ down to <0.05 mg/L [214], in order to
prevent metal silicate scaling, including aluminum silicates. Indeed, silicate ion is more abundant at higher pH and occurrence of silicate scaling is highly dependent on the presence of metal cations [81, 110, 116, 124, 243, 253, 300, 307-309]. Accordingly, it has also been proposed that operation at low pH levels may be advantageous, since both silica polymerization and silicate scale formation are inhibited at low pH, and this may be feasible for water sources such as acid mine drainage [124]. In any case, understanding silica surface scaling kinetics is a fundamental step towards effective silica scaling mitigation strategies and facilitating high recovery RO operations.

In RO systems, early detection of silica scaling is desirable in order to trigger the appropriate strategy for mitigating or avoiding silica scaling, as once it is established it can be challenging to remove and may require harsh chemicals [110, 116, 242, 310, 311]. In this regard, various studies have focused on indirect fouling indicators, such as permeate flux decline (for constant pressure operation) or transmembrane pressure rise (for constant flux operation) in order to determine the onset and severity of silica scaling [134, 135]. These approaches, however, are of insufficient accuracy for detecting the onset of silica scale formation. Moreover, there has yet to be a demonstration of real-time visual detection for silica scale formation and quantification of its growth kinetics on a membrane surface.

Accordingly, the present chapter focuses on demonstrating a real-time direct membrane surface monitoring approach for the early visual detection and elucidation of the kinetics of silica scaling (relative to flux decline measurements) on a commercial RO membrane. The kinetics of silica scaling (in terms of both surface coverage and surface number density of silica particles) were then quantified as a function of the level of silica supersaturation at the membrane surface. In addition, the morphology and surface roughness of silica scale on the membrane surface were
characterized at high resolution, via scanning electron microscopy (SEM) and atomic force microscopy (AFM), to illustrate the complex nature of silica scaling and demonstrate the presence of silica particles, aggregates, and gel-like silica film coverage.

3.2 Experimental

3.2.1 Membrane Monitoring System

Membrane scaling tests were performed with a novel membrane monitoring system [212] consisting of a transparent high pressure plate-and-frame RO (PFRO) membrane cell (Fig. 3-1) [85-89, 139, 156], having flow channel dimensions of 3.1 cm (width) x 8.8 cm (length) x 0.25 cm (height) with an active membrane surface area of 27.4 cm$^2$. Given the above small active membrane surface area, the attainable recovery was < 1%. The hydrodynamics and mass transfer characteristics of the PFRO membrane cell have been previously described, along with detailed quantification of concentration polarization [88, 89, 139].

Figure 3-1. RO membrane monitoring system used in total recycle mode for silica scaling studies.
Specialized external lighting was arranged along the membrane cell to provide high contrast relative to the native membrane background. Real-time surface images were captured with a digital microscope at high resolution (2592 x 1944) and transmitted to a computer for real-time monitoring and analysis.

All silica scaling experiments were carried out in a total recycle mode whereby the RO concentrate and permeate streams were returned to the feed vessel with the feed solution continuously mixed (using Stirrer Type RZR1; Caframo Limited, Georgian Bluffs, Ontario, Canada) (Fig. 3-1). The feed solution was pumped to the RO monitoring cell from a 25-liter plastic feed vessel using a 3/4 hp (559 W) positive displacement pump (Hydra-Cell Model P100; Wanner Engineering, Inc., Minneapolis, MN) controlled using a variable-frequency drive (VFD) (VS1MX11-4D Microdrive; Baldor Electric Company, Fort Smith, AR). The feed stream, prior to the pump inlet, was filtered through a 200 mesh (~75 µm) polyethylene strainer (Ron-Vik, Inc., Minneapolis, MN). The RO concentrate was filtered using a 0.35 µm pleated cartridge filter (Harmsco, Inc., North Palm Beach, FL) prior to returning to the feed vessel. Transmembrane pressure (TMP) was adjusted using the pump VFD and a back-pressure control valve (Jordan LowFlow Model MK708 LMO; LA Valves & Automation, Inc., Corona, CA) at the concentrate stream exit and monitored using both a digital pressure transducer and a mechanical pressure gauge (Model A-10, Model 232.53, respectively; Wika Instrument LP, Lawrenceville, GA). The feed and permeate volumetric flow rates were monitored using digital flow meters (Feed: Model 2000 Micro Flow, Georg Fischer Signet, El Monte, CA; Permeate: (FlowCal 5000 HPLC Liquid Flow Meter; Tovatech LLC, South Orange, NJ). RO permeate conductivity was monitored using an inline digital conductivity sensor (Model 2850; Georg Fischer Signet, El Monte, CA).
All scaling experiments were performed in a constant TMP mode. The feed solution temperature was maintained at 20±1°C using a recirculation water chiller (Neslab RTE-111; ThermoFisher Scientific, Waltham, MA) connected to a stainless steel cooling coil within the feed vessel. The feed solution electrical conductivity was measured using a conductivity meter (Con 110; Oakton Instruments, Vernon Hills, IL). The feed solution pH and temperature were monitored using a digital pH meter with built-in temperature sensor (sensION 4; Hach Company, Loveland, CO) and pH probes (PHG211-8 and REF201; Radiometer Analytical SAS, Lyon, France).

### 3.2.2 Materials and Reagents

A commercial flat-sheet brackish water RO membrane (UTC-70AC; Toray Membrane USA, Poway, CA) was used for all silica scaling experiments. This membrane was selected given its suitability for RO desalination of brackish water. Prior to testing, each membrane coupon was cut from a flat-sheet roll, rinsed for 1-2 minutes and soaked in distilled water (electrical conductivity ≤1 µS/cm) in a covered beaker for 1-2 hours. The membranes were first conditioned in the RO cell with distilled water for 1 hour. The hydraulic membrane permeability was determined using distilled water to be 6.5±0.5 x 10^{-3} m^3/(m^2·hr·bar), over a TMP range of 0.47–2.07 MPa (4.7–20.7 bar). Subsequently, the membrane was conditioned with a 2000 mg/L NaCl solution at a steady TMP of 1.38 MPa (13.8 bar) until the permeate flow rate stabilized (typically ~4 hrs), during which time the observed membrane salt rejection (R_o) was also determined to be 98±0.5% (R_o = 1 – (C_P/C_F), where C_P and C_F are the salinities of the permeate stream and the feed solution, respectively). At the end of each membrane test, the membrane was
removed from the PFRO cell, briefly immersed in distilled water to remove residual solution, dried in air, and stored in sealed plastic containers for further analysis.

Silica feed solutions were prepared by dissolving and mixing sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) as a silica source (99% purity in powder form; Strem Chemicals, Inc., Newburyport, MA) as recommended in previous studies on RO membrane silica scaling [110, 134, 137, 138]. The feed solution also included sodium chloride (NaCl) (99% granular; Fisher Scientific, Pittsburgh, PA), and sodium bicarbonate (NaHCO₃) (99% powder; Fisher Scientific, Pittsburgh, PA) as a pH buffer. Upon preparation and prior to acidification, the feed solution pH was ~11, at which the silica (SiO₂) concentration is predicted to be well below its solubility limit (Fig. 3-2).

3.2.3 Silica Scaling Experiments

Prior to each silica scaling run, the PFRO system was cleaned with an aqueous solution of NaOH (50% in H₂O; Sigma-Aldrich Corporation, St. Louis, MO) diluted in distilled water to a pH of ~12. The cleaning solution was pumped through the PFRO system in recycle mode for 2 hours to dissolve residual silica. The cleaning solution was then purged and the PFRO feed vessel was rinsed with distilled water that was circulated through the system for at least 1 hour. The process of refilling the feed vessel with distilled water, circulation, and draining was repeated at least twice, and until the feed vessel solution reached a pH ≤ 7. The feed vessel was then drained and filled with the silica feed solution for the next silica scaling test.

The feed solution contained 360 mg/L Na₂SiO₃·5H₂O, 85 mg/L NaHCO₃, and 2000 mg/L NaCl (Table 3-1). However, for the two experiments at the lowest SIm (i.e., 1.60 and 1.93, Table 2) NaCl concentration in the feed was raised to 4,000 mg/L in order to increase the feed osmotic
pressure and thus avoid operating at low TMP levels for the required initial permeate flux (<0.34 MPa (3.4 bar)) which would have resulted in feed pump pressure oscillations. It is noted that although salinity may decrease silica solubility [124, 253, 254, 300, 307, 308, 312], over the range of 2,000-4,000 mg/L NaCl there was less than 1% change in silica saturation index (SI). The feed solution was acidified, while mixing, by gradually adding concentrated HCl into the feed vessel to reach an initial pH of 6.0 prior to the start of each experimental run. The above pH level was set in order to minimize changes in solubility due to pH fluctuation and maintain the pH < 8, (i.e., since silica solubility increases rapidly at pH > 8). The saturation index of silica was calculated as $SI_{SiO_2(s)} = a_{SiO_2(aq)} / K_{sp, SiO_2(s)}$, in which $K_{sp}$ is the solubility constant, and where $a_{SiO_2(aq)} = \gamma_{SiO_2(aq)} \cdot x_{SiO_2(aq)}$ is the activity of SiO$_2$ in the aqueous phase with $\gamma_{SiO_2(aq)}$ and $x_{SiO_2(aq)}$ being the activity coefficient and mole fraction of silica, respectively. The calculations of $SI_{SiO_2(s)}$ were performed using the OLI thermodynamic multi-electrolyte package [248] for the present experimental conditions (Tables 3-1 and 3-2).

### Table 3-1. Silica feed solution.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed constituents</strong></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$·5H$_2$O</td>
<td>360</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>85</td>
</tr>
<tr>
<td>NaCl</td>
<td>2000–4000</td>
</tr>
<tr>
<td>SiO$_2$ (a)</td>
<td>102</td>
</tr>
<tr>
<td>SiO$_2$ solubility (a)</td>
<td>104</td>
</tr>
<tr>
<td>Silica (SiO$_2$) bulk saturation index (a)</td>
<td>0.987</td>
</tr>
<tr>
<td>pH (a)</td>
<td>6.0</td>
</tr>
<tr>
<td>Temperature (°C) (a)</td>
<td>20</td>
</tr>
</tbody>
</table>

(a) Calculated using the approach in [248].
Table 3-2. Experimental conditions for silica scaling tests\(^{(a)}\).

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Initial Permeate Flux (L/m²-hr)</th>
<th>Initial Average CP</th>
<th>( \text{SI}<em>m ) at the monitored region and average value ( \text{SI}</em>{\text{m}} )</th>
<th>Initial Local (and Average) Surface SiO₂ Conc. (mg/L)</th>
<th>Equivalent Recovery (average) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.6</td>
<td>1.60</td>
<td>1.60 (1.58)</td>
<td>165 (163)</td>
<td>36.7</td>
</tr>
<tr>
<td>2</td>
<td>24.1</td>
<td>1.80</td>
<td>1.93 (1.79)</td>
<td>199 (184)</td>
<td>44.1</td>
</tr>
<tr>
<td>3</td>
<td>28.5</td>
<td>1.95</td>
<td>2.10 (1.94)</td>
<td>220 (199)</td>
<td>48.4</td>
</tr>
<tr>
<td>4</td>
<td>43.4</td>
<td>2.45</td>
<td>2.72 (2.39)</td>
<td>281 (244)</td>
<td>58.1</td>
</tr>
<tr>
<td>5</td>
<td>63.5</td>
<td>3.10</td>
<td>3.50 (3.10)</td>
<td>361 (316)</td>
<td>67.7</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Crossflow velocity for each test was maintained at 4.2 cm/s for which Re=107; the Reynolds number is defined as \( \text{Re} = u \cdot H / \nu \), where \( u \) is the average crossflow velocity, \( H \) is the channel height, and \( \nu \) is the solution kinematic viscosity at 20°C; \( \text{SI}_m \) and \( \text{SI}_{\text{m}} \) are the silica saturation indices at the membrane surface in the monitored region and the axially average value along the membrane surface.

Figure 3-2. Effect of pH on silica saturation index for the RO feed solution used in the present study (\( T=20°C \)), total silica concentration = 1.7 mM (102 mg/L SiO₂).

At pH=6.0, the feed was nearly saturated with respect to silica (Section 3.2.2, Fig. 3-2), with SI=0.99 (\( T=20°C \)). During each run, the pH gradually increased from its initial pH~6.0 to a stable pH value of 7.2±0.2; the above behavior was expected due to carbon dioxide degassing.
until equilibrium was reached with respect to the bicarbonate in solution. Over the above range of pH increase, the bulk SI decreased by < 1% (i.e., from 0.987 to 0.981). At the above experimental conditions, the condition of SI<1 (Table 3-1) was maintained such that silica precipitation did not occur in the feed solution. Given the above solution composition, it was not anticipated that any form of fouling other than by silica could take place.

The feed crossflow velocity in the RO channel was maintained the same (4.2 cm/s) for all scaling tests. Therefore, in order to achieve the desired level of silica supersaturation at the membrane surface, the transmembrane pressure was set so as to control the permeate flux and thus the CP level at the membrane surface [88, 89, 92]. The CP level (defined as CP = Cm/Cb, where Cm and Cb are the silica concentrations at the membrane surface and in the bulk solution, respectively) was determined (Table 3-2) at the location of the membrane surface monitored region and average value over the channel length given the detailed CFD characterization available for the present PFRO cell [88, 89]. For the range of present experimental conditions, the resulting initial SI_m at the membrane surface (in the monitored region) was in the range of 1.60–3.50 (with channel average values in the range of $\bar{SI}_m$ =1.58-3.10). It can be shown, following the approach described in [43], that the SI range (Table 3-2) above, with the current silica feed solution (102 mg/L silica), would be expected in a spiral-wound RO plant operating at a recovery of 36.7–67.7%. It is noted that silica concentration in brackish groundwater is typically reported in the range of ~12-60 mg/L [43, 75, 87, 138, 212, 287] for which the present range of SI_m would be reached at recovery levels of ~62-95%. Therefore, it can be stated that the present experimental approach does cover the range of SI_m that would be expected under a reasonable range of practical high recovery RO field operations.
3.2.4 Membrane Surface Scale Analysis

3.2.4.1 Real-time Membrane Image Analysis

The monitored membrane area (field of view of ~36.2 mm²) was located between the center and downstream sections of the membrane channel (total membrane area: 27.4 cm²), centered at 6.1 cm from the channel inlet. Image analysis of the membrane surface images was conducted using the software described in [156] (Appendix B), with incorporation of adaptive image segmentation to highlight and quantify persistent surface changes due to mineral scaling or fouling [313]. Images were first converted to grayscale and subsequently aligned to enable accurate image comparison. Image subtraction was then carried out by subtracting the initial image at t = 0 (regarded as clean) from each subsequent image, in order to identify the evolution of surface changes over time (Fig. 3-3). The resulting image was enhanced based on histogram equalization in order to account for undesired lighting effects (e.g., shadows) and background noise [314, 315]. The resulting subtracted image was segmented (i.e., using a threshold) to yield the final processed binary image. The current analysis approach enabled detection of surface objects (particles) of size encompassing 50 pixels (~0.35 μm²) and larger. The identified scaled areas were quantified with respect to the scale surface area coverage, and the identified scaled entities (i.e., particles) were enumerated to track the temporal evolution of the particles SND and the fractional coverage in the field of view.

3.2.4.2 SEM-EDS Analysis of Membrane Samples

Membrane samples were analyzed using scanning electron microscopy (JSM-6700F Field Emission SEM; JEOL, Ltd., Tokyo, Japan) and EDS (EDAX Genesis Spectrum; EDAX Inc., Mahwah, NJ). Prior to analysis, membrane samples were pre-coated using a vacuum sputtering system with a 15-20 nm layer of gold in order to increase the electrical conductivity of
the samples (Hummer 6.2 Sputtering System; Anatech USA, Union City, CA). EDS enabled determination of the major elements present in the membrane foulant layer. Samples were also sectioned and imaged via Focused Ion Beam (FIB) SEM (Nova 600 NanoLab DualBeam SEM/FIB; FEI Company, Hillsboro, OR). These samples were first coated with 50–60 nm of gold and a thin strip of platinum was coated on the sample above the cross-sectioned location just prior to FIB sectioning.

**Figure 3-3.** Example of real-time membrane surface images (Left) and segmented binary images (Right) of the grayscale images obtained from silica scaling Run 5 ($SI_m = 3.50$).
3.2.4.3 AFM Surface Analysis of Membrane Samples

Membrane surface topography was analyzed via atomic force microscopy (AFM) (Dimension Icon; Bruker Corp, Santa Barbara, CA). AFM scans were taken in PeakForce Tapping mode in ambient air using a Bruker ScanAsyst-Air probe (a triangular silicon nitride cantilever with 0.4 N/m nominal spring constant, 70 kHz nominal resonance frequency, and 2 nm nominal tip radius). AFM scans (20 μm x 20 μm or 50 μm x 50 μm) were taken at a scan rate of 0.5–0.9 Hz for 3–5 locations on each membrane sample surface; scans were replicated at the same location at 0º and 90º to verify that the images were free of directional errors. Membrane surface roughness was quantified in terms of the root-mean-square (RMS) surface roughness, 

\[ R_{\text{rms}} = \sqrt{\left[ \frac{1}{N} \sum (Z_i - Z_{\text{avg}})^2 \right]} \]

where \( Z_i \) is the surface feature height of the \( i \)th sample out of \( N \) total samples, and \( Z_{\text{avg}} \) is the average feature height.

3.3 Results and Discussion

3.3.1 Permeate Flux Decline and Early Detection of Scaling

Measurable permeate flux decline was observed for all the silica scaling tests (Runs 1-5) for which the average silica saturation, at the membrane surface (\( \overline{SI}_m \)), was in the range of 1.58–3.10 (Fig. 3-4). Permeate flux decline was gradual for Runs 1-3 for which \( \overline{SI}_m \) was in the range of 1.58–1.94. For example, flux decline was only ~2 and 3% by 80 hrs of operation for \( \overline{SI}_m \) of 1.58 and 1.79, respectively, and ~10% for \( \overline{SI}_m = 1.94 \). Although flux decline was low (<5%) for \( \overline{SI}_m = 1.58 \) and 1.79, it reached levels of ~5% and ~15% (not shown) after operation
of ~200 hours. At the higher $\text{SI}_m$ levels of 2.39 and 3.10, flux decline of 14% and 19%, respectively, was reached within 20 hours of operation. At the latter highest saturation levels there were two noticeable rapid flux decline regions suggesting a high rate of silica scaling; an intermediate moderate flux decline region is also noticed and could be due to silica scale buildup in preferential areas. It is noted that, given the rapid flux decline for the high silica saturation ($\text{SI}_m = 2.39, 3.10$) scaling tests, these runs were terminated after 20-30 hr of operation to avoid excessive system scaling. Here it is noted that RO operation in which silica saturation index is in the above range would likely be infeasible without the utilization of antiscalants specific to retarding silica scaling.

Flux decline behavior for $\text{SI}_m =1.58-1.94$ which demonstrated an apparent scale induction period, is consistent with silica polymerization induction time in solution which is expected to increase with decreasing silica supersaturation [295, 296, 299, 300]. It is noted that in field applications it is typical to consider the induction time as that for which measurable permeate flux decline is indicative of the impact of fouling or mineral scaling. This threshold is typically considered to be ~5-10% flux decline for RO systems [132]. Following the above criterion, it is clear that the observed induction time for silica scaling (Table 3-3) was ≥60 hrs for $\text{SI}_m = 1.58$ and 1.79 and significantly lower ($t_{\text{ind}}=30$ hr) for $\text{SI}_m =1.94$. For the higher silica supersaturation levels the induction time was extremely short (<1–2 hr).

It is emphasized that determination of the onset of silica scaling via flux decline measurements is imprecise. First, silica scaling may occur much earlier than the detection of its influence on flux decline. Second, in field application of RO desalination, flux decline may be due to other types of fouling (e.g., particulates, biofouling, or other types of mineral scaling), as
well as changes in environmental conditions (e.g., temporally changing water temperature or salinity). In contrast, direct and real time image analysis of the membrane surface shows clearly and unambiguously much earlier detection, relative to flux decline, of the onset and evolution of silica scaling in terms of both surface scale coverage (Fig. 3-4B) and surface density of scale particles (Fig. 3-4C). For example, detection of silica scaling at a (monitored area) surface coverage of 0.2% was as early as 79 or 62 hr for $S_{I_m}$ of 1.60 and 1.93, respectively. At the higher $S_{I_m}$ of 2.10, 2.72 and 3.50, 0.2% area scaling occurred within 22 hr, 4 hr and 2 hr, respectively. While the present study was confined to a system where only silica scaling occurs, application of direct surface imaging to more complex (as may be encountered under field conditions) can provide information about the type of surface scaling/fouling [87, 91].

**Table 3-3.** Comparison of the time to reach various possible thresholds as indicators of the onset of scaling for different levels of silica saturation tested.

<table>
<thead>
<tr>
<th>$S_{I_m}$ at the monitored region and average value$^a$ ($\bar{S}_{I_m}$)</th>
<th>Observation Time for 5% Flux Decline (hr)</th>
<th>Scale Coverage at 5% Flux Decline (%)</th>
<th>Silica SND at 5% Flux Decline (#/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.60 (1.58)</td>
<td>165</td>
<td>3.50</td>
<td>16.0</td>
</tr>
<tr>
<td>1.93 (1.79)</td>
<td>92</td>
<td>0.95</td>
<td>9.6</td>
</tr>
<tr>
<td>2.10 (1.94)</td>
<td>52</td>
<td>9.95</td>
<td>15.9</td>
</tr>
<tr>
<td>2.72 (2.39)</td>
<td>1.3</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>3.50 (3.10)</td>
<td>0.14</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

$^a$ The $\bar{S}_{I_m}$ value in parentheses is the axially average value in the membrane channel.

A threshold for detecting the onset of silica scaling can also be set based on the SND. For example, for the local $S_{I_m}$ range of 1.60-3.50 (i.e., at the optically monitored membrane region), silica scale detection at the SND threshold of 50 silica particles/cm² (Fig. 3-4C) was significantly earlier (by a factor of 2–7) relative to the typical 5% flux decline threshold (Table
It has been previously suggested that the majority of silica nuclei are formed during the induction period [296], and that particle nucleation and growth precedes gelling [253]. This appeared to be the case as particles were detected and tracked, although SEM imaging revealed gel-like silica films also eventually formed for all SI\textsubscript{m} levels (Section 3.3.3, Figs. 3-9, 3-10, 3-11, 3-14). Following of the evolution of the silica particle surface number density (Fig. 3-4c) and growth (Section 3.3.2), in the monitored region, was feasible at the early stages of silica scaling (i.e., up to \(~20-50\) hours) (Figs. 3-4B-C, 3-7). At high silica saturation (SI\textsubscript{m} above \(\sim 2.72\)) significant flux decline was observed which was clearly beyond what could be attributed to surface area coverage by particles (Fig. 3-4). It is emphasized that one should not expect to observe congruent (i.e., 1:1) overall percent flux decline (for the PFRO channel) with percent surface scale coverage in the small monitored membrane area given: (a) the stochastic nature of mineral scaling, (b) differences in silica saturation between the local monitored area and other sections of the membrane [88, 89], and (c) silica gel (Section 3.3.3) which contributes to the observed flux decline is not tracked by surface optical imaging. SEM images (Section 3.3.3) and EDS analysis reveal the presence of a silica gel layer (which can be porous, Fig. 3-11H) with embedded silica particles. However, early detection of particles relative to flux decline is apparent in the low silica saturation runs (SI\textsubscript{m} = 1.6 – 2.1). The gel layer does contribute to blockage of the membrane surface; however, real time analysis of surface silica gel coverage is not feasible using currently available (real time) surface analysis methods. The use of batch studies (i.e., multiple scaling experiments of different time periods with surface analysis of membranes sacrificed at the end of each experiment), while feasible, is a daunting and challenging task given the stochastic nature of mineral scaling.
Figure 3-4. Normalized permeate flux (overall) (A), silica scale surface coverage (B) and particle surface number density (SND) (C) for the monitored membrane area for scaling runs at $\text{SI}_m = 1.60-3.50$ ($\text{SI}_m = 1.58-3.10$). (Notes: the SND is shown for the first 25 hr during which distinct particles could be distinguished. $F_t = \text{permeate flux at time } t$, $F_0 = \text{initial permeate flux}$ (Table 3-2)).
Figure 3-5. Comparison of operation times prior to different detection thresholds being met for early scale detection. Note: the SI\textsubscript{m} in the monitored region (where surface coverage and SND were measured) were monitored at SI\textsubscript{m}=1.60, 1.93, 2.10, 2.72, and 3.50, corresponding to the average levels in the range of 1.58–3.10.

3.3.2 Nucleation and Growth Kinetics of Silica Scale Particles

It is instructive to quantify the initial nucleation rates (when the surface is sparsely populated with silica particles and particle growth domains do not overlap) based on the membrane surface images following the approach in [112]. It should be recognized, however, that the current membrane surface observation technique (as well as others) is, at present, incapable of real-time imaging of nano-size nuclei. Nonetheless, observed rate of change of silica surface number density correlates directly with the silica particles nucleation rate given that every site of identified silica particle is also the site at which the tracked particle was nucleated. Accordingly, here the detection rate of silica particles (or observed nucleation rate),
$J_N$, as determined from the silica SND ($\bar{N}$) rate of change, $(J^0_N)_{\text{obs}}$, and the fractional membrane surface area covered by scale ($\phi$), is given as $J_N = (d\bar{N}/dt)/(1-\phi) = (J^0_N)_{\text{obs}}(1-\phi)$. The calculated nucleation rates can then be compared with the nucleation rate predicted based on the classical nucleation theory [112, 230]:

$$J_N = A_N \exp \left( -\frac{a_N}{(\ln(SI))^2} \right)$$

(3-3)

where $A_N$ is a nucleation rate constant, $SI$ is the silica saturation index, and $a_N = (16\pi^3 \nu^2 f(\theta))/(3k_b T^2)$, where $\gamma$ is the specific surface energy at the crystal/particle-solution interface (J/m$^2$), $\nu$ is the molecular volume (cm$^3$/mol), and $f(\theta)$ is the heterogeneous nucleation factor (where $\theta$ varies between 0 and 1), $k_b$ is the Boltzmann constant, and $T$ is temperature (K) [112].

![Graph](image)

**Figure 3-6.** Observed nucleation rates for silica particle nucleation and best fit curve from classical nucleation theory. Error bars represent concentration range for monitored membrane viewing area.
As shown in Fig. 3-6, Eq. (3-3) fits the experimental data reasonably well with the extracted parameters values of $A_N = 20.5 \text{ cm}^{-2}\text{hr}^{-1}$ and $a_N = 0.69$; the value of $a_N$ is in reasonable agreement with the value of $0.47 \pm 0.1$ recently reported for silica bulk phase nucleation (when corrected for temperature) [301].

The growth of the nucleated silica particles, prior to their incorporation/growth into the silica gel layer, was evaluated by analyzing the size evolution of individual silica particles. The particle size was quantified as the particle effective diameter, $d_{eq}$, defined as $d_{eq} = \sqrt{\frac{4A_p}{\pi}}$ where $A_p$ is the projected particle surface area. As shown in Fig. 3-7, for a given $\text{Si}_m$, silica particle growth was essentially linear with time. The growth rate of silica particles, expressed as $d(d_{eq})/dt$, increased by a factor of up to ~23 as the silica $\text{Si}_m$ increased from 1.60 to 3.50. The constant silica particle growth rate is suggestive of diffusional growth that can be described by the following classical model [84, 86]:

$$r_d = \frac{d(d_{eq})}{dt} = \frac{2k(C_m - C_s)}{\rho_p}$$  \hspace{1cm} (3-4)

where $k$ is the particle-fluid mass transfer coefficient, $\rho_p$ is the particle mass density (taken to be 2.196 g/cm$^3$ [316]), and $C_s$ and $C_m$ are the silica concentrations at saturation and at the particle-solution interface, respectively. As shown in Figure 3-8, the silica particle growth rate $(d(d_{eq})/dt)$ varied linearly with the concentration driving force (Eq. 3-4); for the present channel hydrodynamics (i.e., Re=107) the corresponding mass transfer coefficient ($k$) was estimated to be $9.2 \times 10^{-6}$ m/s. Below $(C_m - C_s) \approx 40 \text{ mg/L}$ the particle growth rate was too slow to ascertain to a reasonable level of confidence; at the above condition particle growth could be surface reaction controlled, but further work would be needed to evaluate this hypothesis.
Figure 3-7. Silica particle growth over time ($t_0 = $ initial observation time for each particle, $d_0$ is the initial observed equivalent particle diameter).

Figure 3-8. Correlation of silica particle growth rate with the concentration driving force for diffusional growth for $SI_m=1.60–3.50$ (i.e., difference between silica concentration at the membrane surface and silica solubility). (The horizontal and vertical bars represent the variation in local saturation levels and differences in individual particle growth rates, respectively).
3.3.3 Silica Scale Morphology

The scaled membrane SEM images revealed a range of surface morphologies, showing the presence of silica particles and agglomerates as well as a “gel” like coverage (Figs. 3-9, 3-10, 3-11, 3-14). The scaled membrane surface images for $SI_m=1.60-2.72$ (Runs 1-4) revealed strands of silica scale (silica gel) aligned in the flow direction (Fig. 3-10A,D) that apparently developed from silica particles. The extent of surface coverage and size of silica particles increased at the higher $SI_m$ of 2.10, 2.72 and 3.50 (Runs 3, 4 and 5), and the particles were primarily dispersed and roughly spherical in shape (Fig. 3-10A,B,G,H). Elemental analysis (EDS) confirmed the presence of Si and O atoms (Figs. 3-9F,I & 3-10C,F,I) consistent with the presence of silica scale. As expected, the Si EDS peaks for the lowest silica saturation levels of 1.60 and 1.93 (Runs 1 and 2) were less pronounced than for runs at higher silica saturation of 2.10-3.50 (Runs 3-5). At the lowest $SI_m$ of 1.60 (Run 1) there appeared to be a widespread and relatively uniform film of presumably silica gel (Fig. 3-11D-F), with sparsely dispersed aggregates of silica particles (Fig. 3-9D,E). At the higher $SI_m$ of 1.93 (Fig. 3-9G,H), the SEM images suggest a significantly higher density of silica particles that seem to be embedded within and also present above the silica gel film (Fig. 3-9G,H).
As the silica $S_{l,m}$ increased to 2.10 (Run 3) the surface appeared to be populated by larger discrete particles of about 1–5 $\mu$m in diameter, as well as a rough film (Fig. 3-10A-C). For the higher $S_{l,m}$ of 2.72 test (Run 4), which was of short duration (~20 hr) relative to the other runs, there are patches of silica gel (observed via SEM) (Fig. 3-10D), and a relatively uniform film in between the protruding silica scale patches, that appears to be embedded with silica aggregates (Fig. 3-10E,F). Discrete particles in the size range of 1–10 $\mu$m were also visible. For the scaling
test at the highest SI_m of 3.50 (Run 5), which was kept short (~25 hr) due to the severe fouling and rapid flux decline (Fig. 3-4), surface scaling was in the form of widespread silica “gel” layer with larger embedded silica particles (~10–30 μm) (Figs. 3-10G,H, 3-11); however, in contrast to the silica scale morphologies at lower SI_m, the silica scalant layer appeared to be porous and rough (Figs. 3-10H, 3-11G-I), which could possibly be due to insufficient time for film rearrangement given the relatively short duration of this run. For all supersaturation levels, a “gel” film eventually formed resulting in a widespread degree of surface coverage, as observed in SEM images (Figs. 3-9, 3-10, 3-11, 3-14).
Figure 3-10. SEM images at end of scaling tests, and corresponding EDS spectra for membranes scaled at $S_{I_m}=2.10$ (Run 3) (A-C), $S_{I_m}=2.72$ (Run 4) (D-F), and $S_{I_m}=3.50$ (Run 5) (G-I).
Figure 3-11. SEM images at end of scaling tests, and corresponding EDS spectra for native (i.e., clean) membrane (A-C) and gel-like film regions for membranes scaled at $SI_m=1.60$ (Run 1) (D-F) and $SI_m=3.50$ (Run 5) (G-I).
Surface roughness (determined via AFM) of the silica scaled membranes increased with rising level of silica supersaturation. Correspondingly, the surface feature heights also increased with a feature height distribution that became broader, at higher $SI_m$ levels (Figs. 3-12 & 3-13). For example, the native membrane RMS surface roughness was 84 nm with a mode of the feature height distribution of ~200 nm with a distribution width of ~500 nm (Figs. 3-12 & 3-13). In contrast, the membranes scaled at $SI_m$ of 1.60–3.50 had a significantly higher RMS surface roughness. 

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**Figure 3-12.** 3-D AFM images for feature heights for membranes scaled with silica at various SI levels (B-D) relative to the native (clean) RO membrane (A). Vertical and horizontal axes indicate the range of feature heights and planar location, respectively. RMS roughness values are inset. Scans were taken after the end of the scaling experiments.
roughness in the range of 216–699 nm and feature height mode of 900 nm–2500 nm (Figs. 3-12 & 3-13). It is noted that the broader feature height distributions are consistent with the presence of large aggregates (Figs. 3-9 & 3-10) at the higher levels of silica supersaturation.

**Figure 3-13.** (a) Feature height histograms and (b) mode of the feature height distribution and RMS surface roughness for membranes scaled at different $S_{Im}$ levels and for a clean membrane.
The silica scale layer is likely to be thin at the low SIm levels and there are regions of low coverage even at high silica saturation as suggested by the AFM analysis (Figs. 12 & 13). A confirmation of regions of thin silica layers on the RO membrane was undertaken via imaging of the sectioned membranes from Runs 1 & 2, via dual beam FIB-SEM. As revealed in Fig. 3-14, a foulant layer is present above the active membrane layer (Fig. 3-14). The scalant layer had a thickness in the range of ~250–300 nm for SIm=1.60 (Fig. 3-14D) with uneven thickness for SIm=1.93 ranging from ~300–700 nm (Fig. 3-14F). The “darker” dense layer between the scalant layer and the sponge-like (polysulfone) membrane support is identified as the polyamide RO membrane separation layer, with thicknesses in the range of 70–150 nm.

**Figure 3-14.** Examples of membrane cross-section images obtained via FIB/SEM (Magnification - A-C: 25,000X, D-F: 60,000X). A & B are the native (clean) RO membrane whereas C, D, and E, F are for membranes scaled at SIm of 1.60 and 1.93, respectively. Note that these end of run images reveal a silica scale layer on top of the active membrane layer.
3.4 Summary

Silica scaling of RO membranes was investigated via real-time direct surface imaging, flux decline measurements, SEM and AFM imaging over a range of silica supersaturation. The studies, conducted in an optically transparent RO plate-and-frame cell, demonstrated detection of silica scaling that is significantly earlier (by a factor of 2–7) than suggested by the detection of measurable flux decline (i.e., ≥5%). Real-time membrane surface image analysis also enabled quantification of silica scaling kinetics in terms of both percent scaled area and number density of silica particles. The rate of silica particle nucleation on the membrane surface appeared to follow classical nucleation theory with the growth of individual silica particles governed primarily by a classical diffusion mechanism. Based on present optical monitoring, SEM imaging and AFM analysis, it appears that silica scaling occurs through the formation of primary silica particles and their agglomerates (~1–30 µm), which were generally larger at higher supersaturation levels, as well as a silica gel-like film, which also contributes to flux decline, that can be smooth or rough with embedded silica particles. The silica scale layer thickness was in the range of 0.1–3.5µm and increased with silica supersaturation. Over the range of silica supersaturation of SI_m=1.60–3.50, the membrane surface roughness increased by a factor of 2.6–8.3 relative to the native membrane. At low levels of silica supersaturation, the silica gel film was smoother and appeared less porous than that formed at high supersaturation. At the higher supersaturation levels (i.e., SI_m=2.72-3.50, SI_m=2.39-3.10), silica scaling led to rapid permeate flux decline, attributed to primarily silica gel formation.

The present approach of real-time scale monitoring was demonstrated, for the first time, to be well suited for tracking the early development of silica scale (consisting of polymeric and/or colloidal silica) which is associated with the appearance of silica particles. Although silica
gel developed rapidly at $SI_{m} \geq 2.72$, operation at this supersaturation level without antiscalant
would not be recommended, considering the high rate of flux decline. The current monitoring
approach may be modified or combined with other methods to further elucidate the above. For
example, monitoring of silica scaling over the entire membrane surface would enable a
potentially revealing comparison to flux decline measurements. Developing the approach for
monitoring silica scaling in RO plants under field conditions (e.g., with actual cooling tower
blowdown or brackish water) is also suggested, but will require future efforts to assess the ability
to detect silica scaling in more complex solutions and in combination with other scalants/foulants
as well as antiscalant dosing of the RO feed.
Chapter 4

RO Membrane Mineral Scaling in the Presence of a Biofilm

4.1 Overview

Mineral scaling and other forms of fouling may occur concomitantly during RO desalination of certain types of wastewater, particularly with regard to municipal wastewater effluent. Although it has been shown that wastewater reuse can be beneficial [36, 317-324], reuse of secondary or tertiary treated municipal wastewater typically requires desalting of this water source (containing ~500-1,000 mg/L total dissolved solids (TDS); [36, 95, 325, 326]). However, high recovery RO desalination of municipal wastewater effluent, in which water recovery is typically higher than for seawater RO, can be limited due to biological (biofouling) [141, 194-196, 199, 200, 327], organic [184, 185, 187, 188], and colloidal [181, 182, 186] membrane fouling.

Membrane biofouling is of particular concern in the desalination of secondary treated municipal wastewater due to the significant presence of microorganisms in the source water [141, 200]. A biofilm can form as a result of deposition, attachment and growth of microorganisms onto the membrane surface. Studies have shown that even after 99% removal of microorganisms from the raw RO feed (e.g., via microfiltration and ultrafiltration (MF/UF)), biofouling can still eventually occur on the RO membranes [217, 328]. At the same time, scaling of sparingly soluble mineral salts (e.g., calcium carbonate, calcium sulfate and calcium phosphate) could also impose limits on the achievable RO product water recovery and has also been reported in RO desalting of wastewater effluent [114, 270, 326]. Although many of the above studies focus on one form of membrane fouling at a time, relatively few have focused on the interplay of separate forms of fouling by carrying out experiments with multiple types of
membrane fouling. Practically speaking, multiple types of fouling may be more problematic than a single type. However, there is little or no information available to elucidate the coupling of different types of fouling such as biofouling and mineral scaling.

A number of recent studies have suggested that biofouling can result in enhancement of concentration polarization [198, 231] which in turn could exacerbate the occurrence of mineral scaling, although this has not been explicitly demonstrated. While bacterial adhesion takes place on the RO membrane surface due to the deposition of biological material near the membrane surface and on spacers [329], mineral crystallization occurs only when the concentration of the ion-pair for the mineral salt of concern is above saturation [330]. Therefore, it is expected that biofouling would take place toward the leading elements of the RO process train. In contrast, mineral scaling is typically encountered in the tail membrane elements where the retentate salt concentration is highest. For example, in the Orange County Water District (OCWD) 100 MGD RO Groundwater Replenishment System (GWRS) – an advanced wastewater purification facility located in Fountain Valley, CA, the first stage has been reported to typically exhibit increasing differential pressures and reduced permeability over time – all signs associated with biological and organic fouling. The third stage has experienced mineral scaling, as reflected in reduced permeability and increasing salt passage.

If biofouling indeed exacerbates membrane mineral scaling, it may occur in a more widespread manner and not be isolated to a unit’s tail-end stages. Therefore, it is important to understand the coupling between biofouling and scaling, in order to develop proper fouling mitigation strategies. While it is of importance to ultimately elucidate the concomitant and complex processes of biofouling and mineral scaling, an essential first step is to evaluate the effect of a pre-existing biofilm on local concentration polarization and the ensuing impact on
mineral scaling. Accordingly, the current chapter investigates RO membrane mineral scaling, using gypsum (CaSO$_4$·2H$_2$O) as a model scalant, given its visual detectability, in the presence of a pre-existing biofilm. The biofilm was formed on a commercial RO membrane, in a plate-and-frame RO cell, using secondary wastewater effluent from OCWD. The RO membrane with the pre-existing biofilm was then subjected to mineral salt crystallization induced by desalting under conditions leading to supersaturation of the mineral scalant. The effect of the biofilm was monitored with respect to permeate water flux and the evolution of mineral scale on the membrane surface which was followed optically in real-time [85] to quantify crystals nucleation and growth rate.

4.2 Experimental

4.2.1 Materials

A low-pressure brackish water RO membrane (ESPA2; Hydranautics, Oceanside, CA) was used in this study to investigate the interaction between formed membrane biofilms and mineral scaling. This same membrane, which is also used in the OCWD GWRS RO system, was reported to have RMS surface roughness of 130 nm [21], permeability (based on DI water) of 0.04 ± 0.5 m$^3$/(m$^2$-hr-MPa), and NaCl salt rejection (based on 3000 mg/L feed solution) of 97%. Reagent grade calcium chloride (CaCl$_2$·2H$_2$O), sodium chloride (NaCl) and anhydrous sodium sulfate (Na$_2$SO$_4$) were used to prepare salt solutions (Fisher Scientific, Pittsburgh, PA) for membrane scaling tests. Dextran (12 kDa MW) and ammonium chloride (NH$_4$Cl) were used as nutrient sources to prevent bacterial detachment (Sigma-Aldrich, St. Louis, MO). Ethylenediamine-tetraacetic acid (EDTA) was used as a cleaning agent for the membrane monitoring system (Fisher Scientific, Pittsburgh, PA). Glutaraldehyde and phosphate buffered
saline (PBS) solution were used during membrane fixation for sample preservation (Sigma Aldrich, St. Louis, MO).

Table 4-1. Secondary wastewater effluent quality\(^{(a)}\).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>1100</td>
</tr>
<tr>
<td>pH</td>
<td>7.5 (pH units)</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>4</td>
</tr>
<tr>
<td>Turbidity</td>
<td>3 (NTU)</td>
</tr>
</tbody>
</table>

**Major Constituents**
- Bicarbonate (as CaCO\(_3\)) 200
- Ca\(^{2+}\) 80
- Cl\(^{-}\) 250
- Na\(^{+}\) 200
- SO\(_4^{2-}\) 220
- Total Alkalinity 250

**Minor Constituents**
- K\(^{+}\) 18
- Mg\(^{2+}\) 20
- NH\(_3\)-N 20
- PO\(_4\)-P 1.5
- SiO\(_2\) 20
- Organic N 2
- Total Organic Carbon 15

**Bulk Saturation Indices**
- Calcium orthophosphate (Ca\(_3\)(PO\(_4\))\(_2\)) saturation index 5.92
- Calcite (CaCO\(_3\)) saturation index 1.65
- Silicon dioxide (SiO\(_2\)) saturation index 0.17
- Gypsum (CaSO\(_4\)2H\(_2\)O) saturation index 0.04

(a) Source: Orange County Water District (OCWD) Groundwater Replenishment System (GWRS) treatment facility, Orange County Water District Research Center, Fountain Valley, CA.

Propidium Iodide (PI) solution was used for membrane staining, while the LIVE/DEAD\(^{®}\) BacLight Bacterial Viability Kit from Invitrogen (Carlsbad, CA) was used to assess bacterial
viability. Scaling and cleaning solutions were prepared using de-ionized (DI) water (electrical conductivity of ≤0.2 µS/cm; Milli-Q Water System, Millipore, San Jose, CA).

Biofilm formation on the membrane was achieved using a mixture of unchlorinated secondary treated municipal wastewater (TMW) effluent and tertiary TMW effluent (Table 4-1) from OCWD’s GWRS treatment facility. The secondary TMW effluent consisted of 80% activated sludge effluent and 20% trickling filter effluent (Table 4-1) with average total dissolved solids concentration of ~1100 mg/L, which was then mixed with tertiary TMW (Section 4.2.2.2). Mineral saturation indices for the various feed water sources and scaling solution were calculated as $SI_x = \frac{IAP_x}{K_{sp,x}}$, (where $IAP_x$ and $K_{sp,x}$ are the ion activity and solubility products of mineral scalant $x$, respectively) using a multi-electrolyte thermodynamic simulation software (OLI Systems, Inc., Morris Plains, NJ).

4.2.2 Biofouling and mineral scaling

4.2.2.1 Membrane system

The membrane system (Fig. 4-1) consisted of a transparent plate-and-frame RO (PFRO) cell allowing direct real-time imaging of the membrane surface. Details of the PFRO system and its hydrodynamics are available elsewhere [88, 89]. Briefly, the PFRO cell dimensions were 2.81 cm (width) x 7.7 cm (length) x 0.25 cm (height) with an active membrane surface area of 21.6 cm$^2$. Water was fed to the PFRO channel from a mixed and temperature controlled 20-gallon feed tank via a high pressure ½ hp (373 W) positive displacement pump. Transmembrane pressure was adjusted using a back-pressure regulator with the pressure monitored using a pressure transducer. The feed and permeate flow rates were also monitored continuously.
The PFRO system was operated in two different modes during the biofilm growth (Section 4.2.2.2) and mineral scaling (Section 4.2.2.3) stages of the study (Fig. 4-1). During the inoculation phase of biofilm growth, the solution was circulated in total recycle mode to establish the initial biofilm attachment (with the drain valves closed and feed directly from a feed tank, Fig. 4-1). During the biofilm growth stage, the PFRO was operated in a single pass mode (with the feed provided directly from filtered secondary TMW effluent, Fig. 4-1) with the effluent streams and overflow from the feed tank discharged back to the municipal wastewater treatment facility. During this stage, secondary wastewater effluent was continuously fed into the PFRO system, pre-filtered using 5 µm and 0.2 µm cartridge filters, and stored in the feed tank (with overflow) before being pumped into the PFRO cell.

Figure 4-1. Experimental setup for membrane monitoring of biofouling and mineral scaling. Drain valves DV1 and DV2 are opened to the drain during the biofilm growth step and closed for the biofilm inoculation and mineral scaling steps. Filter cartridge FC1 was is used for the mineral scaling step only, while FC2 and FC3 are used for the biofilm growth step only, and disconnected during mineral scaling.
In the mineral scaling experiments and cleaning steps, the PFRO was operated in a total recycle mode (i.e., retentate and permeate streams returned to the feed tank). The retentate stream was filtered using a 0.2 µm cartridge filter prior to being returned to the feed tank in order to trap and remove any particles or crystals that may have formed in the bulk solution, membrane feed/brine channel or detached from the membrane surface, as detailed elsewhere [43, 78]. The concentration polarization (CP) modulus (i.e., \( CP = \frac{C_m}{C_b} \) where \( C_m \) and \( C_b \) are the solute concentrations at the membrane surface and in the bulk of the flow channel, respectively) in the flow channel was determined from previously published numerical CFD model results for the same PFRO channel geometry [88, 89]. The local CP values were then used to calculate the solution saturation index for the mineral scalant (Section 4.2.1, also [43, 88, 89, 112]).

Prior to biofilm growth, a new membrane coupon was rinsed and soaked in DI water for a period of ~1 h. The membrane was then placed in the PFRO cell and compacted at 1 MPa with DI water for 12 to 24 hours. Membrane permeability was determined over a pressure range of 0.7-1.5 MPa and the observed salt rejection was determined for a NaCl solution (3000 ppm). Biofilm growth on the RO membrane in the PFRO cell was accomplished onsite at the OCWD’s GWRS Research Center, following the procedure described in Section 4.2.2.2. Feed water for biofilm growth (Table 4-1) consisted of secondary wastewater influent to the GWRS treatment facility (provided by the Orange County Sanitation District).

4.2.2.2 Biofilm growth

The biofilm was formed using a previously reported 3-step protocol [205]. The first step was inoculation in a 1:9 ratio mixture of secondary wastewater effluent (SWE) and tertiary TMW (secondary wastewater effluent treated via two-step cartridge filtration through a 5 µm and
0.2 µm filters). This mixture was recirculated through the membrane feed flow channel, at a cross-flow velocity of 35 cm/s and a transmembrane pressure of 1 MPa, for a period of 30 minutes. Although this cross-flow velocity is higher than in typical biofilm formation studies [198], the SWE source water was rich in microorganisms and thus enabled biofilm growth over a significant fraction of the membrane surface over a period of three days [205, 233]. Biofilm growth constituted the second step in which tertiary TMW was passed through the RO membrane test cell (delivered from an intermediary feed tank with the overflow returned to the OCWD plant), at the above cross flow velocity and transmembrane pressure (yielding an initial permeate flux of ~45 L/(m²-hr)) for the biofilm growth period of 3 days (Fig. 4-1). It is noted that the fresh tertiary wastewater effluent provided a constant source of nutrients to promote biofilm growth.

Biofilm formation was monitored visually via the membrane monitoring system, as well as by tracking kinetics of permeate flux decline associated with the proliferation of biofilm on the membrane surface. Traditional laboratory-scale biofilm growth studies track the depletion of dissolved organic carbon (DOC) to determine an acceptable level of biofilm growth [198]. In the present study, however, a continuous supply of wastewater effluent (containing DOC) was delivered (in a single pass) to the membrane and thus DOC measurements were not utilized. Once a sufficient level of biofilm growth was attained (as indicated by flux decline and optical surface imaging), the third step of the biofilm formation protocol was to condition the membrane with a solution containing NaCl (2650 mg/L), dextran (3 mg/L as C) and ammonium chloride (3 mg/L as N) in order to acclimate the biofilm to more highly saline conditions prior to the mineral scaling tests. Dextran was added in order to provide a source of carbon for biofilm formation and
stabilization (note that dextran can also depolymerize to glucose), as shown in previous work [205, 233, 331].

It is noted that in the present work it was desired to form a biofilm over the entire membrane surface. Therefore, the biofilm was allowed to develop until significant flux decline was observed (~30%). It is noted that commercial desalting operations would not operate to the above level of biofouling and fouling mitigation actions (including membrane cleaning) would be would commence at the early signs of significant flux decline (typically ~10% or below). In the present work, however, it was desired to attain sufficient biofilm surface coverage in order to assess the impact on mineral scaling over a reasonable range of local solution supersaturation level at the membrane surface.

4.2.2.3 Membrane mineral scaling tests

Mineral scaling tests in the absence of a biofilm were carried out with a preconditioned membrane coupon. Conditioning consisted of soaking the membrane in DI water for ~1 h, followed by compacting in the test cell by circulating DI water at a cross flow velocity of 15 cm/s and transmembrane pressure of 1 MPa (resulting in an initial permeate flux of 0.045 m$^3$/m$^2$-hr) for a period of up to ~4 h. Membrane permeability and rejection were determined as indicated in Section 4.2.2.1. Equimolar solutions of calcium chloride dihydrate (18 mM) and sodium sulfate (18 mM) were mixed to yield the gypsum scaling solution of 4880 mg/L total dissolved solids with a bulk gypsum saturation index of 0.94 and pH=7.1. For mineral scaling in the presence of a biofilm, the above scaling solution also contained dextran as a carbon source and ammonium chloride (each at 3 mg/L) as a nitrogen source (Section 4.2.2.2). These two nutrients
were added to the scaling feed solution to preserve the viability of the biofilm after removing the secondary treated wastewater [233].

Mineral scaling tests were performed with gypsum as the model scalant in order to illustrate the impact of biofouling on mineral scaling. Gypsum crystals grow up to the millimeter size range and thus can be conveniently followed by direct surface imaging [86, 112]. Given direct monitoring of the evolution of the mineral crystal surface number density [112], one can then determine the local level of solution supersaturation (with respect to gypsum) making use of the quantitative dependence of the rate of gypsum crystal nucleation on its saturation level in solution [43, 78, 86, 112, 113]. The scaling experiments were carried out at a constant temperature of 25°C, maintained with a chilled water recirculator (Model 625, Fisher Scientific, Pittsburgh, PA). Mineral scaling was evaluated at the same initial flux of 0.037 m³/m²-hr (permeate flow rate of ~1.3 cm³/min) which required transmembrane pressures of 2.5 MPa and 1.5 MPa for the membranes with and without a biofilm, respectively. The membrane channel cross-flow velocity was maintained at 13 cm/s (equivalent to 0.040 m³/h volumetric flow rate for the present system). At the above operating conditions the average concentration polarization modulus (CP) along the membrane surface was 1.9 and reached a maximum of 2.3 toward the feed channel outlet. At the above operating condition, the average gypsum saturation index in the membrane channel (at the membrane surface) was ~2. The scaling runs continued for a period of up to ~48 hours after which the membrane coupon was removed and stored for analysis. All mineral scaling tests (with and without the biofilm) were carried out at the same initial permeate flux (accomplished through adjustment of the transmembrane pressure) and cross flow velocity. This approach followed a well-established protocol [86, 113] to ensure that all scaling tests were
compared for the same initial level at the same initial level of solution supersaturation at the membrane surface and thus same initial level of mineral scaling propensity.

4.2.3 Membrane mineral surface scale analysis

Images of the membrane surface were captured at 15-minute intervals during each scaling experiment using a high-resolution digital camera to capture 6 megapixel images through a set of lenses providing optical magnification. Images were analyzed, following a previously established approach [85, 113, 156], using Adobe Photoshop (Adobe Systems Incorporated, San Jose, CA) and the Fovea Pro plug-in (Reindeer Graphics, Asheville, NC), to determine the mineral scaled surface area and crystal count on the membrane surface. The size of individual gypsum surface crystals was quantified as the equivalent diameter of a hemisphere characteristic of gypsum rosette crystals [85, 86, 112], 

\[ d_{eq} = 2\sqrt{A_s/\pi} \]

where \( A_s \) is the projected area of the surface crystal. Gypsum crystals underneath the biofilm were analyzed in the same manner, by tracking the outer perimeter of the bulge created by the subsurface crystal. It is noted that although the rate of nucleation could not be directly measured it is essentially equal to the rate of change of the observed crystal number density since every site of identified crystal (at the same level of size detection) is also the site at which a crystal was nucleated. In other words, the evolution of surface crystals is displaced in time (due to the lag time of detecting the appearance of surface crystals). Accordingly, the measured detection rate of gypsum crystals is the observed nucleation rate corrected for the diminishing surface area for nucleation (due to crystal growth) to obtain the intrinsic nucleation rate [112].

Since the rate of crystal nucleation is related to the supersaturation index (SI), it is feasible to estimate the SI within the biofilm matrix from data on the evolution of the crystal
number density on the membrane surface. The approach follows recent work on mineral scaling on RO membranes [112] in which it was demonstrated that the classical nucleation theory can be effectively used to quantify the dependence of the intrinsic nucleation rate, $J_N$, on $SI$, as described by $J_N = A_N \exp(-a_N / \ln(SI)^3)$ [235, 332, 333] where $A_N$ is a nucleation rate constant and $a_N$ is a lumped heterogeneous nucleation parameter. The above two parameters (i.e., $A_N$ and $a_N$) for gypsum scaling were determined from data on the evolution of the crystal surface number density for the membrane as described by a previously established procedure [112]. This was accomplished by quantifying the time evolution of the crystal number density for 10 equal-width regions along the membrane, but omitting regions of complex hydrodynamics in the immediate vicinity of the exit, entrance and channel wall regions [88, 89]. Subsequently, the nucleation rate was obtained (from magnified surface images) for crystals growing beneath the biofilm with the corresponding SI values estimated using the above nucleation rate expression.

Surface and cross-sectional images of post membrane-biofilm growth and gypsum crystallization were obtained via scanning electron microscopy (JEOL JSM-6700F Field Emission SEM with EDS, Japan) and dual-beam SEM/FIB (Nova 600, FEI Company, Hillsboro, OR). Membrane samples were first cut into 2 cm x 2 cm pieces then sputtered with gold at 70 mTorr and 15 mA for 2 minutes (Anatech Hummer 6.2 Sputtering System, Hayward, CA), resulting in a gold film thickness of approximately 10 nm. SEM imaging was conducted with electron beam voltages ranging 2.5 keV to 10 keV at an average working distance of 8 mm. Platinum coating of the membrane surface was employed prior to Ga-ion beam (focused ion beam or FIB) cross-sectioning. Elemental analysis of the membrane surfaces was carried out via Energy Dispersive X-ray spectroscopy (EDS).
Upon completion of the scaling experiment with the biofouled membrane, the membrane was removed from the RO cell and treated with 4% glutaraldehyde and coated with phosphate buffered saline (PBS) solution at 4°C, in order to preserve the biofilm for further analysis [205]. In order to estimate biofilm density/thickness, the membrane was subsequently stained with 1.5 µg/mL PI, a common bacterial fluorescent stain used in confocal laser scanning microscopy (CLSM), in conjunction with the Baclight Bacterial Viability Kit (Invitrogen Corp., Carlsbad, CA). Membrane imaging by confocal laser scanning microscopy (A LSM 510 Meta laser scanning microscope; Carl Zeiss, Inc., Oberkochen, Germany) was carried out in order to determine the biofilm volume density and distribution on the membrane surface at the entrance, exit and central regions. At least 5 CLSM image stacks were taken for each region and then analyzed to determine the biofilm volume (µm³/µm²) using the COMSTAT software [334]. Additional samples were taken from the same regions of the membrane as those used for CLSM to measure biofilm protein density. The biofilm protein was solubilized by sequentially incubating the membrane in an ultrasonic bath for 6 minutes in 40% ethanol, and a combined solution of 2% EDTA and 1 M NaOH [335]. These solubilization reagents were removed by dialyzing overnight with a 6000 MW Spectra/Por dialysis sack (Spectrum Laboratories, Inc., Rancho Dominguez, CA). Protein concentrations of the extracts were then determined by a Bradford assay (Bio-Rad Laboratories, Inc., Hercules, CA).

4.3 Results and Discussion

4.3.1 Membrane biofouling

Biofilm growth progressed over a period of three days accompanied by significant permeate flux decline as bacteria colonized the membrane surface (Fig. 4-2). Flux decline
reached ~35% at the end of the biofilm growth period with 60% of the final decline occurring within the first 12 hours of biofilm growth. Protein assays indicated measurable protein concentration (~16-24 µg/cm²) at the membrane surface confirming the presence of a biofilm. Formation of the biofilm was marked by the appearance of a dark layer (shown in a contrast enhanced image in Fig. 4-3, flow direction right to left) along the membrane surface, with SEM imaging also indicating a change in surface structure due to the biofilm (Fig. 4-4b).

SEM images of the scaled membrane revealed mineral crystals growing within or underneath the biofilm as illustrated in Fig. 4-4c and 4-4f. Cross-sectioned view (via SEM/FIB) of the scaled membrane clearly showed that the mineral gypsum rods were underneath the biofilm (Fig. 4-4d) with a magnified view suggesting a biofilm layer thickness of ~12 µm (Fig. 4-4e). It is noted that the images shown in Fig. 4-4 (taken from the central region of the membrane coupon; Fig. 4-3) were for the dry membrane and thus the appearance of a relatively thin biofilm layer. The greatest biofilm volume was in the downstream region (0-2 cm axially from channel outlet) as indicated by CLSM images (Fig. 4-5). COMSTAT data from the downstream (toward the exit) region revealed an average biofilm (volume) density of ~39.3 µm³/µm², whereas the biofilm density in the central region (3-5 cm axially from inlet) was significantly lower at 8.8 µm³/µm². A higher biofilm density of 13.2 µm³/µm² was observed in the entrance region (0-2 cm axially from channel inlet). It is typically expected that biofilm growth would be more pronounced toward the entrance of the membrane channel given the higher deposition velocity near the entrance region, with decreased biofilm growth axially as the deposition velocity decreases. However, in this study, the CP modulus (Section 4.2.2.1) in the channel increased toward the exit region up to ~2.3. The CP level was also apparently sufficiently high to provide adequate nutrients to promote greater biofilm growth toward the
channel’s exit region. This biofilm profile did impact the degree of mineral scaling as discussed in Section 4.3.4.

**Figure 4-2.** Permeate flux during biofilm growth and during mineral scaling with and without the presence of a biofilm. Initial flux for biofilm growth: 0.045 m$^3$/m$^2$-hr (TMP=1.0 MPa). Initial flux for mineral scaling (both biofouled and non-biofouled): 0.037 m$^3$/m$^2$-hr (TMP=2.5 MPa for biofouled membrane and TMP=1.5 MPa for non-biofouled membrane).

**Figure 4-3.** Optical images of the membrane surface (a) prior to biofouling, and (b) contrast-enhanced image after the 72-hr biofilm growth period, clearly showing discoloration associated with biofilm coverage (flow from right to left).
Figure 4-4. SEM membrane images from the central region of the RO channel (x/L=0.4-0.6): (a) clean, non-biofouled membrane surface, (b) biofouled membrane surface, (c) view of a biofouled and mineral scaled membrane area prior to FIB sectioning, (d) SEM/FIB cross-section image, and (e) magnified cross-sectioned view of a portion of image (d), regions I, II and III refer to the biofouled region, polyamide active layer, and polysulfone support layer, respectively. (Note that the appearance of a seemingly porous top layer is due to charring from the FIB sectioning process.)
4.3.2 Mineral scaling in the presence of a biofilm

The influence of a biofilm on mineral scaling was quantified via permeate flux decline, monitored over the course of the scaling tests in the presence and absence of the biofilm, for the same level of initial permeate flux and cross-flow velocity. The initial average supersaturation with respect to gypsum was $SI_g \sim 2.0$. At the end of the 48 h scaling test, flux decline of 68% occurred in the mineral scaled biofouled membrane. In contrast, flux declines of approximately 36% and 32% were encountered for the biofouled (but not scaled) membrane and the scaled native membrane, respectively (Fig. 4-2).
Optical imaging of the membrane surface (**Fig. 4-6**) revealed that as the scaling tests progressed, the magnitude of coverage by mineral scale crystals was visibly greater on the biofouled membrane. Also, the degree of membrane mineral scaling was greater toward the exit region of the membrane (higher CP region) as demonstrated in previous studies [86, 89, 113].

The difference in mineral scaling propensity in the presence and absence of a biofilm was first quantified by comparing (at the same cross-flow velocity and initial permeate flux) the extent of membrane mineral scale coverage, and the time evolution of mineral crystal number density (**Fig. 4-7**). For the same initial average gypsum saturation index ($SI_g=2.0$), the total surface area coverage by mineral scale crystals (including crystals above and beneath the biofilm...
surface) increased up to approximately 20% in the absence of a biofilm and 50% in the presence of a biofilm. Surface scale coverage (Fig. 4-7a) correlated to a reasonable degree with flux decline data (Fig. 4-2) and is consistent with the surface blockage model [113]. The surface scale coverage appeared to progress toward a plateau due to diminishing surface area for nucleation and further crystals’ growth, as the membrane surface becomes populated with crystals that begin to encroach on neighboring crystal boundaries [86, 112].

4.3.3 Analysis of mineral crystals above and within the biofilm

SEM imaging of the non-biofouled and biofouled membranes revealed mineral crystal morphologies that were substantially different in the presence and absence of a biofilm. Absent a biofilm, surface gypsum crystals were of the typical rosette structure (Fig. 4-8). In the presence of biofilm, various crystal structures were observed including long gypsum crystal rods protruding from the biofilm surface (Fig. 4-9a), and hemispherical bulges that appear underneath the biofilm (Fig. 4-9b). Elemental analysis via EDS of various areas of the scaled (non-biofouled and biofouled) membranes revealed the presence of calcium, sulfur and oxygen–consistent with

Figure 4-7. Kinetics of gypsum crystallization on the RO membrane with and without the presence of a biofilm. (a) Increase in surface area coverage by mineral scale with time, and (b) Evolution of the crystal number density (CND).
the expected presence of calcium sulfate, given the high level of supersaturation with respect to gypsum at the membrane surface (i.e. \(SI_g \sim 2.0\)).

![SEM image of gypsum rosette crystal structure](image)

**Figure 4-8.** SEM image of gypsum rosette crystal structure, on non-biofouled membrane, showing: (a) single isolated crystal; (b) overlapping crystals.

Throughout the membrane surface, long gypsum crystal rods appeared to protrude from beneath the biofilm surface or were partially covered by the biofilm (Fig. 4-9a). It is possible that the biofilm continued to grow to some extent during the scaling test in which nutrients (i.e., ammonium chloride and dextran) were added to the feed solution to prevent biofilm detachment (Sec. 4.2.3). However, given that the scaling solution was not supplemented with the same level of nutrients and bacteria from the secondary wastewater effluent, it is likely that additional biofilm growth was minimal. A more likely explanation is that mineral crystals within the biofilm grew to sufficient size and broke through the biofilm surface (Fig. 4-9a). Indeed, SEM images of the membrane surface revealed the vast majority of crystals were underneath the biofilm in the form of hemispherical bulges engulfed by the biofilm (Figs. 4-9b). In order to confirm the presence of gypsum crystals within the biofilm bulges, portions of the bulges were etched away with a focused ion beam (Section 4.2.3) and imaged by SEM. A cross-sectional view of the etched bulges clearly reveals the presence of gypsum crystal rods beneath the upper
biofilm surface, thereby confirming that gypsum crystals were also growing within the biofilm (Fig. 4-10).

**Figure 4-9.** SEM images of crystals on the biofouled RO membrane: (a) long gypsum crystal rods protruding from the biofilm surface, including a crystal that grew to sufficient size to break through the biofilm surface (at right), and (b) subsurface bulges within the biofilm containing gypsum crystals (See Fig. 4-10), with central region of the original image magnified for clarity (at right).

**Figure 4-10.** SEM image of subsurface bulge (left) and FIB cross section of a subsurface biofilm “bulge”, revealing a sub-biofilm surface crystal structure (right).
To further elucidate the impact of biofouling on mineral scaling, the growth rates of single crystals located within the biofilm (e.g., Fig. 4-10), above the biofilm and in the absence of a biofilm were compared for crystals in surface regions of initial $S_{SI} \sim 2.1-2.2$ (Fig. 4-11). The growth curves for the above crystals (with the time axis adjusted to the initial time of crystal observation) show that the growth rate is higher for crystals growing within the biofilm (relative to crystals above or in the absence of biofilm) by a factor of two. It is also noted that once a crystal breaks through the biofilm surface (Fig. 4-9a) its growth rate is significantly reduced, and is then comparable to the crystal growth rate in the absence of a biofilm (Fig. 4-11). The above results can be rationalized by noting that the rate of gypsum crystals growth is diffusion-controlled [86], i.e., $dr/dt = k_c (C - C_{sat})$, where $r$ is the equivalent hemispherical crystal radius, $k_c$ is a kinetic growth coefficient which can be considered to be the equivalent of the solution-crystal mass transfer coefficient (when the crystal growth is exclusively due to diffusional growth), and $C$ and $C_{sat}$ are the salt concentrations in the solution and the saturation concentration at the crystal surface, respectively. Therefore, it is reasonable to conclude that, within the biofilm matrix, an increased rate of crystal growth is indicative of a higher solution supersaturation level associated with a higher CP in this region (relative to the fluid region above the biofilm). CP enhancement associated with biofilms is reminiscent of elevated CP levels reported in earlier studies of membrane colloidal fouling in RO desalination [336, 337]. This is also consistent with more recent work suggesting that biofilm enhances osmotic pressure near the membrane surface [198, 206, 231]. CP enhancement within the biofilm can also be rationalized by considering the simple CP film model [92] (i.e., $CP = C_m/C_b = (1 - R_o) + R_o exp(J/k_m)$, in which $C_m$ and $C_b$ are the solute concentrations at the membrane surface and in the bulk solution, respectively, $J$ is the permeate flux, $k_m$ is feed-side mass transfer coefficient, and the $R_o$ is the observed salt rejection).
The salt concentration at the membrane surface will increase with decreasing mass transfer coefficient (which decreases with decreasing cross-flow velocity, such as in the biofilm) and increasing permeate flux. Accordingly, given that the biofilm remains permeable (although at a reduced permeability relative to the native membrane) and the cross flow velocity within the biofilm diminishes, the CP modulus is enhanced relative to the native (i.e., clean) membrane (Fig. 4-12) under the same operating conditions (i.e., cross flow velocity and initial flux). This will result in a higher growth rate of crystals within the biofilm compared to crystals whose growth surfaces are exposed to the flowing fluid in the channel.

Figure 4-11. Comparison of single crystal growth for individual crystals within and above the biofilm and in the absence of a biofilm. Five crystals were analyzed for each case, within the same RO channel region (x/L=0.6-0.8, SlD=2.1-2.2). Note: d and d₀ are the crystal diameters at time t and when the crystal could first be observed at time t₀, respectively. (Analysis beyond t = 10 hrs was infeasible due to crystal overlap).
4.3.4 Nucleation rate and solution supersaturation within the biofilm

The overall mineral crystal number density was higher in the presence of a biofilm by approximately 33%, relative to the non-biofouled membrane (Fig. 4-7b). Since the rate of nucleation on the membrane surface is expected to increase with increasing solution supersaturation, a higher rate of gypsum crystal nucleation for crystals within the biofilm is suggestive of a higher level of solution supersaturation within the biofilm. The level of supersaturation within the biofilm and at the biofilm-free membrane surface was estimated based on the rate dependence of crystal nucleation on solution supersaturation (Fig. 4-13) as described in Section 4.2.3. Results demonstrate that, for the same initial permeate flux and cross flow velocity, the SI level within the biofilm matrix was consistently higher, at the same axial
position, relative to scaling without a biofilm (Fig. 4-14 and Table 4-2). For example, the SI level at x/L=0.8-0.9 (exit region) and x/L=0.2-0.3 (entrance region) was higher by 9% and 6.5%, respectively, within the biofilm relative to the biofilm free case. At first glance the above SI differences may appear small. However, the impact of small SI variation on the rate of nucleation can be significant (Fig. 4-13). For example, a 9% increase in SI (i.e. from 1.93 to 2.11, at x/L=0.8-0.9) would lead to 340% increase in the intrinsic nucleation rate (Table 4-2, Fig. 4-13). Although the rate of nucleation increased along the membrane channel (from entrance to exit; Table 4-2), both in the presence and absence of a biofilm, the percent enhancement of the nucleation rate (and thus mineral scale enhancement) decreased to a minimum toward the central region of the channel where the degree of biofilm coverage was also lowest (Fig. 4-3, Section 4.3.1). As a consequence, the percent SI enhancement was also at a minimum in the central region of the channel as shown in Fig. 4-14.

Table 4-2. Summary of nucleation rate and corresponding level of gypsum supersaturation.

<table>
<thead>
<tr>
<th>Axial Membrane Region (central regions only) (x/L)</th>
<th>Clean Membrane Estimated SI&lt;sub&gt;g,m&lt;/sub&gt;</th>
<th>Clean Membrane Observed J&lt;sub&gt;N&lt;/sub&gt; (cm&lt;sup&gt;2&lt;/sup&gt;hr&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Biofouled membrane Estimated SI&lt;sub&gt;g,m&lt;/sub&gt;</th>
<th>Biofouled Membrane Observed J&lt;sub&gt;N&lt;/sub&gt; (cm&lt;sup&gt;2&lt;/sup&gt;hr&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2-0.3</td>
<td>1.71</td>
<td>0.06</td>
<td>1.82</td>
<td>0.41</td>
</tr>
<tr>
<td>0.3-0.4</td>
<td>1.82</td>
<td>0.61</td>
<td>1.92</td>
<td>1.65</td>
</tr>
<tr>
<td>0.4-0.5</td>
<td>1.91</td>
<td>1.75</td>
<td>1.96</td>
<td>2.34</td>
</tr>
<tr>
<td>0.5-0.6</td>
<td>1.99</td>
<td>2.85</td>
<td>1.98</td>
<td>2.78</td>
</tr>
<tr>
<td>0.6-0.7</td>
<td>2.05</td>
<td>4.01</td>
<td>2.07</td>
<td>5.94</td>
</tr>
<tr>
<td>0.7-0.8</td>
<td>1.96</td>
<td>2.41</td>
<td>2.07</td>
<td>6.01</td>
</tr>
<tr>
<td>0.8-0.9</td>
<td>1.93</td>
<td>1.82</td>
<td>2.12</td>
<td>8.03</td>
</tr>
</tbody>
</table>

(a) SI values were estimated following the method described in Section 4.2.3.
Figure 4-13. Experimental gypsum nucleation data and fit of the rate of nucleation expression (Section 4.2.3). The horizontal error bars represent the locally averaged SI corresponding to the calculated nucleation rate.

Figure 4-14. Percent increase in gypsum SI at the membrane surface due to the biofilm, relative to the biofilm-free (but scaled) membrane surface.
In summary, these data on RO membrane scaling in the presence of a biofilm suggest that mineral crystals can nucleate and grow within the biofilm matrix. Higher degrees of both mineral crystal nucleation and growth rate were revealed for the biofouled membrane relative to the clean membrane, at the same cross flow velocity and initial permeate flux. The results and analyses in the context of classical nucleation theory confirm that a higher level of solution supersaturation (due to higher CP) within the biofilm is responsible for the enhanced scale formation relative to scaling in the absence of a membrane biofilm. The above behavior suggests that the severity of mineral scaling may be greater in biofouled regions of RO membranes.

4.4 Summary

The effect of a pre-existing biofilm on mineral scaling was evaluated using gypsum as a model mineral scalant. The biofilm was established on an RO membrane monitoring cell using secondary treated wastewater effluent, onsite in a wastewater treatment facility. Once the biofilm was established, mineral scaling was monitored via direct real time imaging of the membrane surface. The extent of mineral scaling was found to be greater (in terms of both surface scale coverage and surface crystal number density) in the presence of a biofilm, and was also more pronounced in regions with greater biofilm density. SEM analysis of the membrane surface and of the sectioned biofilm revealed the presence of mineral crystals within as well as some protruding from within the biofilm matrix. The rate of individual mineral crystal growth within the biofilm layer was significantly higher than the growth rate in the absence of a biofilm. The higher observed rates of crystal nucleation and growth suggest that there is enhancement of concentration polarization within the biofilm. This phenomenon suggests that mineral scaling may not be limited solely to RO units tail elements, where scaling
has exclusively been previously thought to occur. Rather, it is feasible that upstream RO unit stages may also exhibit mineral scaling, as biofouling enhances concentration polarization and in turn increasing the level of supersaturation at the membrane surface.
Chapter 5
Rapid Field Assessment of RO Desalination of Brackish Agricultural Drainage Water

5.1 Overview

Mitigation of membrane scaling for brackish water RO desalination requires selection of proper operating conditions with regard to prefiltration, RO recovery level, and antiscalant use. Using antiscalant requires appropriate selection and dose optimization (with respect to the specific water source, membrane type, target water recovery and operating conditions) in order to avoid: (a) overdosing (e.g., when scaling propensity decreases) that is both costly and may facilitate biofouling [75, 282], and (b) under-dosing (e.g., when water source scaling propensity rises) that can result in catastrophic membrane scaling. In addition, appropriate RO feed-filtration (with or without coagulation pretreatment) or other approach (e.g., air floatation) for removal of colloidal matter is needed to minimize RO membrane fouling by organics, microorganisms and colloidal matter and their potential negative impacts on RO operational and maintenance costs. In general, establishing effective RO feed filtration and mineral scale mitigation strategies require site-specific field testing [51, 93].

Rapid field determination of the range of feasible RO operating conditions that addresses the range of needed feed filtration and AS treatment is essential, particularly in a single-pass mode of operation, as used in actual practice. This is especially the case when confronted with the task of assessing source waters of varying water quality from a multitude of geographical locations such as in the California's San Joaquin Valley (SJV) [43] which is the focus of the present study. In this region, which is one of the most productive agricultural regions in the United States [10], there are significant geographical and temporal water quality variations of
groundwater and agricultural drainage water with regard to salinity and ionic composition, with total dissolved solids (TDS) in the range of 3,000–30,000 mg/L [43, 52]. Therefore, cost-effective evaluation of the feasibility of RO desalting for the wide range of water source quality in the SJV would be best achieved through a rapid systematic field evaluation to assess RO feed treatment requirements and feasible product water recovery levels. Accordingly, the present chapter presents an approach for rapid field evaluation of RO desalting feed filtration requirements, optimization of AS treatment, and estimation of the RO water recovery level corresponding to the membrane scaling threshold.

Making use of an automated RO diagnostic system [139, 156], the suitable RO operating conditions were derived using the membrane monitoring system in a single-pass mode of operation (i.e., no concentrate or permeate recycling). Subsequent tests were carried out with a mini-mobile-modular (M3) spiral-wound RO system [139]. These latter field tests served to confirm the suitability of the approach for continuous large scale implementation for optimization and control of the operation of a field RO demonstration plant (Chapter 6).

5.2 Experimental

5.2.1 Reagents, materials and brackish water source

Desalination field tests were carried out with agricultural drainage (AD) water in the Panoche Water District of the San Joaquin Valley [10, 43, 48, 50]. The subsurface drainage water was pumped directly from an underground sump (Drainage Site DP-25) and delivered to the RO systems (Sections 5.2.2-5.2.3). Grab samples of the AD water feed were analyzed following standard methods by a state certified laboratory (Bryte Laboratory, Sacramento, CA) with the water quality data summarized in Table 5-1. It is noted that of the total dissolved solid
content 14,400 mg/L about \(\approx\)46% (6600 mg/L) consisted of sulfate with calcium concentration of 509 mg/L, thus making this water nearly saturated with respect to gypsum at \(SI_g = 0.90\).

Membranes used in the RO pilot plant were spiral-wound elements (Dow FilmTec XLE-2540) each 6.35 cm (2.5 inches) in diameter and 101.6 cm long (40 inches) long, with an active membrane area of 2.6 m\(^2\) (~28 ft\(^2\)). These membrane elements were of average permeability of \(4.57\times10^{-3} \text{ m}^3/(\text{m}^2\cdot\text{hr}\cdot\text{bar})\) and observed rejection of 97.7% (at 18.7 bar and 63% recovery for the water feed composition given in Table 5-1). Although the spiral-wound membrane system was typically used under safe (i.e., non-fouling, non-scaling) conditions, as established with the prior diagnostic tests (Section 5.2.5), membrane cleaning was carried out when initiating new series of tests or when specific scaling tests were conducted. Cleaning of the M3 membrane elements was accomplished by periodically flushing the system with permeate or D.I. water, followed by cleaning with aqueous 0.1 wt% NaOH (pH~12). When not in use, the spiral-wound membranes elements were stored in a preservative solution of 1 wt% sodium metabisulfite.

Flat-sheet membrane coupons used in the membrane monitor RO cell (Section 5.2.2), of the type used in the spiral-wound membrane, had active membrane area dimensions of 3.16 x 8.1 cm. Prior to use in the monitoring cell, each membrane coupon was first rinsed in DI water (for ~5 min) and subsequently stored submerged in DI water (for 1-2 hours prior to testing). At the termination of each diagnostic test, membrane samples were analyzed via scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) (JEOL JSM-6700F Field Emission SEM with EDS, Japan).
Table 5-1. Water quality data for the field study source water.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Reported Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductance, µS/cm</td>
<td>14,810</td>
</tr>
<tr>
<td>Dissolved Boron, mg/L</td>
<td>39</td>
</tr>
<tr>
<td>Dissolved Calcium, mg/L</td>
<td>509</td>
</tr>
<tr>
<td>Dissolved Chloride, mg/L</td>
<td>2,650</td>
</tr>
<tr>
<td>Dissolved Magnesium, mg/L</td>
<td>455</td>
</tr>
<tr>
<td>Dissolved Nitrate, mg/L</td>
<td>597</td>
</tr>
<tr>
<td>Dissolved Potassium, mg/L</td>
<td>7.6</td>
</tr>
<tr>
<td>Dissolved Selenium, mg/L</td>
<td>1.7</td>
</tr>
<tr>
<td>Dissolved Silica (SiO₂), mg/L</td>
<td>34.6</td>
</tr>
<tr>
<td>Dissolved Sodium, mg/L</td>
<td>3,890</td>
</tr>
<tr>
<td>Dissolved Sulfate, mg/L</td>
<td>6,660</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
</tr>
<tr>
<td>Dissolved Hardness, mg/L as CaCO₃</td>
<td>3,145</td>
</tr>
<tr>
<td>Total Alkalinity, mg/L as CaCO₃</td>
<td>235</td>
</tr>
<tr>
<td>Total Dissolved Solids, mg/L</td>
<td>14,440</td>
</tr>
</tbody>
</table>

Two antiscalants were selected for scale suppression of gypsum, namely, Flocon 260 (BWA Water Additives, Tucker, Georgia) and PermaTreat PC-504T (Nalco Co., Naperville, Illinois), hereinafter referred to as AS1 and AS2, respectively. These antiscalants were previously evaluated to be suitable for scale suppression [111, 112].
5.2.2 Mineral scale monitoring and diagnostic RO system

**Figure 5-1.** System setup for M3 and membrane monitoring system operation. The initial filtration scheme (A) included only 5 µm and 0.45 µm cartridge filtration. The media filter and 0.2 µm cartridge filter were used only in the upgraded filtration scheme (Filtration scheme B). Valves V1, V2, and V3 were used to switch between the stand-alone and RO concentrate monitor modes.

Monitoring of membrane fouling and scaling was accomplished with an ex-situ plate-and-frame membrane monitor (Fig. 5-1, [86, 139, 156]). Briefly, the monitoring system consists of a high pressure transparent plate-and-frame reverse osmosis cell (feed channel dimensions of 3.16 cm wide, 8.1 cm long and 2.66 mm in height) suitable for operational pressures for both brackish and seawater desalting. This system allowed for real-time membrane surface imaging (in the cell), as well as monitoring of permeate flux, feed flow rate, transmembrane pressure, as well as conductivity and temperature of feed and permeate streams. Feed, retentate, and permeate flow rates, along with temperature, pH, and conductivity of these streams were recorded digitally using a computerized data acquisition system described elsewhere [139]. Feed to the membrane...
monitor was provided via a partial stream from one of the two positive displacement pumps of the M3 RO pilot (Section 5.2.3) when in a stand-alone mode. The membrane monitor feed was a side-stream from the RO plant when it was used as a process monitor for the plant. In this process monitoring mode, the membrane monitor operation was controlled by the integrated M3 control system. In both cases, feed to the Membrane monitor was provided post M3 system filtration (Section 5.2.3) and the Membrane monitor is operated in a single-pass mode. In the stand-alone mode, the Membrane monitor feed flow rate and pressure were adjusted by a computer-controlled variable frequency drive (VFD) of the high pressure pump, a bypass valve before the RO cell and an actuated valve on the membrane monitor retentate line (located after the membrane monitoring cell). In both operational modes, pressure and flow rates are adjusted via a specialized model-based controller for the system [139] in order to establish the desired level of concentration polarization (CP) in the plate-and-frame RO monitoring cell. Results from previous hydrodynamics and mass transfer CFD modeling work, for this specific membrane monitoring RO cell [88], enabled precise characterization of the CP profile in the membrane channel for the range of operating conditions in the present study (cross flow velocity and feed pressure ranges of 4-8 cm/s and 1.0-2.8 MPa, respectively), and thus the level of solution supersaturation throughout the membrane monitor channel.

Lighting arrangement in the membrane monitor cell was set at a near dark-field condition in order to increase contrast for imaging of surface crystals. Surface imaging is with a high resolution CCD (charge-coupled device) camera attached to a monoscope that focuses on the desired zone of the membrane coupon in the membrane monitor RO cell. In the present work, the monitored zone was a 1.0 cm x 1.3 cm area centered approximately a distance of 6 cm from the cell channel inlet. The entire membrane surface was also imaged by a high resolution digital
camera. Membrane surface images were recorded at specified time intervals (typically 5 or 10 min) and analyzed online by specialized software [156] to detect and quantify the percentage of the monitored area that is covered by particulate or other matter (including mineral scale), as well as the number density of mineral crystals. Given information on: (a) local level of solution supersaturation (at the membrane surface) at the imaged location, and (b) permeate flux and salt rejection, it is possible to establish the operating conditions (e.g., product water recovery, AS dose) at which mineral scaling/fouling would be expected to occur (or be averted) in a larger-scale RO desalting system [43]. The premise of this approach is that $SI_g$ in the monitored plate-and-frame membrane channel, at the observation zone, can be set (via control of the membrane monitor operation) so as to either match or be above or below the $SI_g$ level expected in the spiral-wound RO plant (Sections 5.2.4 and 5.2.5, [43, 139]). Finally, it is noted that once significantly scaled or fouled, the membrane in the monitoring cell was cleaned (online) with DI or previously stored permeate water [139] or using standard cleaning protocols [338] in order to restore the monitor to its original state (as verified by flux and rejection monitoring).

5.2.3 M3 spiral-wound pilot RO system

A mini-mobile-modular (M3) spiral-wound pilot RO system [139] was utilized for rapid field assessment of the optimal/feasible RO operating conditions. The M3 (Fig. 5-1) consisted of the following modular unit operations: pretreatment, pumping, and RO desalting; each of which is connected to a central control system. In the present study, the M3 was loaded with six spiral-wound Dow FilmTec XLE-2540 elements with each element housed in a separate fiberglass pressure vessel (rated up to 68 bar). In the above configuration, the M3 was capable of permeate production of up to ~0.47 m$^3$/h (~3,000 GPD) at 63% recovery for the field feed water source
(14,440 mg/L TDS). The M3 filtration module (Filtration scheme A) contained a series of 5 and 0.45 μm filter cartridges (Keystone Filter, Hatfield, PA). Improvements in feed filtration (Filtration scheme B) in the field study were also evaluated with the addition of an auxiliary media filtration system that included a standard water filter silica sand (silver sand, US mesh #20, average sieve size 0.85 mm) as well as a 0.2 μm filter cartridge (Keystone Filter, Hatfield, PA). Once the source water was pre-filtered, it was fed to the RO elements via two positive-displacement high pressure pumps (Danfoss Model CM 3559, 3 HP, 3450 RPM, Baldor Reliance Motor, Danfoss Sea Recovery, Carson, California) controlled by variable frequency drives (VFDs) (Model FM50, TECO Fluxmaster, Round Rock, Texas). An electrically actuated needle valve (Model VA8V-7-0-10, ETI Systems, Carlsbad, California) on the retentate stream of the M3 RO system, along with the pump VFD, enabled control of the retentate flow rate and pressure in the RO unit using a model-based controller. Antiscalants, when employed, were metered into the feed water prior to RO desalting by using a metering pump (Model EHE31E1-V6, Walchem, Holliston, MA). Feed and retentate pressures were monitored using two pressure transducers (0-68 bar range, Model PX409-1.0KG10V, Omega, Stamford, Connecticut). Flow meters were present on the feed, permeate, and retentate streams. A pH sensor (GF Signet Model 2750) and an inline turbidity meter (Micro TOL Model 20055, HF Scientific, Fort Myers, Florida) were installed at the RO feed (post-filtration) to monitor the feed pH and turbidity. Real-time data from all sensors were recorded via a computerized data acquisition system with all actuators (e.g., automatic valves and pump VFDs) under automated system control. Finally, it is noted that in normal M3 desalting, the membrane monitoring system operated under the M3 control system (Fig. 5-1). In this configuration a concentrate side stream, from the tail element
of the M3 pilot, was fed to the membrane monitoring RO cell in order to monitor for mineral scaling, which was expected to first occur in the M3 tail RO element.

5.2.4 Estimation of recovery limits from membrane monitoring field tests

A relatively high CP level may be achieved in small plate-and-frame RO (PFRO) systems [43, 86, 88] even though these are operated at a low recovery (≤1–2%). Given knowledge of the salt concentration at the membrane surface, in the exit region of the PFRO RO cell (when operated in a single-pass mode and being fed with RO feed water), the equivalent recovery in a full-scale spiral-wound RO plant can be estimated for a specified acceptable level of concentration polarization (McCool et al. 2010). In this approach, surface salt concentrations at the membrane monitor channel were first calculated, for the membrane monitor operating conditions using the numerical procedure developed specifically for the present RO cell geometry [88]. At the present level of analysis, the concentration polarization modulus, $CP$, (defined as $CP = C_M / C_b$ where $C_b$ and $C_M$ are salt concentrations in the bulk and at the membrane surface, respectively) was taken to be the same for all ions. Given the above information (at various locations on the membrane surface), the mineral salt saturation indices and osmotic pressures for the feed and various solution compositions (e.g., for different recovery levels) were then calculated using a multi-electrolyte thermodynamic simulation software [339]. Subsequently, given the above solute concentration at the membrane surface ($C_M$) of the membrane monitor, the acceptable operational ratio of $C_M$ to the mixed cup retentate concentration, $C_R$ (i.e., the average concentration of the retentate in the RO feed channel), in the tail element of the spiral-wound RO plant can be estimated by introducing a CP allowance factor (i.e., $\alpha = C_M / C_R$). In practice, spiral-wound RO plants are operated such that CP for an element
is typically no greater than 1.2 (i.e., a CP allowance of 20%; [43, 180]. Since $\alpha<CP$ for a given operating condition, a conservative value of $\alpha=1.1$ was selected to ensure that the practical limitation on CP is not exceeded. $C_R$ can be estimated for a given operation for which $C_M$ is determined from knowledge of CP along the membrane surface in the RO membrane monitoring cell.

**Figure 5-2.** Variation of saturation indices for selected mineral scalants (gypsum, strontium sulfate, calcite, and silica) with product water recovery. Saturation is reached at SI = 1 indicated by the horizontal dashed line. Note: analysis was based on the water quality data given in Table 5-1.

Given the above, the equivalent recovery ($Y = Q_P/Q_f$, where $Q_P$ and $Q_f$ are the permeate and feed flow rates, respectively) for a spiral-wound RO plant can be obtained, as in Eqn. 2-9, from [43]:

118
\[
Y = \frac{1 - CF}{1 - CF - R_s} \tag{5-1}
\]

where the retentate concentration factor is defined as \( CF = C_R / C_f \) \[43\], \( C_f \) is the feed concentration, and the membrane salt rejection is given as \( R_s = 1 - C_P / C_f \), where \( C_P \) is the permeate solute concentration. It is noted that \( C_P \) for the RO plant tail element can be estimated as \( C_{Pt} = C_M / C_B = k \cdot \exp \left[ \frac{2Y_t}{(2-Y_t)} \right] \) \[180\], where \( Y_t \) is the recovery for the tail element, and \( k \) is an element-specific parameter (taken to be 0.98 for the present 40 inch long spiral wound elements). In the present work, flux from the tail element was monitored enabling estimation of \( C_{Pt} \) and accordingly verifying that the system operation was within the recommended operational guidelines \[180\].

Prior to field determination of the recovery limits imposed by mineral scaling, the potential limits on recovery as imposed by the saturation indices for the sparingly soluble mineral salts (Section 5.1) was determined from information on the feed composition (Table 5-1) and using Eq. 5-1. The resulting saturation indices, based on the retentate mixed-cup concentration, for different recovery levels (Fig. 5-2) demonstrate that recovery would be limited due to gypsum scaling (i.e., \( SL_g = 1 \)) to <10% and to just below 60% with the use of antiscalants (i.e., at \( SL_g = 2.3; \) [340]). It is noted that calcite scaling has a lesser impact (Section 5.2.5) with saturation being reached at recovery of 0% and 72% at pH of 7.9 (or higher) and 6.5, respectively. The results in Fig. 5-2 provide an upper limit estimate of the recovery since \( C_R < C_M \), and accounting for \( C_P \) a lower limit recovery estimates are obtained depending on the \( C_P \) allowance (\( \alpha \)) as depicted in Fig. 5-3. The above recovery estimates were then assessed relative to field estimates based on the operation of the membrane monitor and the RO plant.
Figure 5.3. Variation of gypsum saturation index ($S_{G}$) with product water recovery for RO desalting (based on the water quality given in Table 5-1) at various concentration polarization allowances.

5.2.5 Rapid diagnostic field evaluation of RO operating conditions

Field assessment of the suitable range of RO operating conditions was first carried out with the membrane monitor (in a stand-alone mode) in order to determine the necessary feed filtration, test AS performance and optimize its dose, and establish the maximum feasible recovery. The protocol for establishing the adequacy of RO feed filtration is depicted in Fig. 5-4. In this protocol the membrane monitor is initially operated in a stand-alone mode at a CP level that would be equivalent to RO plant operation at the recovery limit imposed by mineral scaling. This level is set to the mineral scaling threshold considering a CP allowance of $\alpha=1.1$; Section 5.2.3, without AS feed dosing. The filtered feed is monitored to check if its turbidity is below the maximum recommended guidelines for RO feed (~1 NTU; [104]). The membrane surface in the membrane monitor is then observed optically over a period of ~1-2 h. In this diagnostic protocol,
if the filtered feed turbidity is above the recommended level or if significant deposition of particulate matter, or mineral crystals are observed on the monitored membrane surface (even if the RO feed turbidity is $<1$ NTU), this would suggest needed feed filtration upgrade/improvement to further reduce the particulate concentration and thus turbidity. The reason being that fine particulate matter, which deposits onto the membrane surface, can enhance nucleation of mineral salt crystals when the solution in the RO feed channel is supersaturated. Therefore, turbidity alone may be an insufficient indicator of the adequacy of feed filtration, hence the advantage of direct monitoring of the membrane surface in the RO monitoring cell.

**Figure 5-4.** Protocol for evaluating the adequacy of feed filtration.

**Figure 5-5.** Field protocol for antiscalant selection and optimization protocol with the membrane monitoring system.
Once RO feed filtration is deemed adequate, one can proceed to assess the need for AS usage (delivered via a metering pump; Section 5.2.4), AS selection and dose optimization (Fig. 5-5). In this experimental protocol, the membrane monitor operation is first set (by adjusting the crossflow velocity and transmembrane pressure) such that the saturation index at the membrane surface, for the scalant of concern (i.e., gypsum for the present water source), is elevated to a level corresponding to the desired recovery level (without AS addition). If mineral scaling is not detected (over a period of up to ~12 h) [112], this would suggest that AS use is unnecessary for the set recovery level. However, if scaling is detected, or if it is desired to identify the maximum attainable recovery level with AS dosing, one can proceed with field comparison of scale suppression effectiveness (Fig. 5-5) for the selected pool of AS candidates. This evaluation should be done at a reasonable AS dose, via direct membrane surface observation with the membrane monitoring system. AS dose is typically established on the basis of its scale suppression effectiveness at the desired recovery, with considerations of feed water chemistry and the maximum manufacturer recommended level, as well as the impact of AS use on overall process economics.

The present water source (Table 5-1, Fig. 5-2) was supersaturated and nearly saturated with respect to calcite and gypsum, respectively. However, recent work has shown [78] that calcium carbonate scaling is suppressed even under alkaline conditions (pH~7-8) for feed water that is lean in carbonate and of high gypsum saturation when antiscalant is used for gypsum scale suppression. The attainable water recovery, with AS feed dosing, for the recommended bulk $SI_g$ range of 2.3-4.0 [340] (for the residual brine stream), as estimated via mineral solubility analysis (Section 5.2.4; Fig. 5-2), was expected to be in the range of 60%-77%. Accordingly, field evaluation of candidate antiscalants was carried out with the membrane monitor at an initial $SI_{g,m}$
of 3.1 at the membrane surface; this is about the average recommended limit for gypsum $SI$ for its scale suppression by AS dosing [340], which was equivalent to RO desalting of the present field water source at water recovery of 67%. Two candidate antiscalants (Section 5.2.1) were evaluated at a dose of up to 3 ppm. Once the better performing AS and suitable dose were determined, the recovery limit imposed by mineral scaling was verified by operating the monitoring system at incrementally increased levels of equivalent RO water recovery (Section 5.2.4) until detection of the onset of mineral scaling. Subsequently, validation of the selected operating conditions for set recovery limits, as determined via membrane monitor field tests, were carried out with the spiral-wound RO pilot (Section 5.2.3). In these field tests, the membrane monitor received a side stream of M3 concentrate from the tail RO element in order to monitor the onset of mineral scaling in the M3 plant. Mineral scaling detected in the membrane monitor was interpreted as an early warning of scaling occurring in the tail element of the M3, given that $SI_{g,m}$ in the membrane monitor was set at the same initial level as in the M3 tail element. Observed flux decline for the M3 tail element served as a confirmation of scale detection in the membrane monitor RO cell. The monitored membrane was cleaned, after each discrete experiment, with either D.I. water or M3 RO permeate, which enabled effective removal of gypsum scale [139]. Membrane coupons were replaced when scale removal by the above approach was ineffective.

### 5.3 Results and Discussion

#### 5.3.1 Evaluation of feed filtration requirements for RO of agricultural drainage water

Adequacy of the initial feed filtration system (5 and 0.45 micron cartridge filters; designated as Filtration A) was evaluated with the membrane monitoring system in standalone
mode, based on short (60 min) desalting tests, without AS treatment, at an average surface $S_{I_{g,m}} \approx 1.4$ in the membrane monitoring system observation zone (27\% equivalent recovery, $\alpha=1.1$). During the above filtration tests, deposition of fine particulate matter was observed that rapidly covered the monitored membrane surface (Fig. 5-6 a-b) as is particularly noticeable in Fig. 5-6b. Significant permeate flux decline (~42\% within 1 h) was also encountered (Fig. 5-7i) with about 80\% membrane surface scale coverage at the monitored observation zone (Fig. 5-6). Post analysis of the membrane (via SEM-EDS) indicated the presence of calcium sulfate precipitate, although previous mineral scaling studies have suggested that gypsum scaling should not be expected for the above gypsum saturation level until after ~5 h [78, 86].

Given the high gypsum saturation in the raw feed water ($S_{I_g} \approx 0.90$, Table 5-1), $S_{I_{g,m}}$ was expected to exceed unity for recovery above ~10\% (Figs. 5-2, 5-3). Therefore, the effectiveness of AS treatment was first evaluated, via flux decline monitoring, for membrane monitor operation at $S_{I_{g,m}}=2.5$ (equivalent RO plant recovery of ~58\% with $\alpha=1.1$) with a reasonable 3 ppm dosage of AS1 as suggested in previous work [111, 112, 128]. Despite an increase in operational $S_{I_{g,m}}$ from 1.4 to 2.5, flux decline was reduced to ~14\% (Fig. 5-7ii), indicating partial suppression of mineral scaling by the added AS1. Nonetheless, the above level of AS1 dosing should have enabled scale free operation as reported for similar water source [43].
Figure 5-6. Membrane surface images of the membrane monitor observation zone for desalting of agricultural drainage water in a stand-alone operation. Images (a) and (b) are for operation at 27% equivalent recovery ($Sl_{g,m} = 1.4$) with Filtration A (using a series of cartridge filters) without antiscalant dosing, at t=10 min and 1 hr, respectively, showing widespread particulate matter deposition observed in (a) and particularly in (b). Images (c) and (d) are for membrane monitor operation at 58% equivalent recovery ($Sl_{g,m} = 2.5$) with upgraded Filtration B (media filtration and cartridge filters) without antiscalant treatment, showing a clean membrane surface (c), except for some initial mineral scaling on the right-hand region of (d). Observation area: 1.3 x 1.0 cm.

Therefore, it was surmised that insufficient filtration was likely the cause of the observed rapid fouling and contributor to enhanced scaling (due to seeding of crystals) even with reasonable AS dosing. Although Filtration scheme A (Fig. 5-1, Section 5.2.3) reduced feed water turbidity from ~6 NTU to ~0.5-1.0 NTU, cartridge filtration was observably insufficient for mitigating
particulate deposition which is likely to have enhanced heterogeneous nucleation of mineral crystals [51].

In order to improve feed filtration, a media filter was installed upstream of cartridge filtration and a 0.2 micron cartridge filter added just downstream of existing M3 filter cartridges (Fig. 5-1). With enhanced filtration B the filtered RO feed turbidity was reduced to <0.2 NTU. Although membrane monitor operation at initial $S_{lg,m}$ of 2.5 (equivalent to 58% RO plant recovery with $\alpha=1.1$) without AS dosing did reveal a degree of scaling (Fig. 5-6c-d), there was significant reduction in the observed surface fouling in the membrane monitor test zone. Also, flux decline, relative to operation at the same $S_{lg,m}$ of 2.5 but with AS1 dosing, was somewhat lower for the test period of 1 h (Fig. 5-7iii). Upon AS1 dosing of 3 mg/L (also for membrane monitor operation at the above $S_{lg,m}$ level) mineral scale formation was effectively suppressed as indicated by the negligible flux decline in the short diagnostic test (Fig. 5-7iv). Membrane monitor surface imaging at a higher $S_{lg,m}$ of 3.1 (equivalent RO plant recovery of 67%) provided further confirmation that the upgraded filtration along with AS dosing was effective in suppressing mineral scaling (Fig. 5-8), with noticeable scaling occurring only after about 5 h of operation. The above diagnostic tests suggest that suspended particulates (even for feed water of turbidity <1 NTU) in source feed water of high mineral scaling propensity could serve as seeds for promoting gypsum surface crystal nucleation. Therefore, for such water sources effective removal of suspended particulates is needed prior to RO desalting.
Figure 5-7. Permeate flux decline for membrane monitor tests of feed filtration adequacy for two different filtration schemes (Section 5.2.3). Filtration A (cartridge filters: 5 and 0.45 μm): i. Initial $S_I_{g,m} = 1.4$ (27% equivalent recovery) without AS dosing, and ii. $S_I_{g,m} = 2.5$ (58% equivalent recovery) with 3 mg/L dosing of antiscalant AS1. Filtration B: iii. Initial $S_I_{g,m} = 2.5$ (58% equivalent recovery) without antiscalant dosing, and iv. Initial $S_I_{g,m} = 3.1$ (67% equivalent recovery) with 3 mg/L dosing of antiscalant AS1.

5.3.2 Rapid antiscalant selection and dose optimization for mitigation of mineral scaling

Final antiscalant selection and dose optimization were accomplished via a sequence of mineral scaling tests using the membrane monitoring system post optimization of the feed filtration scheme (Section 5.2.2). Selection of the two candidate antiscalants, for field testing of scale suppression, was based on previously reported laboratory AS testing results [78, 128]. Both antiscalants, AS1 and AS2, were compared at the same dose (3 mg/L) for the same initial $S_I_{g,m}=3.1$ (in the observation zone), corresponding to an equivalent RO plant water recovery of 67% (for $\alpha=1.1$; see Section 5.2.4). Real-time membrane surface monitoring revealed that the evolution of surface mineral scale coverage on the RO membrane was significantly slower with AS2 than with AS1 as shown in Fig. 5-8. Scale coverage of about 44% was observed without AS
use after 3 h, with 9% and 2% scale coverage after 10 h with AS1 and AS2, respectively, at the
dose of 3 mg/L. Flux decline due to scaling (Fig. 5-9) was consistent with the observed surface
coverage (at the same initial $SI_{g,m}=3.1$ for each antiscalant dosage). AS2 was more effective in
delaying the onset of scaling (i.e., nucleation) and reducing the growth rate of gypsum crystals
on the membrane surface, (i.e., retarding gypsum scaling), thereby resulting in fewer gypsum
crystals on the membrane surface. Antiscalant feed dosing increased the observed scaling
retardation time to ~1.5 h and ~8 h for AS2 dose of 1 mg/L and 2 mg/L, respectively, relative to
6 h for AS1 at 3 mg/L and only 20 minutes without AS use. AS2 was more effective in delaying
the onset of mineral scaling, and at 3 mg/L dose reduced surface scale coverage (at the
membrane monitor observation zone; Section 5.2.2) from ~45% to below 3% for the 10 h test
(Figs. 5-8, 5-10).

![Image](image1.png)

**Figure 5-8.** Evolution of the extent of gypsum scale coverage of the membrane surface in the
membrane monitor observation zone for stand-alone membrane monitor operation
at equivalent 67% recovery (initial $SI_{g,m}=3.1$) without antiscalant addition and
which feed dosing with antiscalants AS1 (3 mg/L) and AS2 (1-3 mg/L).
Figure 5-9. Permeate flux decline for field evaluation of antiscalant performance in membrane monitor stand-alone operation corresponding to the scaling test conditions of Fig. 5-8. (Initial $SI_{g,m}=3.1$, all tests were conducted for the same initial flux, $F_0$).

Although the above tests indicated that AS dosing at 3 mg/L was reasonable for operation of the RO plant at about 67% recovery, a more refined testing was undertaken (Fig. 5-10). In this test, the membrane monitoring system was operated at successively increasing $SI_{g,m}$ (at the membrane surface in the observation zone) from ~1.9 to ~3.1 over a 45-hour period (Fig. 5-10) with the equivalent recovery estimated based on $\alpha=1.1$ in Eq. 5-1 (also see Fig. 5-3). Scale formation was first detected near the end of a 7-hour membrane monitor desalting run at $SI_{g,m}$ of 2.9 ($t=25-32$ h) representing an equivalent recovery of 64%. Upon increasing $SI_{g,m}$ to 3.1 (equivalent recovery of 67%, $\alpha=1.1$) during a subsequent 12-hour period ($t=33-45$h), the appearance and growth of gypsum crystals on the membrane surface became more readily observable. The above gypsum supersaturation level was sufficiently high to overcome the AS2 capacity (at 3 mg/L dose) for suppression of gypsum crystallization. From the above results, it
was reasonable to conclude that the membrane scaling threshold would be expected to be at an equivalent RO plant recovery of ~64% (assuming $\alpha=1.1$ and retentate $S_{i_{g,m}}\approx2.9$).

Figure 5-10. Field estimation of the mineral scaling threshold whereby the membrane monitor is operated at a stand-alone mode, with 3 mg/L feed dosing with antiscalant AS2, at different equivalent recovery levels of 45%, 51%, 57%, 64% and 66% corresponding to initial gypsum saturation at the membrane surface (in the monitored observation zone) of 1.9, 2.1, 2.4, 2.9 and 3.1.

5.3.3 Field demonstration of AD water desalination with the M3 Spiral-Wound RO Pilot

In order to confirm the RO operating conditions identified as suitable for scale free operation in the diagnostic field testing described in Sections 5.3.1 and 5.3.2, RO desalting was carried out with the spiral-wound M3 pilot system at a feed flow rate of 0.79 m$^3$/h with the membrane monitor was installed for online scale detection (Fig. 5-1). The operational recovery range was 58-65%, producing permeate of salinity in the range of 370-400 mg/L total dissolved solids, for the set RO feed flow rate of 0.79 m$^3$/h. Initially, desalting was carried out at about
65% recovery ($SI_{g,m} = 3.0$ at the exit region of the M3 tail element) (**Section 5.2.4**) with a low AS2 dosage of 0.5 mg/L. This test was undertaken, whereby operation of the membrane monitor was set such that $SI_{g,m} = 3.0$ in the observation zone, in order to confirm the ability to monitor the onset and progress of scale formation in the RO plant. At the above operating condition mineral scaling was expected to occur (see **Figs. 5-2, 5-3**) as was indeed verified in the membrane monitor scale detection (**Fig. 5-11**).

**Figure 5-11.** (Top) Normalized permeate flux for membrane elements 1-6 and for the tail element (element 6) of the M3 pilot for desalting operating at feed flow rate of 0.79 m$^3$/h and 65% recovery (tail element retentate initial $SI_{g,m} = 2.9$) with 0.5 ppm AS2 feed dosage. (Bottom) Membrane surface images from the membrane monitor observation zone set to operate with $SI_{g,m} = 2.9$ at the observation area. Initial overall and tail (6$^{th}$) element permeate fluxes of 0.198 m$^3$/h (117 GFD) and 0.009 m$^3$/h (5.30 GFD), respectively. Right: entire membrane surface image (t=2 h) reveals widespread mineral scaling that increases toward the RO channel exit (flow is in the arrow direction). Rectangle indicates the membrane monitor observation zone.
Mineral crystals were visually detected on the monitored membrane (Fig. 5-11a-b) within the first 1 h of operation, prior to any significant measurable permeate flux decline either for the overall system (i.e., collective flux from M3 elements 1-6) or the M3 tail (Fig. 5-11, Table 5-2).

Indication of scaling could also be inferred from membrane monitor flux decline that reached about 20% within the first 0.5 h while there was no measurable change in flux detected for the M3 RO plant. The membrane monitor flux declined progressively reaching 62% after 1 h, relative to only ~3% flux decline (within measurement uncertainty) for the M3 6th element (Table 5-2, Fig. 5-11). The above results indicated that monitoring RO plant flux decline did not provide sufficient sensitivity for early warning regarding membrane mineral scaling [112]. Early detection of mineral scaling and its progression can, however, be quantified with the membrane monitor as a scale detector on the basis of membrane surface scale coverage (Fig. 5-11) and also by the number density of mineral crystals (in the monitored observation zone). In principle, the first observed crystal in the membrane monitor could be considered as the earliest observed sign of the onset of mineral scaling. In the present study, for which images were captured every 5 minutes, the first instance of observed scale was as early as t=5 min with the crystal number density (CND) being 40 crystals/cm² with a surface coverage of 1.1% of the detection zone (Table 5-2, Fig. 5-12). Clearly, the above is a highly practical and sensitive test of the onset of mineral scaling.
Table 5-2. Operating conditions for test of RO pilot scale detection\(^{(a)}\).

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Percent flux decline for the monitor (initial SI(_{gm}=2.9))</th>
<th>Percent flux decline for the M3 RO tail element (initial SI(_{gm}=2.9))</th>
<th>Overall percent flux decline in the M3 RO system</th>
<th>Gypsum crystal number density (CND) in the monitored observation zone (cm(^{-2}))</th>
<th>Mineral scale surface coverage (%) in the monitored observation zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>20%</td>
<td>&lt;1%</td>
<td>~0%</td>
<td>89</td>
<td>13</td>
</tr>
<tr>
<td>1.0</td>
<td>60%</td>
<td>1%</td>
<td>~0%</td>
<td>216</td>
<td>23</td>
</tr>
<tr>
<td>1.5</td>
<td>80%</td>
<td>10%</td>
<td>3%</td>
<td>523</td>
<td>48</td>
</tr>
<tr>
<td>2.0</td>
<td>&gt;80%</td>
<td>39%</td>
<td>10%</td>
<td>820</td>
<td>75</td>
</tr>
</tbody>
</table>

\(^{(a)}\)Test conditions and results are in reference to Fig. 5-11.

Figure 5-12. Product water recovery and permeate flux for M3 RO pilot field testing of AD water desalting at feed flow rate of 0.72 m\(^3\)/hr (4,500 gallons/day) with AS2 feed dosing of 3 mg/L. For 52% recovery: initial overall flux was 0.11 m/hr (65.6 GFD). For 63% recovery: initial overall and 6\(^{th}\) element permeate fluxes were 0.17 m/hr (100 GFD) and 0.01 m/hr (5.89 GFD), respectively. Initial, maximum and average recovery were 60%, 64% and 62.9%, respectively. Membrane monitor operation was set at initial SI\(_{gm}=2.8\) at the observation zone (equivalent RO plant recovery of 63%).
Given the above validation of scale detection for the spiral-wound M3 plant operation, desalting with the M3 was then carried out with 3 mg/L AS2 dosing. The M3 plant was first operated at a safe recovery level of ~52% (Fig. 5-12). Subsequently desalting testing was increased to a recovery range of 60-64% (Fig. 5-12), just below the previously determined mineral scaling threshold (Figs. 5-2, 5-3, 5-10, Section 5.3.2). At the above recovery range, it was determined that the RO tail element recovery was 8.8-10%, corresponding to a CP level in the tail element of ~1.08-1.09, consistent with recommended industry guidelines and the present CP allowance (Section 5.2.4) used for estimating the attainable recovery based on membrane monitoring diagnostic tests. The M3 plant was operated with the membrane monitor serving as an online monitor receiving a side stream from the last (i.e., 6th) element of the plant (Fig. 5-1). The membrane monitor was operated such that $S_{g,m}=2.9$ at the observation zone (equivalent to RO plant recovery of 64%). The RO plant operation was initiated at 60% recovery with the recovery gradually set to increase up to a maximum of 64% for a short duration ($t=1.0-1.5$ h). The recovery was then gradually decreased and set to 63%, which was just below the mineral scaling threshold as ascertained in the stand-alone membrane monitoring diagnostic tests (Fig. 5-10, Sections 5.2.5, 5.3.2). As expected, RO plant operation was scale free over the test period as indicated by both the lack of RO plant permeate flux decline and scale free membrane surface in the monitored detection zone (Fig. 5-12). Overall, results of the study demonstrate the benefit of field deployment of the membrane monitoring diagnostic system for establishing both suitable RO feed pre-treatment and RO operating conditions. Further utilization of an online membrane fouling detection system enables one to ensure safe RO operating conditions. Moreover, with appropriate interface of the membrane monitoring system with RO plant control system, it
should be possible to adjust plant operating conditions (e.g., feed flow rate, transmembrane pressure, antiscalant dose) to aid in mitigation of fouling and mineral scaling.

5.4 Summary

Rapid field evaluation of RO feed filtration requirements, selection of effective antiscalant type and dose, and estimation of suitable scale-free RO recovery level for a given source water was achieved using a novel approach based on direct observation of mineral scaling and flux decline measurements. In this approach, an automated membrane monitor was operated in a single-pass desalting mode in the field. In terms of feed filtration, suspended particulates (even for feed water of turbidity <1 NTU) in the brackish RO feed water of high mineral scaling propensity were found to contribute to more severe flux decline and serve as seeds for promoting additional surface crystal nucleation, as visualized via the membrane monitoring system. Therefore, for such water sources, effective removal of suspended particulates (beyond the typical recommended level for RO feed) is needed prior to RO desalting.

Scale-free RO operating conditions were determined via standalone rapid membrane monitoring diagnostic tests. Extended operation of an integrated system, with real-time evaluation of scaling mitigation is presented in Chapter 6 for field optimization of RO operating conditions of a RO demonstration plant integrated with a membrane monitoring cell for guided operation.
Chapter 6

RO Recovery Optimization and Mineral Scaling Mitigation for Agricultural Drainage Water Desalination

6.1 Overview

The desalination of agricultural drainage (AD) water in the San Joaquin Valley of California is challenging due to its high scaling propensity and high salinity (~3,000–30,000 mg/L TDS) which can vary locally and temporally [43, 52, 74, 87]. As stated in Chapter 5, early detection of mineral scaling via direct membrane monitoring is clearly necessary for AD water desalination, and it is essential to establish effective site-specific RO operating conditions in the field.

As discussed previously (Sec. 2.2.2), optimizing RO operating conditions (e.g., water recovery, antiscalant selection and dose, etc.) is important for effective scale control [81, 111, 112, 118, 281, 282]. However, in conventional RO plants, antiscalant selection and testing for a given recovery level may require tedious long-term studies in order to verify causal relationships between operating conditions and membrane mineral scaling. This is due, in part, to the reliance on monitoring permeate flux decline which typically may suggest a fouling or scaling problem when there is at least ≥5% flux reduction (i.e., the accuracy limit of the measurements) [127, 130-133]. Determination of the onset of mineral scaling via flux decline measurements is imprecise, since incipient scaling can occur much earlier than detection of its influence on flux decline [85-87, 133, 140]. Secondly, temporal changes in environmental conditions may affect operating conditions (e.g., changes in water salinity or temperature), further complicating the conventional approach of flux normalization. For example, significant local and temporal
variability has been reported for AD water salinity in the San Joaquin Valley (~3,000–30,000 mg/L total dissolved solids) [43]. Therefore, site-specific evaluation of scaling potential is essential in order to determine the optimally feasible RO water recovery, as limited by salinity or mineral scaling [43, 87]. Given the potential variability in feed water quality, effective real-time membrane monitoring (i.e., for fouling and mineral scaling) would be invaluable in order to optimize RO operating conditions (i.e., prefiltration, antiscalant dose, mineral scaling mitigation methods, etc.) and maximize the feasible RO water recovery.

Direct membrane monitoring, using a high-pressure optical monitoring cell [85-87, 91, 112, 156, 157], has previously been used for early detection and investigating mineral scaling kinetics relevant to brackish water desalination in Chapters 3–5 and in previous studies [85, 86, 112, 156]. This approach was also demonstrated as a useful tool for quantifying antiscalant impact on mineral scaling kinetics and for comparing antiscalant effectiveness [112]. In Chapter 5, the feasible operating conditions for RO desalination for similar AD water were evaluated, in the field, using a membrane monitoring system and small RO pilot system for verification of the diagnostic study [87]. However, demonstration of the practicality of the approach necessitates verification of the approach with continuous RO operation at a reasonable demonstration plant scale. Accordingly, the present chapter presents an approach whereby a specialized optical RO membrane monitoring system was developed and interfaced with the UCLA SIMS RO plant. The membrane monitoring system was utilized to guide both the optimization of feed pretreatment and scaling mitigation strategies (e.g., antiscalant selection and dose optimization in addition to periodic fresh water flush and RO recovery setting).
6.2 Experimental

6.2.1 Brackish Agricultural Drainage Water Source

A field optimization study for inland RO desalination was carried out for subsurface agricultural drainage water at the Panoche Drainage District (PPD) of the San Joaquin Valley (SJV) in California. Influent water quality in the field site varied temporally (Table 6-1) with salinity being in the range of 11,380–16,030 mg/L total dissolved solids (TDS). The sparingly soluble mineral CaCO$_3$ was above its solubility while CaSO$_4$ was near or above saturation.
# Table 6-1. Summary of AD water source quality.\(^{(a)}\)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Average</th>
<th>Standard Deviation</th>
<th>Observed Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductance (µS/cm)</td>
<td>17374</td>
<td>2387.9</td>
<td>13526–19596</td>
</tr>
<tr>
<td>Turbidity (NTU)(^{(b)})</td>
<td>0.66</td>
<td>0.3</td>
<td>0.15–1.17</td>
</tr>
<tr>
<td>pH (pH units)</td>
<td>7.6</td>
<td>0.12</td>
<td>7.5–7.8</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS) (mg/L)</td>
<td>14405</td>
<td>1722</td>
<td>11380–16030</td>
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<tr>
<td>Total Suspended Solids (mg/L)</td>
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<td>3.3</td>
<td>1–10</td>
</tr>
<tr>
<td>Total Organic Carbon (mg/L)</td>
<td>8.4</td>
<td>1.2</td>
<td>6.9–9.9</td>
</tr>
<tr>
<td>Total Alkalinity (mg/L as CaCO(_3))</td>
<td>317</td>
<td>63</td>
<td>229–377</td>
</tr>
<tr>
<td>Total Barium (mg/L)(^{(c)})</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
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<tr>
<td>Dissolved Boron (mg/L)</td>
<td>50.5</td>
<td>6.3</td>
<td>41–58</td>
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<tr>
<td>Dissolved Calcium (mg/L)</td>
<td>549</td>
<td>34.5</td>
<td>520–614</td>
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<td>Dissolved Chloride (mg/L)</td>
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<td>850</td>
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<td>Dissolved Magnesium (mg/L)</td>
<td>348</td>
<td>78.9</td>
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<td>Dissolved Silica (mg/L)</td>
<td>38.2</td>
<td>1.6</td>
<td>36–41</td>
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<td>Dissolved Sodium (mg/L)</td>
<td>3760</td>
<td>715</td>
<td>2819–4708</td>
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<tr>
<td>Total Strontium (mg/L)</td>
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<td>3.2</td>
<td>1.0–9.8</td>
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<td>Dissolved Sulfate (mg/L)</td>
<td>6104</td>
<td>319.7</td>
<td>5500–6401</td>
</tr>
<tr>
<td>(SI_{\text{CaCO}_3})</td>
<td>7.2</td>
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<td>6.54–8.11</td>
</tr>
<tr>
<td>(SI_{\text{CaSO}_4})</td>
<td>0.97</td>
<td>0.03</td>
<td>0.93–1.01</td>
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<tr>
<td>(SI_{\text{SiO}_2})</td>
<td>0.32</td>
<td>0.01</td>
<td>0.30–0.33</td>
</tr>
<tr>
<td>(SI_{\text{SrSO}_4})</td>
<td>0.66</td>
<td>0.29</td>
<td>0.09–0.84</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Note: Water samples were taken from the tile sump at the field site (Figures 6-1, 6-2). Raw influent water was first passed through a hydrocyclone separator for removal of large particles prior to sampling.

\(^{(b)}\) NTU: nephelometric turbidity units. \(^{(c)}\) Barium levels were below the detection limit.
6.2.2 Smart Integrated Membrane System (SIMS)

The mobile demonstration-scale RO system, the “SIMS”, developed at UCLA, was housed inside a 40 ft.-long (12.2 m) ISO container positioned on a trailer, capable of redeployment in remote areas (Figs. 6-1, 6-2). The plant’s treated water production capacity was up to 151 m$^3$/day (~40,000 gallons/day). The SIMS RO feed pretreatment train consisted of a hydrocyclone (centrifugal separator, Lakos, Lindsay Corporation, Fresno, CA), followed by microfiltration using a 300 µm self-cleaning disk filter (2” Brushaway Filter, Amiad, Mooresville, NC) and subsequently ultrafiltration using 2 parallel multibore inside-out hollow fiber modules (Dizzer XL 0.9 MB 60 W; Inge GmbH, Greifenberg, Germany). Raw agricultural drainage feed water was delivered by a large sump pump on-site with a capacity of up to 100 gallons/min delivered at a pressure of up to 50 psi (3.4 bar) (P-1, Fig. 6-2). Once treated for removal of large suspended matter (>850 µm), feed water was diverted to a storage tank (T-1, Fig. 6-2). A centrifugal pump (P-2, Fig. 6-2, CRNE5-6 A-P-G-E HQQE 2 HP; Grundfos, Bjerringbro, Denmark) provided feed water from the storage tank (T-1) to the UF modules. The UF filtered water was diverted to a UF filtrate tank (T-2) from which a low pressure pump (CRN5-4 A-P-G-E-HQQE 1.5 HP; Grundfos, Bjerringbro, Denmark) delivered water to the RO unit.

The plant was instrumented with digital sensors for monitoring the various streams with respect to pressure (Model S-10 & S-11; Wika Instrument LP, Lawrenceville, GA), flow rate, temperature, pH, electrical conductivity and turbidity (Models 2551/2537, 2350, 2750, 2850, and 4150 respectively; Georg Fischer Signet, LLC, El Monte, CA). Sensor data were collected in real-time by the onboard control and monitoring system and transmitted wirelessly to a data
acquisition and control server. In addition, periodic water quality analyses of the influent and RO process streams were performed offsite by a State of California accredited laboratory (Bryte Chemical Laboratory, Sacramento, CA). Inline coagulation of the UF feed stream was accomplished using metering pumps (SMART Digital DDA; Grundfos, Bjerringbro, Denmark), and utilized a 5 wt. % aluminum solution of ACH (aluminum chlorohydrate) (Qemipac 7580; Qemi International, Inc., Kingwood, TX) injected to the UF feed stream at a dosage of 0.8 mg/L (Al).

Figure 6-1. Location of field testing site in the San Joaquin Valley of California (adapted from [43]) (A), external view of SIMS trailer on-site (B), internal view of SIMS (C), and membrane monitor inside the SIMS trailer (D).
Figure 6-2. Simplified process diagram for the SIMS RO desalination plant with integrated membrane monitoring system (MMS). A sump pump (P-1) delivered raw water to the pretreatment system and feed tank (T-1). The centrifugal UF feed pump (P-2) delivered water to the UF membranes or to the membrane monitoring system (MMS) using a sampling valve (V-1). UF filtrate was delivered from a storage tank (T-2) to the MMS with a sampling valve (V-2) or to the high-pressure RO pump system (P-3) which included a low pressure pump and interstage pump (not shown). For pretreatment diagnostics, the MMS booster pump (P-4) was fed water from storage tanks T-1 or T-2 using a diverting valve (V-3). Valves V-4 and V-5 allowed RO concentrate monitoring. Diverting valve (V-6) allowed for fresh water flushing of the SIMS and MMS. Control valves V-7 & V-8 serve to control the pressure and crossflow velocity in the SIMS and MMS, respectively. The regions within the dotted and dashed lines indicate the standard prefiltration train and ultrafiltration train, respectively. Note: CF = cartridge filter.

The RO system consisted of two RO membrane trains. The first stage pump had a capacity of 24 GPM (5.45 m³/hr) (CRNE3-23 HS-P-G1-E-HQQE 10 HP; Grundfos, Bjerringbro, Denmark) and the interstage pump capacity was 12.5 GPM (2.84 m³/hr) (CRNE1-23 HS HS-P-G1-E-HQQE 6.2 HP; Grundfos, Bjerringbro, Denmark). The first stage contained 14 brackish water RO membrane elements of 4” (10.2 cm) diameter and 40” (1.02 m) length, while the second stage consisted of 7 seawater RO membrane elements of the same dimensions (TM710D
and TM810V, respectively; Toray, Poway, CA). These membranes were selected for their high salt rejection and high permeability, suitable for brackish water desalination. Overall observed salt rejection for the RO system was ~99.5%. RO permeate water was stored in a 400 gal. (1.51 m³) tank (T-3, Fig. 6-2).

6.2.3 Membrane Monitoring System (MMS)

The RO system was integrated with a membrane monitoring system (MMS) (for scale detection) (Figs. 6-1D, 6-2), consisting of a transparent plate-and-frame RO (PFRO) membrane cell adapted from a previous approach [85-89, 139, 156]. The brackish water (BW) or seawater (SW) membrane coupons used in the monitor (UTC-70AC and UTC-82V, respectively; Toray, Poway, CA) had observed salt rejection of 97.5±0.6% and 98.0±0.5%, respectively (determined for a 4000 ppm NaCl solution at a transmembrane pressure of 250 psi (17.2 bar)). The PFRO cell has rectangular flow channel dimensions of 3.1 cm (width) × 8.8 cm (length) × 0.25 cm (height) with an active membrane surface area of 27.4 cm². Given the small membrane surface area, the water recovery due to permeate withdrawal in the monitoring cell was <0.1%. The cell's flow channel has been well-characterized with respect to hydrodynamics and concentration polarization (CP), the details of which can be found elsewhere [88, 89, 139, 156]. The MMS was configured to receive a feed stream directly from the SIMS or operate as a standalone unit receiving its feed via a 3/4 hp (559 W) positive displacement pump (P-4, Fig. 6-2) with capacity of 0.45 GPM (0.10 m³/hr) (Hydra-Cell Model P100; Wanner Engineering, Inc., Minneapolis, MN) from a separate feed tank (not shown). The MMS feed pump inlet was fitted with an 80-mesh (177 μm) stainless steel strainer (Ron-Vik, Inc., Minneapolis, MN). Specialized external lighting was arranged along the membrane cell to direct light towards the membrane cell and provides high contrast illumination of surface foulants/scalants. Real-time surface imaging was
accomplished with a compact digital microscope with high resolution imaging (2592 × 1944 resolution). Images were captured automatically and transmitted to the monitoring and control system for direct observation and online image analysis as discussed in Section 6.2.5.1 (Appendix B).

6.2.4 Field Optimization Scheme for RO Water Recovery and Antiscalant

The first stage of the field optimization scheme (Fig. 6-3) entails a water quality analysis in which the concentrations of dissolved salts in the RO feed (Table 6-1) are used to identify sparingly soluble mineral salts (i.e., potential mineral scalants). For each potential mineral scalant, a recovery survey is performed on the water quality data, whereby the concentration factor \( CF = C_c / C_f \), where \( C_c \) and \( C_f \) are the salt concentrations in the RO concentrate and feed, respectively) is used to simulate RO water recovery from the feed stream (Eqn. 6-3). Using an aqueous multi-electrolyte simulation software package [248], thermodynamic plots of saturation index (SI) (in the RO concentrate stream) versus RO water recovery are generated. Such data is then used to determine: (a) projected water recovery levels at which SI=1 for a given mineral scalant, and (b) projected feasible water recovery ranges for a recommended range of SI values (e.g., for effective antiscalant use) (Sec. 6.3.1).

The second stage of RO field optimization, pretreatment diagnostics, includes standalone, one-pass testing of the RO feed stream using the MMS (Sec. 6.3.2). The membrane monitor was configured to receive a slipstream from either the "raw" UF feed, UF filtrate (RO feed), or high-pressure RO concentrate in a single-pass mode of operation (Fig. 6-2). The SIMS UF pump delivers the raw feed to the membrane monitor pump (P-4), whereas the UF filtrate tank (T-2) was used to feed the MMS pump directly with UF filtrate (Runs 1, 2) (Fig. 6-2). Standard sand media filters (#20 sand, ~0.85 mm average sieve size) were available on-site for filtration of AD
water influent. As a precautionary step, the turbidity of each feed stream was tested to ensure they met minimum RO feed water standards (i.e., <0.5 NTU average [104]). During pretreatment diagnostics (Fig. 6-3), the UF feed and UF filtrate are initially monitored over a range of operating conditions, without antiscalant, such that the water recovery level was at or above that projected where SI=1 (i.e., mineral scaling is possible). In these runs, the UF filtrate is not processed by the RO plant. These short tests serve to assess the potential for mineral scaling as well as the effectiveness of the prefiltration units for preventing introduction of particulate matter to the RO feed. Additionally, since antiscalant is not used in these tests, they serve as a baseline for kinetic rates of mineral scaling (i.e., crystal nucleation and growth rates).

![Figure 6-3](image)

**Figure 6-3.** Field optimization procedure for assessing mineral scaling and its mitigation for brackish water RO desalination.
The local salt concentration at the membrane surface \( (C_m) \) in the membrane monitoring cell is elevated according to the CP factor, \( CP = C_m/C_b \), where \( C_b \) is the concentration in the bulk solution, and \( CP \) is estimated using models previously developed for the present membrane cell \([88, 89]\). It is noted that the CP level in the monitored area of the membrane cell can be tuned by controlling the feed pressure that dictates permeate flux as well as the cross-flow velocity using the membrane monitor pump and control valve (Figure 6-2). The CP can therefore be selected to mimic the conditions that exist in the SIMS RO plant concentrate in the tail element.

The equivalent recovery, \( \text{Y}_{eq} \), is the RO water recovery with RO brine salt concentration equivalent to the salt concentration at the observed membrane surface (due to CP in the membrane monitoring system). The equivalent recovery is calculated from the SIMS RO plant recovery \( (Y) \) or corresponding concentration factor \( (CF=C_c/C_f) \) calculated from Eqn. 6-1, and \( CP \):

\[
\text{Y}_{eq} = 1 - \frac{1}{CP \cdot CF}
\]  

(6-1)

or in terms of the SIMS RO recovery, \( Y \) and \( CP \):

\[
\text{Y}_{eq} = 1 - \frac{1-Y}{CP(1-\beta Y)}
\]  

(6-2)

in which \( \beta \) is the salt passage \( (\beta=C_p/C_f \text{, where } C_p \text{ is the salt concentration in the permeate}) \). Therefore, when the membrane monitor is used to monitor the UF or RO feed in a standalone mode, \( CF=1 \text{ (Y=0)} \), and the equivalent recovery depends only on \( CP \).

Lastly, RO field optimization requires the determination of the critical RO water recovery level (with antiscalant dosing) at which mineral scaling will occur. To accomplish this, the membrane monitoring system is used as a 2nd stage RO concentrate monitor for mineral scale detection and RO recovery optimization. This also involves antiscalant selection and dosage.
optimization. In the above operational mode, a slipstream of high-pressure RO concentrate is fed directly to the membrane monitoring system. If no scaling occurs at a given recovery, the recovery is periodically increased until scaling begins to occur (Fig. 6-3). When scaling occurs in the membrane monitor, the current recovery level is regarded as potentially unsafe for the current water quality and operating conditions (e.g., antiscalant dose). Thereafter, corrective actions are initiated for mineral scaling mitigation (e.g., antiscalant dosage adjustment or freshwater flush).

6.2.5 Membrane Surface Scale Analysis

6.2.5.1 Real-time Membrane Image Analysis

Real-time surface imaging was accomplished with a compact digital microscope with high resolution (2592 × 1944) imaging. Images were captured and transmitted to the monitoring and control system for image analysis using specialized in-house software [156]. The image analysis algorithm relied on adaptive image segmentation to highlight and quantify surface changes due to mineral scaling. Images were first converted to grayscale and enhanced based on histogram equalization in order to increase image contrast (Appendix B) [314, 315], and subsequently aligned to enable accurate image comparison. Image background subtraction was then carried out in order to identify the evolution of surface changes over time. Subsequently, the identified scaled areas were quantified with respect to the surface area covered by detected crystals, and the number of identified scaled entities (i.e., crystals) was enumerated and crystal number density (CND) was calculated in units of number of crystals/cm² or number of crystals/mm². The above surface scaling parameters can be used as a basis for setting thresholds to trigger operational adjustments that include, for example, water recovery, increasing AS dosage, initiating a permeate water flush sequence, or a combination of the above.
Individual crystal growth rates were also estimated from the analyzed images, by assuming a hemispherical geometry for the imaged crystals. The equivalent crystal diameter, \( d_{eq}=(4 \cdot A_c/\pi)^{1/2} \), was calculated from the measured projected 2-D area of each scale crystal, \( A_c \), following a previous approach [78, 85, 86, 91, 112]. Crystal growth rate was quantified as the equivalent crystal diameter rate of change, \( r_d=d(d_{eq})/dt \).

6.2.5.2 EDS Analysis of RO Membrane Samples

At the end of RO experiments, the membrane coupons were removed from the membrane monitor cell and subsequently analyzed via energy dispersive x-ray spectroscopy (EDS). Prior to analysis, membrane samples were pre-coated using a vacuum sputtering system with a 15-20 nm layer of gold in order to increase the electrical conductivity of samples (Hummer 6.2 Sputtering System; Anatech USA, Union City, CA). Pre-coated samples were analyzed with respect to major elements present in the surface scale crystals (EDAX Genesis Spectrum; EDAX Inc., Mahwah, NJ).

6.3 Results and Discussion

6.3.1 Field Water Quality Analysis

The expected level of saturation of calcite, silica and gypsum in the RO brine were calculated as a function of product water recovery given the feedwater quality (Table 6-1, Fig. 6-4). Water recovery is defined as \( Y=Q_p/Q_f \), where \( Q_p \) and \( Q_f \) are the volumetric flow rates of permeate and feed, respectively. Water recovery is related to the concentration factor \( CF \), \( (CF=C_c/C_f) \) and the observed salt rejection, \( R_o=1-(C_p/C_f) \), (or salt passage, \( \beta \)). It follows from a mass balance that \( CF \) can be expressed as:
\[ CF = \frac{C_C}{C_F} = \frac{1-Y(1-R_o)}{1-Y} = \frac{1-Y\beta}{1-Y} \]  

(6-3)

or \( Y \) in terms of \( CF \):

\[ Y = \frac{CF - 1}{CF - (1-R_o)} = \frac{CF - 1}{CF - \beta} \]  

(6-4)

The saturation index of a mineral salt is given by \( SI_x \), where \( x \) denotes the mineral salt of concern. The \( SI \) for gypsum (i.e., calcium sulfate), calcite, and silica are given by:

\[ SI_g = \frac{(Ca^{2+})(SO_4^{2-})}{K_{sp,g}}, \quad SI_c = \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp,c}}, \quad SI_s = \frac{(SiO_2)_{aqueous}}{K_{sp,s}} \]  

(6-5, 6-6, 6-7)

where \((Ca^{2+})\), \((SO_4^{2-})\), \((CO_3^{2-})\), and \((SiO_2)_{aqueous}\) are the activities for each species. \( K_{sp,x} \) is the equilibrium solubility constant (e.g., defined as \((Ca^{2+})_{eq}(SO_4^{2-})_{eq}\) for gypsum). For calcite, \( K_{sp,c} = (Ca^{2+})_{eq}(CO_3^{2-})_{eq}\), and \( K_{sp,s} = (SiO_2)_{eq}\) for silica in aqueous solution.

Figure 6-4. Saturation indices for sparingly soluble minerals vs. water recovery for the water sample taken at the beginning of experimental runs. Overall salt rejection is 99.5%. SI values calculated from [248]. Note: Error bands indicate variability in water quality.
Analysis of the expected saturation indices for calcite, gypsum and silica for the source water at PDD revealed SI variations corresponding to about ±13.6–17.9%, ±8.4–18.2% and ±6.3–10.3%, respectively, about the mean value (at the average water quality). It is noted that the variation in calcite saturation index was likely due, in part, to the observed feed pH range of 7.5–7.8 (Table 6-1). Based on previous studies, gypsum was expected to be the recovery-limiting mineral scalant for this water source [43, 74, 87]. Indeed, the source water was consistently at or near saturation with respect to gypsum ($SI_g = 0.93–1.01$). Additionally, at recovery levels higher than 70%, silica was also supersaturated. Calcite scaling was not expected since it has been shown that calcium sulfate inhibits calcite scaling due to antagonistic effects [78] and for the observed pH range of 7.5–7.8, $SI_c$ remained below the industry guidelines for RO operation (for effective antiscalant use) of $SI_c = 60$ [123] for $Y \leq 0.80$ (Fig. 6-4). Barium sulfate scale was not anticipated given that the total barium concentration in the RO feed and concentrate was consistently below 0.1 mg/L (Table 6-1, Appendix C), or $SI_{BaSO_4} \leq 15$, well below the recommended limit (with antiscalant) of $SI_{BaSO_4} = 60–80$ for RO operation [123].

Based on the above analysis, it was concluded that the major potential mineral scalants were calcium sulfate (gypsum) and silica. Therefore, two candidate antiscalants were selected based on their recommended usage for controlling silica and gypsum scale formation, hereafter referred to as AS-1 and AS-2 (Flocon 260 and 135, respectively; BWA Water Additives, Tucker, GA).
6.3.2 Assessment of Prefiltration and its Impact on Mineral Scaling

Based on prior studies on RO desalination of AD water at the PDD field site, it was expected that feed pretreatment (i.e., filtration of submicron particulate matter down to at least 0.2 μm) would be important to minimize RO membrane fouling and scaling [52, 87]. It has been suggested, for example, that foreign particulates in the RO feed can provide surface area for heterogeneous nucleation resulting in reduced crystallization induction times [230]. Therefore, effective removal of particulate matter is essential in order to establish an effective scale mitigation strategy.

Based on the RO water quality analysis to determine SI in the RO concentrate over a range of RO recovery levels (Sec. 6.3.1), it was determined that gypsum would be supersaturated (SIg=2) at 50% water recovery level. Water recovery of 50% is also a conservative target recovery for brackish water RO, and may be considered the minimum acceptable recovery, Indeed, below 50% recovery, more brine is produced than fresh water. Moreover, based on previous studies of gypsum scaling, significant mineral scaling was expected at $\text{SI}_g \geq 2$ within a relatively short period of ~12–24 hours [78, 112]. Therefore, operating at $\text{SI}_g=2$ enabled mineral scaling diagnostic tests to be accomplished over a short period of time. Moreover, the above testing also enabled a comparison of mineral scaling kinetics (i.e., nucleation rates) relative to previous RO membrane scaling data at the same conditions (SIg=2). This enabled inductive determination of whether the mineral scaling nucleation rate was abnormally high (e.g., due to the presence of suspended particles, etc.). Therefore, a series of RO diagnostic experiments using the MMS (without antiscalant) were carried out at 50% equivalent recovery (CP=2) in the membrane monitor with SI of gypsum at the membrane surface (SIg,m) of 1.9–2.0.
Membrane monitor surface images during desalination of raw water without antiscalant (Run 1, Table 6-2) (without UF) at crossflow velocity of 4.5 cm/s, initial permeate flux of 33 L/m²-hr (19 gallons/ft²-day) and $S_{g,m} = 1.9–2.0$ (50% equivalent recovery) exhibiting early particulate deposition or crystal nucleation.

From the resulting membrane surface images, it was apparent that the present prefiltration (with media filtration) was an inadequate means of avoiding particle deposition and mineral scaling. Although the level of feed turbidity achieved via media filtration was, on average, 0.66 NTU (less than the industry-recommended maximum of 1.0 NTU [104], Table 6-1), the extensive appearance of particles and/or small crystals was observed on the monitored membrane surface within 30 minutes after beginning operation (Figure 6-5). It has been suggested that the presence of foreign particles in solution reduce the energy required for nucleation to take place [230]. Therefore, if prefiltration is insufficient (and there are significant
suspended particles in solution) then mineral scale crystals may nucleate at a faster rate than they normally would and also appear on the surface more rapidly than they would in the absence of suspended particles.

In order to determine if different levels of prefiltration can affect crystal nucleation, the nucleation rates were quantified whereby detected surface crystals were enumerated. Although it was currently infeasible to visually detect crystal nuclei in the nanosize range in the membrane monitoring system (in real-time), the observed crystals represented surviving nuclei at a given location that had grown to visually detectable size (typically ~20-30 µm). Therefore, the rate of crystal nucleation, $J_N$, was quantified following a previous approach where the observed nucleation rate of change is given by [112]:

$$
J_N = \frac{1}{1-\phi} \frac{d\bar{N}}{dt}
$$

(6-8)

in which the crystal number density (CND) is $\bar{N}$, and $\phi$ is the degree of fractional surface scale coverage (i.e., $\phi=0$–1, where $\phi=0$ indicates a surface free of mineral scale). In the initial RO diagnostic test with the MMS operating at 50% equivalent recovery without UF pretreatment, the nucleation rate on the monitored surface was calculated as 7.23 crystals/(cm$^2$-hr). However, when compared to a previous study of gypsum membrane scaling without antiscalant for $SI_{gm}=1.9$–2.1, this nucleation rate was significantly higher (by a factor of 3–13) than previously observed [112]. Therefore, it was deduced that the presence of suspended particulate matter most likely contributed to a higher degree of particulate deposition on the membrane surface and thus a higher than expected observed surface crystal number density and nucleation rate. As a result, the media filters were subsequently removed and the RO feed was switched to the MF/UF train (Fig. 6-2).
Using UF pretreatment resulted in feed water turbidity that was consistently < 0.2 NTU, below the recommended average of 0.5 NTU for RO feed water [104]. The ultrafiltered raw source water was then used as the RO feed and the previous experiment was repeated using the membrane monitoring system at the same hydrodynamic conditions and resulting SI_{g,m}=1.9–2.0 for 50% equivalent recovery in the MMS. The resulting membrane surface images and comparative permeate flux decline data indicate that using ultrafiltered feedwater as RO feed resulted in a lesser degree of mineral scaling (Fig. 6-6, 6-7). Indeed, the flux decline after 10 hours was ~22% relative to ~38% flux decline without UF pretreatment, and the differences in the observed scale surface coverage and CND evolution revealed substantial difference in the mineral scaling kinetics (Figs. 6-7, 6-8). Without UF pretreatment, the mineral scale coverage and CND reached nearly 10% and 3 crystals/cm² after 10 hours, respectively, whereas the scale coverage with UF pretreatment was less than 2% with a CND of less than 1 crystal/cm². The observed crystal growth rate of 7.2 × 10⁻² mm/hr was also consistent with crystal growth rates measured in two previous studies of gypsum membrane scaling at SI_g=2 [78, 112]. Additionally, the nucleation rate (1.38 cm⁻²hr⁻¹) determined for RO operation with UF pretreatment was found to be consistent with a previous gypsum scaling study using a synthetic solution (at SI_g=1.9–2.1) [112]. Although surface scale coverage was nearly 10% higher in the raw water run, the individual crystal growth rates were comparable (Table 6-3), and the higher surface scale coverage is attributed primarily to a more widespread nucleation within the viewing area (Figs. 6-5, 6-8).
Figure 6-6. Real-time membrane monitor surface images (A) during desalination of RO feed water without antiscalant (Run 2, Table 6-2) (pretreated with UF). Crossflow velocity = 4.5 cm/s, initial permeate flux = 33 L/m²-hr (19 gallons/ft²-day) and SIg,m=1.9–2.0 (50% equivalent recovery) and (B) EDS scan of scale crystals on the membrane monitor surface. Note: Sample was coated with gold (Au) prior to EDS analysis.
Figure 6-7. Normalized permeate flux in membrane monitoring system during desalination testing with and without UF pretreatment (Runs 1 and 2, Table 6-2). Crossflow velocity = 4.5 cm/s, initial permeate flux = 33 L/m²-hr (19 gallons/ft²-day) and S_I_{g,n}=1.9–2.0 (50% equivalent recovery). Note: F = measured permeate flux, F_0 = initial permeate flux.

Real-time membrane images revealed a rod-like or rosette-like crystal morphology on the surface suggesting that the mineral scale consisted of gypsum (Figs. 6-5, 6-6), which is in agreement with expectations from water quality analyses (Sec. 6.3.1). EDS analysis was subsequently carried out on a scaled membrane sample from the membrane monitoring system in order to confirm the presence of calcium sulfate (Fig. 6-6B). EDS analysis revealed major intensity peaks for Calcium, Oxygen and Sulfur, suggesting the scale consists of calcium sulfate.
Figure 6-8. Comparison of surface coverage and crystal number density analyzed from real-time membrane images during prefiltration testing indicating a comparison of observed mineral scaling with and without UF at $S_{l,m}=1.9–2.0$ at 50% recovery without antiscalant dosing.

In previous work, antiscalant effectiveness in retarding nucleation was quantified as a nucleation retardation factor $\Theta_{N}$ [112], defined as:
\[
\Theta_N = 1 - \frac{J_{N,2}}{J_{N,1}}
\]  
(6-9)

in which \(J_{N,2}\) and \(J_{N,1}\) are the nucleation rates with and without antiscalant, respectively. Nucleation is unhindered (\(J_{N,2} = J_{N,1}\)), when \(\Theta_N = 0\), and completely suppressed when \(\Theta_N = 1\). In terms of the impact of prefiltration effectiveness, a nucleation retardation factor can be defined as \(\Theta_{N,UF} = J_{N,UF} / J_{N,raw}\) where \(J_{N,UF}\) and \(J_{N,raw}\) are the nucleation rates for mineral scaling using UF pretreated water and the raw water, respectively. The determined value of \(\Theta_{N,UF} = 0.81\) (Table 6-3) (i.e., nucleation rate reduced by \(~81\%)\), is attributed to the removal of fine particulate matter from the raw feed water. The above indicates that UF pretreatment of the feed water significantly diminished the extent of mineral scaling by decreasing the UF filtrate turbidity and thus heterogeneous nucleation on the membrane surface. It is noted that in both cases (Runs 1 & 2), the 80-mesh (177 μm) strainer was in place on the membrane monitor pump (P-4, Fig. 6-2), after the pretreatment units, for removal of particles size smaller than the 300 μm screen filter that was used in conjunction with the UF system. Therefore, the reduction in scaling can be attributed to the removal of smaller particles by the UF membranes (and with coagulation) rather than the screen filter itself. Although UF pretreatment somewhat reduced the severity of mineral scaling, antiscalants that impede CaSO₄ mineral scaling would be needed for long-term RO desalting at even moderate recovery levels of 50% and above, given that gypsum mineral scale crystals were beginning to form after only 10 hours of operation.
6.3.3 Real-time Recovery Optimization and Evaluation of Antiscalant Effectiveness for Mineral Scale Control

Long-term RO pilot plant operation was carried out with a RO plant concentrate slipstream fed to the membrane monitoring system (in single-pass) with antiscalant dosing to the RO plant feed stream. Following the RO recovery optimization scheme (Fig. 6-3), the membrane monitor was run in tandem with the SIMS RO plant, in which conditions were periodically adjusted (e.g., recovery, antiscalant).

In order to maintain a recovery difference (for early warning) between the MMS and the SIMS, it was necessary to increase the CP factor up to 1.4, above the industry recommended maximum for any given RO element of 1.2 [43, 180]. This was done in order to operate the SIMS RO plant at a safer recovery level relative to the MMS. As a result, the equivalent recovery in the membrane monitor was at least ~5–10% higher than the actual RO plant recovery due to CP development in the observed membrane channel, as determined by Eqn. 6-2 (Fig. 6-9). Therefore, if mineral scaling did occur in the RO plant, it was expected that it would occur to a lesser extent relative to the membrane monitor, particularly when using conservative incremental upward adjustments of water recovery. Thus, during membrane cleaning, the membrane monitor was used to dictate the required flush time for complete mineral scale removal.

Prior to beginning RO recovery optimization, the initial antiscalant dosages were selected for mineral scaling control. The initial dose for AS-1 was selected based on previous work that demonstrated significant mineral scaling at a dosage of 3 ppm for brackish water desalination at SI₉ levels of ~2–3 [87, 112]. Therefore, a dose greater than 3 ppm was deemed necessary. Additionally, the maximum allowable dosage of AS-1 for safe drinking water production (NSF/ANSI 60) was 5 ppm. Therefore, the tested AS-1 dosage was initially 5 ppm. Although the
maximum dosage for AS-2 was 10 ppm (NSF/ANSI 60), the initial dose used for AS-2 was also 5 ppm, for comparison.

Incremental RO recovery testing consisted of either non-scaling tests (i.e., safe or moderate recovery levels) or tests in which scaling was detected visually in the membrane monitoring system (Table 6-2, Fig. 6-9). The latter types were: (a) runs where AS dosage was adjusted in order to observe an impact on mineral scaling, and (b) runs in which only permeate water flushing was tested. However, following an adjustment to the AS dosage, the SIMS and membrane monitor were also flushed with permeate in order to clean the membranes prior to the next test. Permeate flushes were carried out at a feed pressure of 50 psi (3.4 bar) and flow rate of 18 GPM (4.09 m³/hr) in the SIMS RO and 14 psi (0.97 bar) and 0.2 GPM (0.045 m³/hr) in the membrane monitoring system. When scaling did not occur, water recovery was increased after a scale-free period of at least 3 days (72 hr). As water recovery reached or surpassed the projected limit of antiscalant effectiveness of $\text{SI}_{\text{e}} = 4$ ($\geq 75\%$ equivalent recovery) (Figures 6-4, 6-9), this period was increased to 5–7 days (120–168 hr) (or until scaling was detected), in case effective antiscalant dosing resulted in the formation of slow growing crystals. The monitored membrane coupon was replaced if it could not be completely cleaned or suffered permanent rejection loss ($\beta \geq 0.10$) after scaling and fresh water flushing.
Table 6-2. Testing conditions for mineral scaling during AD water RO desalination.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Feed Stream</th>
<th>Duration (hr)</th>
<th>AS Type</th>
<th>AS Dosage (mg/L)</th>
<th>Equivalent Recovery (%)</th>
<th>Scale Detected?</th>
<th>Scaling Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(a)</td>
<td>UF Feed</td>
<td>14</td>
<td>n/a</td>
<td>0</td>
<td>50</td>
<td>Yes</td>
<td>n/a</td>
</tr>
<tr>
<td>2(a)</td>
<td>UF Filtrate</td>
<td>14</td>
<td>n/a</td>
<td>0</td>
<td>50</td>
<td>Yes</td>
<td>n/a</td>
</tr>
<tr>
<td>3(b)</td>
<td>RO Conc.</td>
<td>120</td>
<td>AS-1</td>
<td>5</td>
<td>60</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>4(b)</td>
<td>RO Conc.</td>
<td>72</td>
<td>AS-1</td>
<td>5</td>
<td>64</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>5(b)</td>
<td>RO Conc.</td>
<td>96</td>
<td>AS-1</td>
<td>5</td>
<td>68</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>6(b)</td>
<td>RO Conc.</td>
<td>72</td>
<td>AS-1</td>
<td>5</td>
<td>70</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>7(b)</td>
<td>RO Conc.</td>
<td>72</td>
<td>AS-1</td>
<td>5</td>
<td>74</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>8(b,e)</td>
<td>RO Conc.</td>
<td>132</td>
<td>AS-1</td>
<td>5</td>
<td>78</td>
<td>Yes</td>
<td>FWF</td>
</tr>
<tr>
<td>9(b)</td>
<td>RO Conc.</td>
<td>66</td>
<td>AS-1</td>
<td>5</td>
<td>78</td>
<td>Yes</td>
<td>FWF</td>
</tr>
<tr>
<td>10(b)</td>
<td>RO Conc.</td>
<td>168</td>
<td>AS-1</td>
<td>5</td>
<td>74</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>11(b)</td>
<td>RO Conc.</td>
<td>144</td>
<td>AS-1</td>
<td>5</td>
<td>65</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>12(b)</td>
<td>RO Conc.</td>
<td>168</td>
<td>AS-1</td>
<td>5</td>
<td>77</td>
<td>Yes</td>
<td>FWF</td>
</tr>
<tr>
<td>13(b,e,d)</td>
<td>RO Conc.</td>
<td>55</td>
<td>AS-1</td>
<td>5,6,7</td>
<td>78</td>
<td>Yes</td>
<td>AS Dose, FWF</td>
</tr>
<tr>
<td>14(b)</td>
<td>RO Conc.</td>
<td>168</td>
<td>AS-2</td>
<td>5</td>
<td>70</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>15(b)</td>
<td>RO Conc.</td>
<td>168</td>
<td>AS-2</td>
<td>5</td>
<td>75</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>16(b)</td>
<td>RO Conc.</td>
<td>168</td>
<td>AS-2</td>
<td>5</td>
<td>76</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>17(b)</td>
<td>RO Conc.</td>
<td>144</td>
<td>AS-2</td>
<td>5</td>
<td>77</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>18(b)</td>
<td>RO Conc.</td>
<td>168</td>
<td>AS-2</td>
<td>5</td>
<td>78</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>19(b,d)</td>
<td>RO Conc.</td>
<td>183</td>
<td>AS-2</td>
<td>5</td>
<td>80</td>
<td>Yes</td>
<td>FWF</td>
</tr>
<tr>
<td>20(b,e)</td>
<td>RO Conc.</td>
<td>253</td>
<td>AS-2</td>
<td>4,5</td>
<td>80</td>
<td>Yes</td>
<td>AS Dose</td>
</tr>
<tr>
<td>21(b,e)</td>
<td>RO Conc.</td>
<td>230</td>
<td>AS-2</td>
<td>2,5,3,4,5</td>
<td>80</td>
<td>Yes</td>
<td>AS Dose</td>
</tr>
</tbody>
</table>

(a) Pretreatment diagnostics tests: Runs 1 & 2 (Sec. 6.3.2).
(b) Recovery optimization tests: Runs 3–21 (Sec. 6.3.3).
(c) Antiscalant dose tests: Runs 13, 20, 21 (Sec. 6.3.3).
(d) Fresh water flush tests: Runs 8, 13, 19 (Sec. 6.3.4).

Note: Conc. = RO concentrate (brine). FWF = fresh water flush.
Figure 6-9. Operation timeline indicating recovery levels in the SIMS RO plant (lower) and equivalent recovery in the membrane monitoring system (upper). Periods of AS-1 and AS-2 dosing (at initial dosage of 5 ppm) are indicated.

The maximum recovery limit imposed by mineral scaling (with antiscalant use) was tested over the equivalent recovery range of 60–80% (in the MMS) (Fig. 6-5). Based on the suggested upper supersaturation limit for effective antiscalant use for calcium sulfate scale control of $Si_g=4$ in the RO concentrate [123], it was projected that the RO recovery limit imposed by scaling would be in the range of 75–78%, depending on variations in water quality (Figure 6-4). However, incremental recovery testing suggested that the recovery limit imposed by mineral scaling was in the range of ~74-78% with AS-1 at a dosage of 5 ppm and ~78-80% with AS-2 at a dosage of 5 ppm, depending on temporal water quality variations. It was observed on the membrane monitoring images (and EDS analysis, Sec. 6.3.2) that calcium sulfate
(gypsum) scaling occurred on the membrane surface. However, further testing is recommended to determine if silica scaling could also occur at higher recovery levels (e.g., >80%), since silica was projected to be supersaturated in the RO concentrate at ≥70% recovery (Fig. 6-4).

At moderate equivalent RO recovery levels (60–70%), it appeared that mineral scaling could be avoided for long-term operation for the tested range of antiscalant doses (Runs 3-7, 10, 11, 14-18, Table 6-2, Fig. 6-10). However, as expected, antiscalant (at a dose of 5 ppm) did not completely prevent mineral scaling at progressive water recovery levels of ≥78%, but rather delayed its onset while also impeding scale crystal nucleation and growth (Table 6-3). During SIMS RO operation, real-time observation of mineral scaling in the membrane monitor revealed substantial differences in scale control performance between antiscalants AS-1 and AS-2. While AS-1 enabled effective scale control up to \( Y_{eq} \leq 0.74 \) (\( S_{l,m} \leq 3.6-3.8 \)) at a dosage of 5 ppm (Fig. 6-10), significant mineral scaling was detected when the equivalent recovery was increased to 78% (i.e., at \( S_{l,m} \)=4.1–4.4) (Fig. 6-11). However, the change in the monitored normalized permeate flux in the membrane monitor was less sensitive to the initial occurrence of scaling, at ~10% flux decline, while significant mineral scaling developed on the surface (Fig. 6-12).

At the above equivalent recovery level (78%), after scaling began, the impact of antiscalant dose on mineral scaling kinetics was investigated by adjusting the AS in real-time while monitoring the membrane surface (Run 13). AS-1 dosage was increased at \( t=42 \) hr to 6 ppm and subsequently at \( t=47 \) and 52 hours to 6.5 and 7 ppm, respectively, in order to evaluate the possibility of further mineral scaling. However, this approach was largely ineffective at halting the progression of scaling, observed by the continuing increase of surface area coverage (Fig. 6-13a) and crystal growth (Fig. 6-14). There was however a small but measurable decrease (of about ~33%) in the nucleation rate after the dosage was increased (Fig. 6-13b). Indeed, it was
observed that regions of the observed membrane surface which were clear of mineral scaling tended to remain clear of new crystals as the AS dose was increased (final image, Fig. 6-11), as manifested in the minor slowdown of the CND evolution (Fig. 6-11b). The above suggests that AS-1 was specifically formulated to suppress crystal nucleation, sequester nuclei, and/or stabilize particle suspensions.

![Initial Membrane Image](image1) ![Final Membrane Image](image2)

**Figure 6-10.** Membrane surface image (Left) from the membrane monitoring system after operating for 15 days at equivalent recovery level in the range of 60–70% in the membrane monitor (Runs 3-6, Table 6-2), and (Right) membrane surface image after operating for 3 days with the same membrane at 74% equivalent recovery in the membrane monitor (Run 7, Table 6-2).
Figure 6-11. Real-time membrane surface images during AS-1 dose increase operating at 78% equivalent recovery in the membrane monitor (Run 13, Table 6-2). Circled areas indicate regions relatively free from mineral scale coverage.
Figure 6-12. Normalized permeate flux decline data for the membrane monitoring system during mineral scaling (78% equivalent recovery, Run 13, Table 6-2). Note: $t_0$ is the time at which crystal nucleation was first detected.

Given that further increase in antiscalant dosage (i.e., from 5 to 7 ppm) had no measurable effect on the change in the evolution of mineral scale coverage or crystal growth rate (Figs. 6-11, 6-13), it is hypothesized that the extent of mineral scaling (~8% surface scale coverage) was too high for increased antiscalant dosage to prevent further scale growth, given the additional surface area available on crystal surfaces. Indeed, it has been suggested that antiscalant molecules can retard gypsum growth by adsorbing onto crystal surfaces [81, 234, 236]. As the AS dose was increased, from 5 ppm to 7 ppm, existing crystals continued to grow (Fig. 6-14). It is plausible that the antiscalant dose was insufficient for effective adsorption onto the large area offered by the growing crystals. Therefore, the observed scale surface area coverage continued to increase, hence suggesting that it is critical to establish an effective antiscalant dose that will prevent or significantly retard the onset of surface scaling.
Figure 6-13. (a) Surface area coverage by gypsum scale and (b) CND for gypsum scale crystals detected at 78% equivalent recovery during operation with progressively increasing antiscalant dosage (Run 13, Table 6-2).
Figure 6-14. Crystal growth during AS-1 dosage increases from 5 ppm to 7 ppm for RO operation at 78% equivalent recovery (Run 13, Table 6-2). Note: \( d_0 \) = initially detected crystal diameter, \( t_0 \) = initial detection time for first crystal.

It was not feasible to operate the SIMS RO plant at 78% or higher RO recovery without antiscalant dosing due to the risk of severe system fouling and scaling. Therefore, for comparison of AS performance with respect to scaling kinetics, a baseline case of 50% recovery with no AS (Run 2) or a model predicted value can be used, with the diffusive crystal growth model using the average \( S_{Ig,m} \) value in the observed range, as this model has been used previously to describe gypsum crystal growth on RO membranes [78, 84, 86, 112]. The impact of AS dosing on retardation of crystal growth was quantified by a growth retardation factor, \( \Theta_G \), defined as:

\[
\Theta_G = 1 - \frac{\dot{r}_{d,AS}}{\dot{r}_{d,NoAS}} \tag{6-10}
\]

where \( \dot{r}_d \) is calculated as described in Sec. 6.2.5.1. At AS-1 dose range of 5-7 ppm, RO operation with the membrane monitor led to measurable retardation of crystal growth, both
relative to the observed case of 50% equivalent recovery (Si\text{g,m}=2) as well as the predicted growth rate at 78% equivalent recovery, as expected (i.e., \(r_d=0.17\) mm/hr at 78% equivalent recovery, Si\text{g,m}=4.2, Table 6-3). Crystal growth with AS-1 was retarded by \(\sim82\%\), when compared to the predicted crystal growth rate for antiscalant-free RO operation at 78% equivalent recovery. In terms of retarding nucleation AS-1, the crystal nucleation rate was higher (i.e., by a factor of \(\sim3.2\)) for AS-1 at 5 ppm (at 78% equivalent recovery) relative to AS-2 at 5ppm (at 80% equivalent recovery) (Table 6-3).

AS-2 was effective in retarding both crystal growth and nucleation, at the initial dose of 5 ppm for operation in the range of 60–80% equivalent recovery in the membrane monitor (Fig. 6-9, Table 6-3). At 80% equivalent recovery, after minimal mineral scaling was detected after \(\sim2.5\) days (i.e., <0.01% surface scale coverage and CND=0.02 mm\(^{-2}\), Fig. 6-16), the AS-2 dose was reduced gradually in order to determine if antiscalant could be conserved while still effectively suppressing scale formation. However, it was observed that the CND and scaled surface coverage evolution accelerated as the AS dose was decreased from 5 ppm to 2.5 ppm (Figs. 6-15, 6-16, 6-19); this trend suggested that AS-2 performance was sensitive to the dose level. The nucleation rate increased by a factor of \(\sim7\) and the surface scale coverage increased up to a level of 0.1% coverage over the next 50 hours. However, the corresponding retardation factor for crystal growth with AS-1 at 2.5 ppm (at 80% equivalent recovery) was still significant (i.e., \(\Theta_G=0.98\)) (Table 6-3).
Table 6-3. Summary of antiscalant performance for AS-1 and AS-2 relative to the operation without antiscalant addition.

<table>
<thead>
<tr>
<th>Run</th>
<th>Antiscalant (AS)</th>
<th>AS Dosage (ppm)</th>
<th>SIMS RO Recovery (%)</th>
<th>Eq. Water Recovery in MMS (%)</th>
<th>SI of Gypsum (monitored surface)</th>
<th>Nucleation Rate, ( J_n ), (#/cm²-hr)</th>
<th>Crystal Growth Rate (mm/hr)</th>
<th>( \Theta_G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None (UF Feed)</td>
<td>n/a</td>
<td>50</td>
<td>1.9–2.0</td>
<td>7.23</td>
<td>6.8 ( \times 10^{-2} )</td>
<td>–</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>2</td>
<td>None (UF Filtrate)</td>
<td>n/a</td>
<td>50</td>
<td>1.9–2.0</td>
<td>1.38</td>
<td>7.2 ( \times 10^{-2} )</td>
<td>–</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>(b)</td>
<td>–</td>
<td>–</td>
<td>78</td>
<td>4.2</td>
<td>–</td>
<td>( 1.7 \times 10^{-1} )</td>
<td>–</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>(b)</td>
<td>–</td>
<td>–</td>
<td>80</td>
<td>4.7</td>
<td>–</td>
<td>( 1.9 \times 10^{-1} )</td>
<td>–</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>3-7, 10, 11</td>
<td>AS-1</td>
<td>5</td>
<td>50–65</td>
<td>60–74</td>
<td>2.3–3.8</td>
<td>n/a</td>
<td>n/a</td>
<td>( \sim 1 )</td>
</tr>
<tr>
<td>13</td>
<td>AS-1</td>
<td>6–7</td>
<td>68</td>
<td>78</td>
<td>4.1–4.4  ( \times 10^3 )</td>
<td>2.6 ( \times 10^{-2} )</td>
<td>0.82</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>13</td>
<td>AS-1</td>
<td>5</td>
<td>68</td>
<td>78</td>
<td>4.1–4.4  ( \times 10^3 )</td>
<td>2.5 ( \times 10^{-2} )</td>
<td>0.82</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>16-20</td>
<td>AS-2</td>
<td>5</td>
<td>60–72</td>
<td>70–78</td>
<td>3.0–4.4</td>
<td>n/a</td>
<td>n/a</td>
<td>( \sim 1 )</td>
</tr>
<tr>
<td>21</td>
<td>AS-2</td>
<td>4</td>
<td>75</td>
<td>80</td>
<td>4.5–4.9  ( \times 10^{-3} )</td>
<td>2.2 ( \times 10^{-1} )</td>
<td>0.989</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>21</td>
<td>AS-2</td>
<td>3</td>
<td>75</td>
<td>80</td>
<td>4.5–4.9  ( \times 10^{-3} )</td>
<td>2.8 ( \times 10^{-3} )</td>
<td>0.985</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>21</td>
<td>AS-2</td>
<td>2.5</td>
<td>75</td>
<td>80</td>
<td>4.5–4.9  ( \times 10^{-3} )</td>
<td>3.0 ( \times 10^{-3} )</td>
<td>0.984</td>
<td>( \text{---} )</td>
</tr>
</tbody>
</table>

(a) Note: The SI ranges are the result of water quality variations corresponding to Fig. 6-4.
(b) Crystal growth rates at these conditions were estimated using the diffusive crystal growth model [78, 84, 86, 112].
Figure 6-15. Membrane surface images taken during periodic AS-2 dose reduction within the range of 5 ppm and 2.5 ppm at 80% equivalent recovery in the membrane monitoring system (SI$_{g,m}$=4.5-4.9) (Run 21, Table 6-2).
As previously discussed, increasing the AS-1 dose to the RO feed from 5 ppm to 7 ppm was largely ineffective at controlling mineral scaling after significant scaling (~8% scale surface coverage) was detected at 78% equivalent recovery (Run 13, Table 6-2). As noted earlier, it appeared that establishing an optimal AS dosage at the early stages of scaling (i.e., prior to widespread nucleation and growth) is critical to mitigating membrane scaling. In order to test the
above hypothesis, a test at 80% equivalent recovery (in the MMS) was continued at 4 ppm AS-2 dose where mineral scaling was expected to occur earlier than with 5 ppm AS-2 dosage. At the above equivalent recovery, 4 ppm was an effective AS-2 dose for preventing detectable scaling for about 7 days. Limited mineral scaling was detected thereafter, with a single crystal observed to be growing. After a period of about 2.5 days (i.e., 9.5 days after the beginning of the run, Run 20, **Table 6-2**), the antiscalant (AS-2) dose was increased to 5 ppm and it appeared that the crystal growth slowed significantly, as the growth rate was reduced by a factor of ~5.5 (**Figs. 6-17, 6-18**), further confirming that AS-2 effectiveness at retarding crystal growth is highly dose-dependent. The results as shown in **Figs. 6-15–6-19** and **Table 6-3** suggest that AS-2 was effective in retarding both the nucleation and growth of calcium sulfate scale crystals.

**Figure 6-17.** Real-time membrane surface images depicting single crystal growth before and after AS-2 dose increase from 4 to 5 ppm at 80% equivalent recovery in the MMS (Run 20, Table 6-2). The observed crystal was circled for clarity.
Figure 6-18. Mineral scale crystal growth before and after AS-2 dose increase from 4 to 5 ppm at 80% equivalent recovery (in the MMS) (Run 20, Table 6-2).
Figure 6-19. Comparison of crystal growth during the antiscalant-free RO operation with ultrafiltered feed and with tests using AS-1 and AS-2 (Tables 6-2 & 6-3); Note: the specified recovery level is the equivalent recovery in the membrane monitoring system.

Mineral scale control for desalting the PDD source water (Table 6-1) was more effective with AS-2 relative to AS-1 (Fig. 6-19). At AS-2 dose of 5 ppm, mineral scaling kinetics were significantly impeded. Based on the above results, it is suggested that even if water quality improves and mineral scaling is not detected, it may be risky to reduce antiscalant dosage (from the optimal value). As observed in Figs. 6-15 & 6-16, there is a risk that mineral scaling may accelerate as a result of reducing the AS dose.

6.3.4 Scale Removal via Permeate Flush

Given that mineral scaling was not completely avoided (but significantly impeded) by antiscalant addition (at AS-2 dose of 5 ppm) at higher equivalent recovery levels (i.e., 78–80%),
an approach was implemented of periodic flushing of the RO elements with permeate water. This approach was undertaken given previous work in which it was shown that calcium sulfate scale can be dissolved by undersaturated feed and mitigated via operation in the mode of feed-flow reversal (FFR) [85, 139, 261]. In FFR, the feed crossflow direction is periodically reversed using a network of automated valves, thereby reversing the axial CP profile [139, 152, 260, 261]. However, in the present study, the source water was already saturated \((SI \approx 1)\) with respect to gypsum, and thus dissolution of this mineral scalant with feed flow reversal was infeasible. Other methods such as osmotic backwash, while effective for dislodging membrane fouling cake layers, require a high salinity (HS) feed solution and interruption of normal operation [262, 263].

In the present work, given the ability to detect the onset of mineral scaling, fresh water flush was implemented for scale dissolution. The present RO plant permeate was expected to be effective at mineral scale dissolution, having only \(62\pm13\) mg/L total dissolved solids (TDS) (electrical conductance \(87\pm19\) \(\mu\)S/cm). In the above approach, once mineral scaling is detected, fresh water flush is triggered for scale removal. At the highest membrane surface scale coverage (of 13%) and CND (of 5.3 crystals/mm\(^2\)) (i.e., multiple large crystals detected), the required fresh water flush time was substantial, taking up to \(~50\) minutes for complete scale removal. Real-time membrane images show that while some crystals were removed within the first 20 minutes, additional crystals remained requiring an additional 30 minutes for complete removal (Fig. 6-20, top row). In Run 8 (78% equivalent recovery, Table 6-2), a single large crystal was detected in the viewing area, and complete removal via fresh water flush was achieved in about 20 minutes (Fig. 6-20, middle row). The required flush time was about 14 minutes when scale was detected early (prior to 1% flux decline) as a smaller single crystal (0.08% scale coverage) (Fig. 6-20, bottom row), Table 6-4). Based on permeate flux decline measurements alone,

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however, one would have to trigger a fresh water flush (at a threshold of \( \sim 10\% \) flux decline) when the mineral scale was already developed on the membrane surface (Figs. 6-11, 6-12, 6-20). The above further confirms the utility of direct membrane monitoring for early detection to trigger corrective actions (i.e., fresh water flush) for mineral scaling mitigation.

It has been previously demonstrated that undersaturated feed solutions can be used to dissolve and remove gypsum scale crystals from RO membrane surfaces, as confirmed via direct visual membrane monitoring [85]. Indeed, the removal of calcium sulfate scale using a pure water flush was also evaluated in a previous study, in which ultrasonic monitoring was used for scale detection and verification of scale removal [146]. This approach, known as ultrasonic time domain reflectometry (UTDR), measures the reflection of ultrasonic waves in a membrane channel, where a change in amplitude can be interpreted as due to membrane fouling or scaling. While the method previously had signaled mineral scaling on the membrane, during the pure water flush, the ultrasonic signal subsequently stabilized, suggesting the scale was removed. However, there was no direct confirmation of scale removal until the membrane was removed from the module and analyzed via SEM, where it was indicated that some small crystals remained. Therefore, direct visual surface monitoring has the advantage of verifying complete scale removal.

Although fresh water flushing of the RO membranes consumes part of the produced permeate water, a scale mitigation strategy involving fresh water flushing twice per week would only require \( \sim 0.6\% \) of the overall produced permeate, if carried out sufficiently early (at a flow rate of 18 gallons/min for 15 min). Accordingly, it is estimated that extended RO operation for the present water source may be achievable with 80% recovery or above, with effective antiscalant dosing (e.g., AS-2 dose of \( \geq 5 \) ppm) combined with periodic fresh water flushing. It is
noted that the above recovery level corresponds to operating at bulk $\text{SI}_g=4.5–4.9$ in the RO concentrate, which is higher than the industry recommended upper limit of $\text{SI}_g=4$.

Table 6-4. Summary of fresh water (permeate) flush for scale removal (a)

<table>
<thead>
<tr>
<th>Run</th>
<th>Equivalent Recovery (b) (%)</th>
<th>$\text{SI}_{g,m}$</th>
<th>AS</th>
<th>Surface Scale Coverage (%)</th>
<th>Surface CND (# of crystals/viewing area)(c)</th>
<th>Permeate Flux Decline Prior to Flush (%)</th>
<th>Flush Time Required (min)</th>
<th>Flush Volume Required (gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>78</td>
<td>4.1–4.4</td>
<td>5 ppm AS-1</td>
<td>13.0</td>
<td>405</td>
<td>12</td>
<td>50</td>
<td>900</td>
</tr>
<tr>
<td>8</td>
<td>78</td>
<td>4.1–4.4</td>
<td>5 ppm AS-1</td>
<td>1.3</td>
<td>2</td>
<td>7</td>
<td>20</td>
<td>360</td>
</tr>
<tr>
<td>19</td>
<td>80</td>
<td>4.5–4.9</td>
<td>5 ppm AS-2</td>
<td>0.08</td>
<td>1</td>
<td>&lt; 1</td>
<td>14</td>
<td>252</td>
</tr>
</tbody>
</table>

(a) The reported scale coverage, CND, and permeate flux decline levels were measured before the start of each fresh water flush.

(b) Recovery equivalent to operation at the indicated gypsum saturation index value at the membrane surface ($\text{SI}_{g,m}$). $\text{SI}_{g,m}$ values provided as a range due to water quality variation.

(c) Membrane monitoring viewing area = 76.4 mm$^2$. 
Figure 6-20. Membrane surface images during fresh water flush testing for scale removal. Top: $Y_{eq}=78\%$ and 5 ppm AS-1 (Run 13), Middle: $Y_{eq}=78\%$ and 5 ppm AS-1 (Run 8), Bottom: $Y_{eq}=80\%$ and 5 ppm AS-2 (Run 19). Smaller crystals are circled in white for clarity.

6.4 Summary

An approach for field optimization of RO desalination of brackish agricultural drainage water of high scaling propensity was demonstrated in a field study with a demonstration scale RO plant. An optically transparent membrane observation cell was used for real-time membrane surface scale detection with a slipstream from the 2nd stage RO concentrate from a spiral-wound RO plant. The monitoring system enabled real-time evaluation of the scale mitigation strategies of antiscalant adjustment and permeate water flushing, enabling extended operation at up to 80% equivalent water recovery. The membrane monitor enabled direct comparison between standard media filtration and ultrafiltration pretreatment for minimizing membrane scaling and fouling by particulate matter. Comparison of antiscalant performance for mineral scale suppression was also performed in real-time to optimize the plant RO water recovery. Real-time image analysis
indicated that UF pretreatment reduced mineral scale nucleation by \(-81\%\) (at 50\% equivalent recovery without antiscalant). and that the second antiscalant, AS-2, reduced crystal growth rates by \(\geq99\%\) at moderate doses of 2.5–5 mg/L and was also more effective than AS-1 (by a factor of \(~3\)) for reducing crystal nucleation rates. Operation at 80\% equivalent recovery (RO concentrate \(S_{Ig}=4.5–4.9\)) was feasible with: (a) antiscalant dosing of 5 mg/L (AS-2) and (b) periodic fresh water flushing (twice per week) with stored permeate water, which consumed \(\leq0.6\%\) of the product water. Real-time membrane monitoring enabled visual verification of complete scale removal from the membrane surface using a permeate water flush. In order to further improve the RO desalination process and the feasibility of fresh water flushing for long-term operation, it is plausible that the used fresh water flush solution could be recycled to the feed pretreatment system and thus provide a minor dilution of the RO feed stream, and whereby any suspended crystals and particulate matter would be removed by the UF system.

If brine disposal costs become too high or if the value of produced water demands it, the 2\(^{nd}\) stage RO concentrate could undergo demineralization (e.g., using seeded precipitation) to \(S_{Ig}=1\) before a tertiary RO stage operating at 50\% recovery (to \(S_{Ig}=2\)) or perhaps higher. The achievable overall recovery in such a system would be 90\% or higher, reducing the brine volume to \(\leq10\%\) of the feed. Additionally, more frequent monitoring of ion concentrations (e.g. calcium) in the RO feed, along with real-time estimates of \(S_{Ig}\) values in the RO feed and concentrate could further help guide operation towards the optimal recovery (e.g., safe operating range of \(S_{Ig}\)), rather than relying on periodic manual water sampling (e.g., every \(~1–2\) weeks).
Appendix A

Membrane Monitoring System (MMS) Operation

A.1 System Description

The membrane monitoring system (MMS) consisted of a transparent plate-and-frame RO (PFRO) crossflow cell (Figs. A-1 – A-3) able to withstand the pressure ranges required for RO desalination. The MMS can be used as a standalone tool for membrane fouling or scaling experiments, either in a mode of total recycle (using a feed vessel) (Ch. 3, 4) or in a single-pass (i.e., once through) mode of operation (Ch. 5, 6). Additionally, the MMS was interfaced with larger RO pilot systems for desalination field studies (Ch. 5, 6). The monitoring cell was constructed with a transparent feed channel block in order to enable real-time optical monitoring of membrane surface changes (i.e., surface fouling or mineral scaling). The transparent block must be thick relative to the flow channel height, for structural integrity and safety when pressurized. However, the transparent block should not be too thick so as to prevent microscopic observations. The transparent side-walls of the feed channel block enabled low-angle (e.g., LED) lighting, along the length of the membrane channel, to provide high-contrast and illumination of surface objects for either wide-field photography of the entire membrane surface or microscopic observation of a selected region of the membrane. Quantification of surface number density of particles or crystals and fractional scaled surface area coverage via image analysis was then performed with the captured images (Appendix B). The permeate collection block (with porous sintered stainless steel insert) was not transparent, and was constructed from an acetal-based plastic resin. The transparent interior (i.e., flow channel) and exterior of the membrane cell should be gently cleaned and polished periodically by hand.
Figure A-1. (A) Side-view of assembled membrane monitoring cell and (B) Top-down view of membrane monitoring cell, with major dimensions shown.
Figure A-2. Exploded schematic view of membrane monitoring cell with major cell assembly components. Note: SS = stainless steel.

Figure A-3. Photograph of membrane monitoring cell assembled and mounted in the system using brackets and threaded stainless steel mounting studs with inlet and outlet ports connected to high-pressure stainless steel tubing.
A.2 System Operation

Whether operated as a standalone diagnostic system or interfaced with a RO plant for mineral scale detection, the membrane monitoring system can be operated manually or through a graphical user interface (GUI). The GUI enables one to record sensor readings and set the pressure and crossflow velocity using the feed pump (controlled with variable frequency drive, VFD), and various valves according to the system schematic (Fig. A-4).

A.2.1 Membrane coupon preparation

Note: If stored in a wet solution for extended periods, membranes should not be allowed to dry and should be stored in a preservative solution of 0.5 – 1 wt.% sodium meta-bisulfite in sealed plastic bags.

1. Cut at least 2 membrane coupons from a larger sheet of the membrane to a size that would overlap the flow channel and fritted steel (~4 inches × 2 inches), being careful to not touch or scrape the active layer of the membrane. Trim the membrane coupon as necessary with sharp scissors or utility knife.

2. Rinse the membranes with running de-ionized (DI) or distilled water for several minutes.

3. Place the membranes in a 600 mL beaker of ultra pure DI water, cover the beaker with parafilm and place in refrigerator for at least ~2 hours and up to 3 days. Discard if stored for more than 3 days.
A.2.2 Solution preparation

**Note:** If field water is being used, simply fill the feed tank with the field water or feed directly to the feed pump or monitoring cell, as needed.

1. Fill enough beakers with DI water to accommodate the number of different salts or chemicals to be used in the feed solution and cover with parafilm. Dissolve only 1 chemical in each beaker.

2. Measure out the required mass of each solid chemical by placing a weighing boat on a digital scale and taring the scale thereafter. Then fill the weighing boat with the required mass of the solid chemical. Repeat this process for each chemical using a clean weighing boat.

3. Dissolve each chemical in DI water in the beakers using a stirbar and stirplate. When the chemicals are completely dissolved, remove the stirbar using another stirbar or stirbar retriever.

4. Cover each beaker with parafilm during solution preparation to prevent particle or dust contamination, or if the solutions are being prepared for future testing.
Figure A-4. Process flow diagram of membrane monitoring system (MMS). Feed water was supplied from a feed vessel (Feed 1) or from a pressurized source such as a larger RO plant (Feed 2). When a pressurized source is used, Feed 1 and the pump are disconnected. A shut-off valve (V1, normally open) is used in conjunction with a flush valve (V2, normally closed) for cleaning the membrane system. Pressure and crossflow were controlled using the feed pump and an automated control valve (V3). When flushing or cleaning the system a bypass valve (V4, normally closed) was used to enable higher flow rates. If needed to make further adjustment to pressure or crossflow, a manual valve was added (V5, normally closed). Online sensors include feed pressure (P), concentrate flow rate (F), and permeate flow rate and conductivity (F, C). Note: When using total recycle with a feed vessel, it is recommended to use a microfilter of the RO retentate (rated at ≤1 μm) in order to remove foreign or formed suspended particles prior to recycling to the feed vessel.

A.2.3 System operating procedure

1. Using a squirt bottle, lightly rinse the interior of the membrane cell and the membrane coupon one final time with DI water.
2. Check the MMS cell o-ring gasket for cracks or other damage and re-insert into its groove. Periodically re-lubricate the o-ring gasket with a compatible lubricant. Do not use excessive amounts of lubricant or drip lubricant on the membrane coupon.

3. Place the membrane coupon flat inside the MMS cell.

4. If using a flat gasket, insert it over the four studs and the membrane coupon.

5. Clamp the cell shut. If required, hold the cell shut with one hand while lightly fastening the tightening knobs or threaded nuts onto the studs. Note: if the cell falls open due to gravity, the membrane coupon may need to be cleaned, replaced and re-inserted.

6. If using hand-tightening knobs, securely tighten each of the four cell studs in a criss-cross or circular fashion to avoid overtightening any single knob. If using threaded nuts, use a socket wrench or adjustable or open-ended wrench of the appropriate size to tighten each of the four cell studs to the nuts in a criss-cross or circular fashion to avoid overtightening any single stud.

7. Immediately verify that the membrane is lying flat and there are no folds or creases of the membrane coupon. If there are such anomalies, replace the membrane coupon.

8. Open the image acquisition software or camera or microscope interface, and immediately verify if the membrane appears clean. If needed, open the membrane cell and squirt DI water to remove particles. If unsuccessful, replace the coupon. Note: prior to pressurization, the membrane image may appear differently, and may contain air bubbles.

9. For membrane water conditioning or permeability testing, first fill the feed vessel with the desired volume DI water. Avoid using less than ~5 L of water in order to adequately supply the suction side of the feed pump and to minimize temperature drift of the solution for total recycle operation.
10. For membrane compaction or salt rejection testing, fill the feed tank with a standard sodium chloride solution or other test solution (e.g., a partial salt scaling solution of Na₂SO₄).

11. Add the test solution (Sec. A.2.2) to the feed vessel, being sure to add any solutions containing Calcium ions last. Mix vigorously, and if possible, maintain mixing (e.g., with a motorized impeller) throughout the experiment.

12. If needed, adjust the solution pH by slowly adding concentrated NaOH or HCl to the feed solution while mixing (i.e., using a pipette), until the desired initial pH is attained.

13. For total recycle operation, insert the cooling coil in the feed vessel, making sure that the mixer does not contact the coil during operation. Fill the chiller’s reservoir. Turn on the chiller and set to the desired set-point temperature.

14. If used, insert the microfilter cartridge into housing and tighten the housing. Note: do not lose the microfilter housing gasket (o-ring), and occasionally check and re-lubricate the o-ring with a compatible lubricant.

15. Fully open the shutoff valve (V1), control valve (V3) and bypass valve (V4). Make sure V2 is closed, unless a fresh water flush or other cleaning is needed using that connection, prior to testing.

16. Start the data acquisition software.

17. Start the image acquisition software and set the interval for time-lapse image capture.

18. Start the feed pump and initially run for at least ~70% of the maximum variable frequency drive (VFD) speed.

19. Turn on the permeate flowmeter.

20. Once all air bubbles are purged from the pump and tubing, close the bypass valve (V4).
21. Slowly reduce the control valve (V3) opening downward from 100% until the desired feed pressure or permeate flow rate is reached. Note: when used with a pressurized feed line (Feed 2), the control valve (V3) controls the crossflow velocity.

22. If needed, adjust the speed of the pump (using the VFD) until the desired crossflow velocity, feed pressure, and initial permeate flow rate are reached.

23. For membrane compaction, set the feed pressure to be at least as high as the operating pressure during experimental testing. Overall compaction time of usually at least 4 hours is required. However, compact the membrane until the permeate flow rate has been stable for at least ~30 minutes. Note: if the permeate flow rate continues to decline for more than ~6 hours, replace the feed solution and the membrane coupon and ensure that the system is clean before restarting the experiment (Sec. A.2.4).

24. Activate any PID control loops in the GUI or data acquisition software that are used to maintain pressure or flow rate on the control valve (V3) or feed pump VFD.

25. For the first ~5–10 minutes of the experimental period, adjust the imaging by doing the any of the following that are necessary: adjust the optical magnification, camera or microscope position, light source intensity, or lighting angle. If needed, use a reference membrane with attached objects of known size prior to testing, in order to verify proper optical and imaging settings.

26. For a given magnification setting, calibrate the actual image size by inserting a marked membrane sample with precisely measured tick marks. Note the image magnification, as this will be needed for subsequent image analysis (Appendix B).

27. At the end of an experiment, open the control valve (V3) to 100% and set the pump VFD to 0%.
28. Allow the pressure to decrease for ~5–10 seconds, then open the bypass valve (V4).

29. Turn off the pump.

30. End the data acquisition and image capture and ensure all data and images are stored for further analysis.

31. Turn off the mixer and the chiller units.

32. Empty the feed vessel.

33. Remove the cooling coil from the feed vessel and rinse with DI water.

34. Rinse the inside of the feed vessel thoroughly with DI water, empty and allow to dry.

35. Open the microfilter housing and remove the microfilter cartridge. Rinse the housing interior with DI water and soak the microfilter cartridge in DI water for up to ~2 hours. Allow both to dry.

36. Open the RO membrane cell and remove the membrane coupon.

37. Dip the membrane coupon briefly into a beaker of DI water to remove residual feed solution.

38. Store the membrane sample for further analysis.

39. Remove o-ring gasket and flat gasket (if used) from the cell and rinse or soak thoroughly with DI water and allow to dry.

A.2.4 System cleaning procedures

**Light Cleaning – NaOH and DI Water**

**Note:** If the system has been used within the last 1-2 weeks, a light cleaning is sufficient, unless a solution containing significant amounts of organic or biological material was used, such as a
waste water solution. This should remove or neutralize small amounts of bacteria and clear the system of small quantities of particles and salt crystals.

1. Disconnect and remove the microfilter cartridge (if used) and re-tighten the filter housing.
2. Place a membrane coupon in the membrane cell and securely tighten the cell studs.
3. Fill the feed tank with 20 L of DI water.
4. Start the pump.
5. Recirculate the DI water through the system for 24 hours at high flow rate and moderate pressure.
6. Turn off the pump.
7. Drain the system.
8. Fill the feed tank with DI water
9. Dissolve NaOH into the feed tank until the pH is 10–11.
10. Start the pump and recirculate this solution for 24 hours.
11. Turn off the pump.
12. Drain the system.
13. Fill the feed tank with DI water.
14. Start the pump.
15. Recirculate the DI water through the system for 24 hours.
16. Repeat steps 11–15 until the pH in the feed tank is approximately equal to 7, or the pH of DI water.
17. Turn off the pump.
18. Drain the system.
19. Open the membrane cell and remove the membrane coupon.
20. Rinse the internals of the membrane cell with DI water.

21. Remove the o-ring gasket from the membrane cell and soak in the cleaning solution for 24 hours, rinsing thoroughly with DI water afterwards.

**Heavy Cleaning – Micro 90 cleaning solution**

**Note:** A heavy cleaning is necessary when the system has not been used for more than several weeks or the system was contaminated.

1. Disconnect and remove the microfilter cartridge (if used) and re-tighten the filter housing.
2. Place a membrane coupon in the membrane cell and securely tighten the cell studs.
3. Fill the feed tank with 20 L of DI water. Pour 10 mL of pure Micro 90 into the feed tank.
4. Fully open the control valve (V3) and bypass valve (V4).
5. Start the pump.
6. Circulate the water mixture through the system for at least 24 hours in order to clean the system.
7. At the end of the 24 hours run, turn off the pump.
8. Empty the water from the feed tank.
9. Fill the feed tank with DI water.
10. Fully open the crossflow and regulator/bypass valves.
11. Start the pump.
12. Place the feed return line into a bucket. Continue to fill the feed tank with DI water as the system runs (make sure the feed tank does not completely empty) and pour the water from the feed return line down the drain. Repeat this for at least 15 full feed tanks.

13. Check the conductivity of the effluent water to ensure it is < 2 µS. If it is > 2 µS, repeat step 12 until the effluent water is < 2 µS.

14. Turn off the pump.

15. Drain the water out of the feed tank, RO cell, tubing, and piping.

16. Open the membrane cell and remove the membrane coupon.

17. Rinse the internals of the membrane cell with DI water.

18. Remove the o-ring gasket from the membrane cell and soak in the cleaning solution for 24 hours, rinsing thoroughly with DI water afterwards.

**Heavy Cleaning – EDTA + NaOH**

**Note:** If a solution containing bacterial or biological material is used, a heavy cleaning with NaOH and EDTA is necessary before and after the experiment.

1. Disconnect and remove the microfilter cartridge (if used) and re-tighten the housing.

2. Place a membrane coupon in the membrane cell and securely tighten the cell studs.

3. Fill the feed tank with DI water containing EDTA dissolved at 1 g/L and NaOH at 4 g/L (final pH ~ 13).

4. Fully open the control (V3) and bypass valves (V5).

5. Start the pump.

6. Circulate the solution at 5-10 bar and 100 L/hr for 10 minutes.
7. Turn off the pump for 20 minutes.
8. Repeat steps 5–7 a total of 3 times.
9. Drain the system.
10. Rinse the feed tank with DI water and recirculate DI water through the system until the pH of discharge water reaches the DI water pH value.
11. Dissolve sodium meta-bisulfite in the feed tank at 1 wt%, and circulate the solution for 45 minutes.
12. To preserves the system for an extended period, turn off the pump and leave sodium meta-bisulfite solution in the system.
13. To use the system immediately, turn off pump and drain the sodium meta-bisulfite solution.
14. Fill the feed tank with DI water.
15. Start the pump.
16. Recirculate the DI water through the system at 100 L/hr and moderate pressure (5–10 bar).
17. Check that the conductivity of the water in the feed tank is the same as the conductivity of DI water (~2–5 µS). If the conductivity is above this value, drain the system and repeat steps 14–16 until the conductivity is below 5 µS.
18. Turn off the pump.
19. Drain the system.
20. Open the membrane cell and remove the membrane coupon.
21. Rinse the internals of the membrane cell with DI water.
22. Remove the o-ring gasket from the membrane cell and soak in the cleaning solution for 24 hours, rinsing thoroughly with DI water afterwards.
Appendix B

Surface Image Analysis Procedures

B.1 Overview

Successive time-series images (e.g., photographs or micrographs) captured of a membrane surface in the membrane monitoring system (MMS) were analyzed via an image processing method in order to quantify mineral scaling kinetics over time, including: individual crystal/particle growth rates, surface scale coverage, crystal number density (CND) or surface number density (SND). Such mineral scale growth parameters can be used, as part of a process control system, to trigger corrective adjustments to operating conditions (e.g., feed flow reversal (FFR), water recovery adjustment, antiscalant type or dosage, membrane cleaning frequency, etc.) in either the MMS or a RO desalination plant to which the MMS is interfaced. For real-time automated image analysis (Sec. B.1.1), the processing software was developed at UCLA specifically for images taken in the MMS. The approach is based on a previous approach [156] in which surface image changes are separated from the background and quantified.

B.1.1 Automated image analysis

Images processed by the image analysis algorithm were 5-megapixel (2592 × 1944), 24-bit color images and contained a standard 10-digit time stamp as a filename. The image analysis algorithm was assembled in order to efficiently analyze the saved images in real-time. The algorithm was designed using image segmentation to highlight and quantify surface changes due to mineral scaling or fouling (Fig. B-1). First, images were pre-processed in order to obtain consistent results. Pre-processing consisted of two steps. First, images were converted to grayscale and enhanced using a standard image enhancement technique based on histogram
equalization that flattens the narrow/skewed spread of pixels (narrow histogram) of an image in order to increase image contrast and adjust for minor irregularities in the image illumination [314, 315]. Secondly, images were aligned in order to account for slight shifts that occasionally occurred in between image capture that may result from external disturbances, vibrations, etc. Subsequently, it was necessary to subtract the initial “clean” (background) surface image from all subsequent images using a standard image subtraction algorithm. This algorithm subtracts each element in the background image from the corresponding element in subsequent images and returns the difference in corresponding elements of an output image. If the difference is positive (i.e., pixel intensity increased) then the element is counted for detection. If the difference is negative (e.g., due to shadows, or lower pixel intensity), then the element was not counted. It should be noted that one could also modify the current algorithm for taking the absolute difference of two images, thereby highlighting all changes (either negative or positive) in pixel intensity.

**Figure B-1.** Flow diagram outlining the automated image analysis procedure.

The remaining subtracted images highlighted any changes that occurred on the membrane surface over time. The resulting images were segmented using a thresholding method that
regards the image as a two class image following a bi-modal histogram (i.e., foreground and background) [313]. This thresholding method iteratively finds the spread in pixel groups and finds an optimal threshold which separates foreground pixels from the background pixels so that the intra-class variance is minimal. Subsequently, the changed area was calculated as a fractional surface coverage, and the number of detected objects on the surface was also quantified. The graphical user interface (GUI) for the automated image processing software is depicted in Figure B-2.

**Figure B-2.** Graphical user interface for automated image analysis program in MATLAB.
Automated Image Analysis Procedure:

1. Click “Select Image Directory” and point the program to the directory where the images are saved.
2. If image shifts (due to vibration or other movement) are expected, check the box “Enable Shift Adjustment”.
3. Select the image range for analysis by inputting the first and last image (e.g., 1 and 10, to analyze the first 10 images). The first image in a series will be taken as the “clean” background image.
4. Click “Test Threshold” and the program will quickly determine and display an appropriate threshold value for analyzing the image set.
5. Click “Analyze Images”.
6. The resulting detected fractional surface area coverage will be saved as “fracc overp.mat” and the number of detected objects will be saved as “CrystalCount.mat”. Open these files in MATLAB in order to access the image analysis results.

B.1.2 Manual image analysis

For further analysis of previously saved membrane images, manual image analysis can also be performed. Manual image analysis was carried out using Adobe Photoshop CS3 Extended (Version 10; Adobe, San Jose, CA) with Fovea Pro plug-in (version 3.0; Reindeer Graphics, Asheville, NC). For quantification of mineral crystal growth kinetics, there are two approaches for manual image analysis outlined below. The first method uses thresholding to
outline surface objects. However, in some cases (e.g., significant shadows) it may be necessary to use a more tedious approach of tracing individual crystals or groups of crystals.

Manual Image Analysis Procedure:

1. Open Adobe Photoshop and the initial “clean” membrane image, as well as the image to be analyzed.

2. To enhance image contrast prior to analysis select Image » Adjustments » Auto Contrast or » Auto Levels. Perform this procedure on both images.

3. Subtract the background image from the image of interest by selecting: Image » Calculations. In the calculations box, select the following settings: Channels: Gray, Blending: Subtract, Source 2: Image of Interest, Source 1: Clean Image. Note: the subtraction is performed in the following manner: Source 2 – Source 1 = Subtracted Image.

4. Using the subtracted image, select Image » Adjustments » Threshold. Select a threshold value that minimizes false positives (background detection) but that also minimizes false negatives (uncounted crystals). If there is no acceptable threshold level, repeat the above process with the raw (pre-enhanced) images.

5. Using the thresholded (segmented) black and white image, select Image » Adjustments » Invert.

6. To measure the area fraction, first select the following: Filter » IP*Measure Global » Calibrate Magnification. A prompt will ask for a known distance to provided on the image. This will calibrate the software to the magnification used in the experiment.
7. To measure the detected surface area coverage select: Filter » IP*Measure Global » Area Fraction (Fig. B-3). Note: a detected object that overlaps or contacts an adjacent object will be counted as a single object.

8. In order to measure the number of detected objects, first add a new transparent layer to the image: Layer » New » Layer, and select Color: None.

9. Select a drawing tool (e.g., pen, pencil) and place a dot on each observed crystal. Then select: Filter » IP*Measure Features » Count.

10. If step (7) above did not appear to produce accurate results based on a visual observation of the raw images, the crystal tracing approach can be used. To begin this method, first add a new transparent layer to the image: Layer » New » Layer, and select Color: None.

11. In order to measure the surface area coverage by crystals, trace each crystal using the pencil drawing tool (Fig. B-4).

12. Fill the outlined objects using the fill bucket tool (Fig. B-4).

13. To measure the detected surface area coverage select: Filter » IP*Measure Global » Area Fraction.

14. Repeat the above for each image of interest. For individual crystals, plot the measured area for a given crystal as a function of the experimental time in order to determine the crystal growth rate.
Figure B-3. Example of manual image analysis approach in Adobe Photoshop with background image (A, Left) and image containing crystals (Right). The images are first subtracted (C), then the resulting image was thresholded (D) and subsequently inverted (E).
Figure B-4. Manual image analysis method using Adobe Photoshop where the crystals are first traced using the pencil tool (A, Top image) and then filled using the fill bucket tool for quantifying surface area coverage (B, Bottom image).
## Appendix C

### Water Quality Analytical Reports

#### C.1 Detailed Water Quality for OCWD Influent (Secondary Wastewater Effluent pertaining to Chapter 4)

**Table C-1.** Secondary wastewater effluent quality*.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>Aluminum (Al)</td>
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</tr>
<tr>
<td>Arsenic (As)</td>
<td>1.5 ppb</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>&lt;1 ppb</td>
</tr>
<tr>
<td>Barium (Ba)</td>
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<tr>
<td>Beryllium (Be)</td>
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<tr>
<td>Boron (B)</td>
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<tr>
<td>Bicarbonate ion (HCO₃⁻)</td>
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<tr>
<td>Biological oxygen demand (BOD)</td>
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<tr>
<td>Calcium (Ca)</td>
<td>80 ppm</td>
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<tr>
<td>Carbonate ion (CO₃²⁻)</td>
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<tr>
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<tr>
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<tr>
<td>Copper (Cu)</td>
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### Analyte and Concentration

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<td>Total Organic Carbon, TOC</td>
<td>15 ppm</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>1.5 ppb</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>15 ppb</td>
</tr>
</tbody>
</table>

*Provided via e-mail communication from OCWD on 04/17/09.*

---

### C.2 RO Feed for Panoche Site DP-25 – 05/29/09 (Pertaining to Chapter 5)

Friday, May 29, 2009

DWR Brute Laboratory  
1450 Riverbank Road, West Sacramento, CA 95605

Inorganic Analyses  
Including Misc Physical Measurements

Report of Analytical Results

---

**Sample Number:** FWA0509B1071  
**Station:** DP25-RO Feed  
**Cost Code:** L10000L00000  
**Collection Date:** 05/19/09 11:12:00 AM  
**Sample Purpose:** Normal Sample 0

**Metric:** Water, Natural  
**Description:** RO Feed  
**Customer Instructions:** Pre-filtered RO Feed  
**Sample Condition:** 2.0 °C when received.

<table>
<thead>
<tr>
<th>Method</th>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>Reporting Limit</th>
<th>Fastness</th>
<th>Chemist</th>
<th>Analysis Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std Method 2510 B</td>
<td>Conductance (EC)</td>
<td>14810 mS</td>
<td>cm</td>
<td>1</td>
<td>1</td>
<td>Chan, Esline</td>
<td>5/21/2000</td>
</tr>
<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Boron</td>
<td>30.9 mg/L</td>
<td></td>
<td>0.3 R4</td>
<td>5 R4</td>
<td>Quiambao, Josie</td>
<td>5/22/2000</td>
</tr>
<tr>
<td>EPA 200.7 (E)</td>
<td>Dissolved Calcium</td>
<td>506 mg/L</td>
<td></td>
<td>5 R4</td>
<td>5 R4</td>
<td>Quiambao, Josie</td>
<td>5/22/2000</td>
</tr>
<tr>
<td>EPA 300.3 24d Hold</td>
<td>Dissolved Chloride</td>
<td>2550 mg/L</td>
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<td>100</td>
<td>1</td>
<td>Quiambao, Josie</td>
<td>5/22/2000</td>
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<tr>
<td>Std Method 2340 B</td>
<td>Dissolved hardness</td>
<td>3145 mg/L as CaCO3</td>
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<td>5 R4</td>
<td>Quiambao, Josie</td>
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<td>EPA 200.7 (D)</td>
<td>Dissolved Magnesium</td>
<td>455 mg/L</td>
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<td>5 R4</td>
<td>Quiambao, Josie</td>
<td>5/22/2000</td>
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<tr>
<td>EPA 300.0 24d Hold</td>
<td>Dissolved Nitrate</td>
<td>597 mg/L</td>
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<td>10</td>
<td>10</td>
<td>Pineda, Maniza</td>
<td>5/22/2000</td>
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<tr>
<td>EPA 356.1 (DWR Mod)</td>
<td>Dissolved Ortho-phosphate</td>
<td>0.07 mg/L as P</td>
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<td>0.01</td>
<td>0.01</td>
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<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Potassium</td>
<td>7.6 mg/L</td>
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<td>0.5</td>
<td>Quiambao, Josie</td>
<td>5/22/2000</td>
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<tr>
<td>EPA 200.3 (D)</td>
<td>Dissolved Selenium</td>
<td>1.68 mg/L</td>
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<td>0.01</td>
<td>0.01</td>
<td>Third, Pritam</td>
<td>5/21/2000</td>
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<tr>
<td>EPA 200.7 (E)</td>
<td>Dissolved Silica (SiO2)</td>
<td>34.6 mg/L</td>
<td></td>
<td>0.5 R4</td>
<td>0.5 R4</td>
<td>Quiambao, Josie</td>
<td>5/22/2000</td>
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<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Sodium</td>
<td>3890 mg/L</td>
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<td>10 R4</td>
<td>Quiambao, Josie</td>
<td>5/23/2000</td>
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<tr>
<td>EPA 300.0 24d Hold</td>
<td>Dissolved Sulfate</td>
<td>6000 mg/L</td>
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<td>100</td>
<td>100</td>
<td>Pineda, Maniza</td>
<td>5/22/2000</td>
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<td>Std Method 2320 B</td>
<td>pH</td>
<td>7.5 pH Units</td>
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<td>0.1</td>
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<td>Std Method 2320 B</td>
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<td>235 mg/L as CaCO3</td>
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<td>1</td>
<td>1</td>
<td>Chan, Esline</td>
<td>5/21/2000</td>
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<tr>
<td>EPA 200.8 (T)</td>
<td>Total Arsenic</td>
<td>0.013 mg/L</td>
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<td>0.01</td>
<td>0.01</td>
<td>Third, Pritam</td>
<td>5/27/2000</td>
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<tr>
<td>EPA 200.8 (T)</td>
<td>Total Barium</td>
<td>&lt; 0.5 mg/L</td>
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<td>0.5</td>
<td>0.5</td>
<td>Third, Pritam</td>
<td>5/27/2000</td>
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<tr>
<td>Std Method 2540 C</td>
<td>Total Dissolved Solids</td>
<td>14440 mg/L</td>
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<td>1</td>
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<td>EPA 200.8 (T)</td>
<td>Total Selenium</td>
<td>1.75 mg/L</td>
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<td>EPA 200.8 (T)</td>
<td>Total Strontium</td>
<td>0.85 mg/L</td>
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<td>0.05</td>
<td>0.05</td>
<td>Third, Pritam</td>
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N.A.: Not Analyzed  
Reporting Limits Adjusted For Dilution

---

**Figure C-1.** RO Feed for Panoche Site DP-25 (05/29/09).

205
C.3 Detailed Influent Water Quality Reports for Panoche Tile Sumps TS-3 and TS-4 (Pertaining to Chapter 6)

C.3.1 TS-3: AD Water Influent (Date: 02/24/15)

<table>
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<td>Normal Sample</td>
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<td>UF-1</td>
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<tr>
<td>Station Name</td>
<td>UF-1 Influent</td>
</tr>
<tr>
<td>Sample Condition</td>
<td>3.0 °C when received, iced.</td>
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<tr>
<td>Depth</td>
<td>1 Ft</td>
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<td>Collection Date</td>
<td>2/24/2015 11:55:00 AM</td>
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<tr>
<td>Matrix</td>
<td>Water, Natural</td>
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<tr>
<td>Cost Code</td>
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### Inorganic Analytical Results

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<tr>
<th>Method</th>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>R.L.</th>
<th>Dilution</th>
<th>ChewID</th>
<th>Analysis Date</th>
<th>Flags and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std Method 2510-B</td>
<td>Conductance (EC)</td>
<td>19696</td>
<td>µS/cm</td>
<td>1.0</td>
<td>20.0</td>
<td>2/26/2016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPA 200.8 (D)</td>
<td>Dissolved Aluminum</td>
<td>&lt;0.2</td>
<td>mg/L</td>
<td>0.2</td>
<td>20.0</td>
<td>13/26/2015</td>
<td>R4</td>
<td></td>
</tr>
<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Boron</td>
<td>57.95</td>
<td>mg/L</td>
<td>2.0</td>
<td>20.0</td>
<td>67/33/2015</td>
<td>R4</td>
<td></td>
</tr>
<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Calcium</td>
<td>613.9</td>
<td>mg/L</td>
<td>20.0</td>
<td>20.0</td>
<td>67/33/2015</td>
<td>R4</td>
<td></td>
</tr>
<tr>
<td>EPA 300.0 26d Hold</td>
<td>Dissolved Chloride</td>
<td>378.0</td>
<td>mg/L</td>
<td>250.0</td>
<td>250.0</td>
<td>9/22/2015</td>
<td>R4</td>
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<tr>
<td>Std Method 2340 B</td>
<td>Dissolved Hardness</td>
<td>347.2</td>
<td>mg/L as CaCO₃</td>
<td>1.0</td>
<td>67</td>
<td>3/33/2015</td>
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<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Magnesium</td>
<td>470.8</td>
<td>mg/L</td>
<td>20.0</td>
<td>20.0</td>
<td>67/33/2015</td>
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<td></td>
</tr>
<tr>
<td>EPA 200.8 (Hg Dissolved)</td>
<td>Dissolved Mercury</td>
<td>&lt;0.004</td>
<td>mg/L</td>
<td>0.004</td>
<td>20.0</td>
<td>13/22/2015</td>
<td>R4</td>
<td></td>
</tr>
<tr>
<td>EPA 300.0 26d Hold</td>
<td>Dissolved Nitrate</td>
<td>152</td>
<td>mg/L</td>
<td>25.0</td>
<td>250.0</td>
<td>9/22/2015</td>
<td>R4</td>
<td></td>
</tr>
<tr>
<td>EPA 415.1 (D) OX</td>
<td>Dissolved Organic Carbon</td>
<td>14.4</td>
<td>mg/L as C</td>
<td>0.5</td>
<td>1.0</td>
<td>86/33/2015</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| EPA 365.1 (DWR Modified) | Dissolved Ortho-phosphate | 0.05 | mg/L as P | 0.01 | 1.0 | 5/27/2016 | |
| EPA 200.7 (D) | Dissolved Potassium | 21.7 | mg/L | 10.0 | 20.0 | 67/33/2015 | R4 |
| EPA 200.8 (D) | Dissolved Selenium | 0.362 | mg/L | 0.02 | 20.0 | 13/26/2015 | R4 |
| EPA 200.7 (D) | Dissolved Silica (SiO₂) | 37.496 | mg/L | 2.0 | 20.0 | 67/33/2015 | R4 |
| EPA 200.7 (D) | Dissolved Sodium | 470.8 | mg/L | 20.0 | 20.0 | 67/33/2015 | R4 |
| EPA 300.0 26d Hold | Dissolved Sulfate | 640.133 | mg/L | 250.0 | 250.0 | 9/22/2015 | R4 |
| EPA 150.1 | pH | 7.5 | | | | | |
| Std Method 2320 B | pH | 7.5 | | | | | |
| Std Method 2320 B | Total Alkalinity | 377 | mg/L as CaCO₃ | 1.0 | 1.0 | 20/26/2015 | |
| EPA 200.8 (T) | Total Aluminum | <0.01 | mg/L | | | | |
| EPA 200.8 (T) | Total Arsenic | <0.001 | mg/L | | | | |
| EPA 200.8 (T) | Total Barium | <0.005 | mg/L | | | | |
| EPA 200.8 (T) | Total Chromium | 0.028 | mg/L | | | | |
| EPA 200.8 (T) | Total Copper | 0.02 | mg/L | | | | |
| Std Method 2540 C | Total Dissolved Solids | 15870 | mg/L | 1.0 | 1.0 | 20/26/2015 | |
| EPA 200.8 (T) | Total Iron | <0.005 | mg/L | | | | |
| EPA 200.8 (T) | Total Lead | <0.001 | mg/L | | | | |
| EPA 200.8 (T) | Total Manganese | <0.005 | mg/L | | | | |
| EPA 200.8 (T) | Total Nickel | 0.03 | mg/L | | | | |
| EPA 415.1 (T) OX | Total Organic Carbon | 9.1 | mg/L as C | | | | |

| EPA 200.7 (T) | Total Potassium | 21.73 | mg/L | 10.0 | 20.0 | 67/33/2015 | R4 |
| EPA 200.8 (T) | Total Selenium | 0.394 | mg/L | | | | |
| EPA 200.7 (T) | Total Silica (SiO₂) | 40.142 | mg/L | | | | |
| EPA 200.8 (T) | Total Strontium | 0.999 | mg/L | | | | |
| EPA 160.2 | Total Suspended Solids | 10 | mg/L | | | | |
| EPA 160.1 | Turbidity | <1 | NTU | | | | |

N.A. = Not Analyzed  R.L. = Reporting Limit (Reporting Limits Adjusted For Dilution)

Figure C-2. TS-3 AD Water Influent (02/24/15).
C.3.2 TS-3: AD Water Influent (Date: 04/01/15)

![Inorganic Analytical Results](image)

**Figure C-3.** TS-3 AD Water Influent (04/01/15).
### C.3.3 TS-3: AD Water Influent (Date: 04/14/15)

**Sample Number**: FW0415B0101  
**Sample Type/Purpose**: Normal Sample  
**StationNumber**: UF-1  
**StationName**: UF-1 Influent  
**Sample Condition**: 1.0 °C when received, Iced.

#### Inorganic Analytical Results

<table>
<thead>
<tr>
<th>Method</th>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>R.L.</th>
<th>Dilution Chem/ID</th>
<th>Analysis Date</th>
<th>Flags and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std Method 2510-B</td>
<td>Conductance (EC)</td>
<td>16755</td>
<td>µS/cm</td>
<td>1.</td>
<td>1.</td>
<td>4/16/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 200.8 (D)</td>
<td>Dissolved Aluminum</td>
<td>&lt;0.2</td>
<td>mg/L</td>
<td>0.2</td>
<td>20</td>
<td>4/17/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Boron</td>
<td>54.51</td>
<td>mg/L</td>
<td>0.5</td>
<td>10</td>
<td>4/22/2015</td>
<td>R4</td>
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<tr>
<td>EPA 200.7 (D)</td>
<td>Dissolved Calcium</td>
<td>560.5</td>
<td>mg/L</td>
<td>5.</td>
<td>5.</td>
<td>4/22/2015</td>
<td>R4</td>
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<tr>
<td>EPA 300.0 28d Hold</td>
<td>Dissolved Chloride</td>
<td>3333</td>
<td>mg/L</td>
<td>200</td>
<td>200</td>
<td>4/17/2015</td>
<td>R4</td>
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<tr>
<td>EPA 300.0 28d Hold</td>
<td>Dissolved Chloride</td>
<td>3330</td>
<td>mg/L</td>
<td>200</td>
<td>200</td>
<td>4/17/2015</td>
<td>R4</td>
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<td>Std Method 2340 B</td>
<td>Dissolved Hardness</td>
<td>3041</td>
<td>mg/L as CaCO3</td>
<td>1.</td>
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<td>4/22/2015</td>
<td>R4</td>
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<tr>
<td>Std Method 2340 B</td>
<td>Dissolved Hardness</td>
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<td>mg/L as CaCO3</td>
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<td>1.</td>
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<td>Dissolved Magnesium</td>
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<td>5.</td>
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<td>R4</td>
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<tr>
<td>EPA 200.8 (Hg Dissolved)</td>
<td>Dissolved Mercury</td>
<td>&lt;0.004</td>
<td>mg/L</td>
<td>0.004</td>
<td>20</td>
<td>4/17/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 300.0 28d Hold</td>
<td>Dissolved Nitrate</td>
<td>140.5</td>
<td>mg/L</td>
<td>20.</td>
<td>200</td>
<td>4/17/2015</td>
<td>R4</td>
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<tr>
<td>EPA 300.0 28d Hold</td>
<td>Dissolved Nitrate</td>
<td>140.3</td>
<td>mg/L</td>
<td>20.</td>
<td>200</td>
<td>4/17/2015</td>
<td>R4</td>
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<td>EPA 415.1 (D) Ox</td>
<td>Dissolved Organic Carbon</td>
<td>9.4</td>
<td>mg/L as C</td>
<td>0.5</td>
<td>1.</td>
<td>4/23/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 365.1 (DWR Modified)</td>
<td>Dissolved Ortho-phosphate</td>
<td>0.1</td>
<td>mg/L as P</td>
<td>0.01</td>
<td>1.</td>
<td>4/15/2015</td>
<td>R4</td>
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<td>Dissolved Potassium</td>
<td>16.3</td>
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<td>5.</td>
<td>4/22/2015</td>
<td>R4</td>
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<td>Dissolved Selenium</td>
<td>0.345</td>
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<td>R4</td>
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<td>Dissolved Silica (SiO2)</td>
<td>36.834</td>
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<td>Dissolved Sulfate</td>
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<td>4/17/2015</td>
<td>R4</td>
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<td>Total Alkalinity</td>
<td>374</td>
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<td>1.</td>
<td>4/16/2015</td>
<td>R4</td>
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<tr>
<td>EPA 200.8 (T)</td>
<td>Total Aluminum</td>
<td>&lt;0.2</td>
<td>mg/L</td>
<td>0.2</td>
<td>20</td>
<td>4/21/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 200.8 (T)</td>
<td>Total Arsenic</td>
<td>&lt;0.02</td>
<td>mg/L</td>
<td>0.02</td>
<td>20</td>
<td>4/21/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 200.8 (T)</td>
<td>Total Barium</td>
<td>&lt;0.1</td>
<td>mg/L</td>
<td>0.1</td>
<td>20</td>
<td>4/21/2015</td>
<td>R4</td>
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<td>EPA 200.8 (T)</td>
<td>Total Chromium</td>
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<td>mg/L</td>
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<td>4/21/2015</td>
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<td>Method</td>
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<td>Date</td>
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<td>4/21/2015</td>
<td>mg/L</td>
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<td>67</td>
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N.A. = Not Analyzed  R.L. = Reporting Limit (Reporting Limits Adjusted For Dilution)

Figure C-4. TS-3 AD Water Influent (04/14/15).
C.3.4 TS-4: AD Water Influent (Date: 05/12/15)

<table>
<thead>
<tr>
<th>Method</th>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>R.L.</th>
<th>Dilution</th>
<th>Chem ID</th>
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<tr>
<td>Std Method 2510-B</td>
<td>Conductance (EC)</td>
<td>13526</td>
<td>µS/cm</td>
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<td>EPA 200.8 (D)</td>
<td>Dissolved Aluminum</td>
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<td>13</td>
<td>5/20/2015</td>
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<td>Dissolved Boron</td>
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<td>10</td>
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<tr>
<td>EPA 300.28d Hold</td>
<td>Dissolved Chloride</td>
<td>1800</td>
<td>mg/L</td>
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<td>9</td>
<td>5/28/2015</td>
<td>R4</td>
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<tr>
<td>Std Method 2340 B</td>
<td>Dissolved Hardness</td>
<td>2402</td>
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<td>1.0</td>
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<td>EPA 200.6 (Hg Dissolved)</td>
<td>Dissolved Mercury</td>
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<td>R4</td>
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<td>EPA 300.28d Hold</td>
<td>Dissolved Nitrate</td>
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<td>EPA 415.1 (D) Ox</td>
<td>Dissolved Organic Carbon</td>
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<td>mg/L as C</td>
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<td>Dissolved Ortho-phosphate</td>
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<td>EPA 200.7 (D)</td>
<td>Dissolved Potassium</td>
<td>12.2</td>
<td>mg/L</td>
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<td>EPA 200.8 (D)</td>
<td>Dissolved Selenium</td>
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<td>&lt; 0.1</td>
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<td>10</td>
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<td>R4</td>
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<td>mg/L</td>
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<td>5/20/2015</td>
<td>R4</td>
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<td>mg/L</td>
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N.A. = Not Analyzed  R.L. = Reporting Limit (Reporting Limits Adjusted For Dilution)

Figure C-5. TS-4 AD Water Influent (05/12/15).
### Inorganic Analytical Results

**Sample Number**: FW0615B0276  
**Sample Type/Purpose**: Normal Sample  
**Station Number**: UF-1  
**Station Name**: UF-1 Influent  
**Matrix**: Water, Natural  
**Depth**: 1 ft  
**Collection Date**: 6/23/2015 12:30:00 PM  
**Cost Code**: U1067200000

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<th>R.L.</th>
<th>Dilution</th>
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<th>Analysis Date</th>
<th>Flags and Notes</th>
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<td>3</td>
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<td>R4</td>
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<td>Dissolved Calcium</td>
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<td>10.</td>
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<td>R4</td>
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<td>EPA 300.0 2Bd Hold</td>
<td>Dissolved Chloride</td>
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<td>10</td>
<td>6/26/2015</td>
<td>R4</td>
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<tr>
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<td>Dissolved Mercury</td>
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<td>13</td>
<td>6/30/2015</td>
<td>R4</td>
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<td>Dissolved Nitrate</td>
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<td>60.</td>
<td>9</td>
<td>7/1/2015</td>
<td>R4</td>
</tr>
<tr>
<td>EPA 415.1 (D) Ox</td>
<td>Dissolved Organic Carbon</td>
<td>6.8</td>
<td>mg/L as C</td>
<td>0.5</td>
<td>1.</td>
<td>67</td>
<td>6/24/2015</td>
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<tr>
<td>EPA 365.1 (DWR Modified)</td>
<td>Dissolved Orthophosphate</td>
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<td>mg/L as P</td>
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<td>Dissolved Potassium</td>
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<td>60.</td>
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<td>6/4/2015</td>
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<td>6/4/2015</td>
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<td>Total Aluminum</td>
<td>&lt; 0.1</td>
<td>mg/L</td>
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<td>13</td>
<td>7/1/2015</td>
<td>R4</td>
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<td>10.</td>
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<td>7/1/2015</td>
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<td>6/26/2015</td>
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**N.A. = Not Analyzed   R.L. = Reporting Limit (Reporting Limits Adjusted For Dilution)**

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**Figure C-6. TS-4 AD Water Influent (06/23/15).**
C.3.6 TS-4: AD Water Influent (Date: 08/04/15)

Note: Membrane monitoring experiments ceased just prior to this sampling date. It was included for comparison of influent water and RO plant performance comparison. On this date, the RO plant was operated with the 2nd stage in 2-pass mode with RO concentrate recycle to the 1st stage.

<table>
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<th>Method</th>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>R.L.</th>
<th>Dilution</th>
<th>ChemID</th>
<th>Analysis Date</th>
<th>Flags and Notes</th>
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<td>8/6/2015</td>
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<td>EPA 200.8 (D)</td>
<td>Dissolved Aluminum</td>
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<td>mg/L</td>
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<td>10.</td>
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<td>8/6/2015</td>
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<td>8/12/2015</td>
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<td>8/12/2015</td>
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<td>Dissolved Nitrate</td>
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<td>mg/L</td>
<td>3.</td>
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<td>Dissolved Organic Carbon</td>
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<td>mg/L</td>
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<td>mg/L</td>
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<td>10.</td>
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<td>8/6/2015</td>
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<tr>
<td>EPA 200.7 (T)</td>
<td>Total Silica (SiO2)</td>
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N.A. = Not Analyzed  R.L. = Reporting Limit (Reporting Limits Adjusted For Dilution)

Figure C-7. TS-4 AD Water Influent (08/04/15).
Appendix D

Supplemental Data – Chapter 3

D.1 Extended Flux Decline Data for Silica Scaling

As is indicated in Figs. 3-4a, 3-5 & D-1, permeate flux decline was not a sensitive indicator of silica scaling at the three lowest silica supersaturation levels. Detectable flux decline was only detected for the silica supersaturation \( \overline{SI}_m = 1.94 \) after about 30 hours of operation. After 200 hrs (> 8 days) of operation, less than 10% flux decline was detected for the lowest silica supersaturation level (i.e., \( \overline{SI}_m = 1.58 \)), and about 15% flux decline was detected for the second lowest supersaturation (\( \overline{SI}_m = 1.79 \)).

![Figure D-1](image)

**Figure D-1.** Long-term permeate flux decline for silica scaling tests at silica supersaturation levels of \( \overline{SI}_m = 1.58–1.94 \).
D.2 Real-time Membrane Images and Image Analysis During Silica Scaling

In contrast to the flux decline behavior, real-time imaging of the membrane revealed significant surface changes prior to gelling at the membrane surface (Figs. D-2–D-4). For the three lowest silica supersaturation levels ($\overline{\text{SI}}_m=1.58–1.94$, Runs 1–3), it is suggested that this gelling process occurred after the initial “induction” period of detectable particle nucleation and growth. In contrast, it was apparent that at the highest two supersaturation levels ($\overline{\text{SI}}_m=2.39$, 3.10, Runs 4 & 5), gelling occurred simultaneously with particle formation resulting in nearly immediate permeate flux decline, rendering “early” detection infeasible.

Optical detection of gel formation was possible to a degree (as indicated in the elongated “strand”-like formations detected on the membrane surface), but comparison of flux decline data to detected surface coverage was infeasible for two reasons: (a) the monitored area was a small fraction of the entire membrane area contributing to permeate flux and may not be representative of scaling on the entire membrane, and (b) as scaling progresses the gel layer should become thicker, as indicated in Fig. 3-14 and previous studies of silica fouling [136], thereby causing greater permeate flux decline. The present monitoring approach was not aimed at tracking development of a fouling "gel" layer in the transverse direction on the membrane. The goal of the present monitoring approach was early detection of incipient scaling, which was indeed accomplished.
Figure D-2. Real-time images of the membrane surface collected for Run 1 (SI_m = 1.60). Binary images (top row) produced by analyzing raw grayscale images (bottom row). Flow direction is from top to bottom. Monitored area = 6.7 × 5.4 mm.

Figure D-3. Real-time images of the membrane surface collected for Run 2 (SI_m = 1.93). Binary images (top row) produced by analyzing raw grayscale images (bottom row). Flow direction is from top to bottom. Monitored area = 6.7 × 5.4 mm.
Figure D-4. Real-time images of the membrane surface collected for Run 3 ($S_{lm} = 2.10$). Binary images (top row) produced by analyzing raw grayscale images (bottom row). Flow direction is from top to bottom. Monitored area = 6.7 × 5.4 mm.

Figure D-5. Real-time images of the membrane surface collected for Run 4 ($S_{lm} = 2.72$). Binary images (top row) produced by analyzing raw grayscale images (bottom row). Flow direction is from top to bottom. Monitored area = 6.7 × 5.4 mm.
D.3 Membrane Image Analysis for Surface Number Density (SND) and Surface Coverage of Silica Scaling: Long-term Data

It is apparent that the rate of nucleation (Figs. 3-4c, 3-6) rises with the level of silica supersaturation, and that nucleation occurred during the “induction” or lag period suggested by flux decline data (Fig. 3-4a). Initially, in Runs 1–3 (SI_m=1.60–2.10), nucleation was relatively slow and generally followed a linear trend in the early stages. After a lag period, the SND and detected surface coverage (Figs. D-6 & D-7) increased sharply until eventually approaching a plateau, presumably due to the decrease in available surface area for scaling, as observed in Figure D-6 for SI_m=2.10 (Run 3). As the level of supersaturation decreased, the duration of this lag time expectedly increased. Notably, at the lowest SI_m of 1.60 this sudden jump in SND was much less pronounced, blurring the concept of an induction period. Rather, a gradual rise in SND indicated a greater buildup of nucleated particles that may act as seeds for further nucleation. This suggests that particle nucleation was more dominant than gel formation at lower supersaturation levels. Moreover, given that nucleation at this level was more gradual, there were less particles growing for extended periods of time (that also grow slower), thus enabling the SND at this condition to reach higher levels than at higher supersaturation levels (Runs 2 & 3) (Fig. D-6). At the higher SI_m=2.72, 3.50 (Runs 4 and 5) expectedly higher rates of nucleation were observed over shorter durations (Figs. 3-4c) and the previously detected lag or induction time was virtually absent as the level of supersaturation was apparently sufficiently high for immediate nucleation and growth of observable particles. Although these levels of supersaturation (SI_m=2.72–3.50) and corresponding degree of CP may be unrealistic in typical RO membrane plants (without antiscalant use), they were included in this study for comparative analysis.
Figure D-6. Surface number density (SND) profiles for detected silica for the three lowest supersaturation levels tested in the observed membrane area (SND = number of detected particles / observed area($\text{mm}^2$)).

Figure D-7. Long-term evolution of surface coverage by silica as a percentage of the observed membrane area at various SI levels.
Appendix E

Supplemental Data – Chapter 6

E.1 Real-time RO Recovery Optimization Scheme

Field optimization of recovery level and antiscalant dose, described in Ch. 6, can be presented as a general incremental optimization approach, and depicted using a decision tree diagram (Fig. E-1). The goal of this approach is to maximize the scale-free RO recovery while minimizing antiscalant use. Clearly, if antiscalant use is unlimited, then this problem would be simplified somewhat. However, excessive antiscalant use is costly and may facilitate biofouling or antiscalant fouling for certain feed waters. Additionally, operating parameters, particularly the time limit (N days) and starting points (C₀, Y₀), would need to be assessed based on relevant field experience or field evaluation studies as discussed in Ch. 5 and 6. Additionally, step sizes in adjustment of antiscalant dose and recovery increments could be aggressive or conservative, depending on a plant’s goals and preferences. However, as one approaches the expected supersaturation limits, one should establish conservative increments. In practice, RO plants utilizing such an optimization scheme would require a sufficiently adaptive supervisory control system (i.e., to account for variable water quality) and automated process actuators. It is noted that the optimization scheme as depicted in Fig. E-1 does not incorporate a long term fresh water flushing approach. However, this should clearly be done whenever there is mineral scale detected, and when significant decline in RO membrane permeability is detected in the plant. Long-term operation may be feasible with an acceptably low scale growth rate, provided that there is a periodic fresh water flushing of the entire system.

Once an appropriate antiscalant dosage and recovery levels are determined, using a similar approach to that outlined in Fig. E-1, these values can be used as initial setpoints for
plant control. Appropriate control schemes will likely be needed to account for temporal variations in water quality that may push the recovery limit lower than the current recovery set point. If the opposite occurs (i.e., recovery limit is higher than the set point) and the recovery limit increases, then it may be possible to increase water recovery, at least temporarily. In this scenario, when mineral scaling is not detected for an extended period, it is not straightforward to determine how far below the recovery limit one is currently operating. Clearly, one can use an incremental approach as was shown here, but this may be tedious and prevent fully capitalizing on the period of improved feed water quality. However, it may be feasible to approach the recovery limit from (slightly) above. Moreover, in practice it may not be possible to operate precisely at the established upper recovery limit. Indeed, observing a minor amount of mineral scale growth may be helpful to signal the proximity of the recovery limit and triggering a fresh water flush.
Figure E-1. Proposed incremental optimization scheme for RO plant recovery while minimizing AS dose for a given selected AS. $Y_0 =$ starting recovery level, $Y_i =$ current rec. level (at start, $Y_i = Y_0$), $\Delta Y =$ rec. increment, $Y_i+1 =$ next rec. level, $C_0 =$ initial AS dose, based on operator experience or manufacturer recommendation, $N =$ number of days for rec. testing period, $C_i =$ current AS dose (at start, $C_i = C_0$), $\Delta C =$ increment for AS dose change, $C_{i-1} =$ reduced dose or previous AS dose, $C_{max} =$ maximum allowable AS dose, $G =$ individual crystal growth rate, $G_{min} =$ acceptable low rate of scale crystal growth.
When operating RO plants in tandem with a membrane monitoring system fed with the RO plant concentrate, assuming the recovery level in the membrane monitoring system is negligibly small, one can calculate the equivalent overall recovery using Eq. 6-2 in Ch. 6 (Fig. E-2):

\[ Y_{eq} = 1 - \frac{1 - Y}{CP(1 - \beta Y)} \]  

(E-1)

The level of CP in the monitored region of the membrane in the membrane monitoring system determines how much greater this overall recovery is than the plant’s operating recovery (i.e., as a safety margin). However, the maximum possible safety margin decreases as the RO plant recovery is increased (Fig. E-2). To increase the CP level, the hydrodynamics in the membrane monitor channel may need to be adjusted (i.e., crossflow velocity) in order to increase the CP level and maintain an acceptable safety margin. However, one could also map the CP profile, using appropriate models and correlations, and monitor regions of the membrane monitor channel where CP may be higher than the average to ensure that mineral scaling is always discovered early. Given the stochastic nature of crystal nucleation, the monitored region should not be overly small, but the magnification should be high enough in order to detect small crystals (of size ~0.05 mm or less).
E.2 Additional Water Quality Analyses

The evolution of saturation index with water recovery was calculated for each of the six AD water sampling events (Appendix C) for the four major potential mineral scalants (Figs. E-3–E-8), with minor differences. This was done by performing a simulated concentration survey in which the amount of water in a given feed solution is varied and the resulting saturation indices were calculated using thermodynamic simulation software. Thereafter, the concentration factor, $CF$, and subsequently the water recovery $Y$ can be calculated from a mass balance (Eqn. 2-8, 2-9). A summary of water quality results is found in Table 6-1, and detailed water quality reports are provided in Appendix C.
Figure E-3. Saturation indices for sparingly soluble minerals vs. water recovery for the 1st water sample (02-24-15). Overall salt rejection taken to be 99.5% (SI values calculated from [248]).

Figure E-4. Saturation indices for sparingly soluble minerals vs. water recovery for the 2nd water sample (04-01-15). Overall salt rejection taken to be 99.5% (SI values calculated from [248]).
Figure E-5. Saturation indices for sparingly soluble minerals vs. water recovery for the 3rd water sample (04-15-15). Overall salt rejection taken to be 99.5% (SI values calculated from [248]).

Figure E-6. Saturation indices for sparingly soluble minerals vs. water recovery for the 4th water sample (05-12-15). Overall salt rejection taken to be 99.5% (SI values calculated from [248]).
Figure E-7. Saturation indices for sparingly soluble minerals vs. water recovery for the 5th water sample (06-23-15). Overall salt rejection taken to be 99.5% (SI values calculated from [248]).

Figure E-8. Saturation indices for sparingly soluble minerals vs. water recovery for the 6th and final water sample taken near the end of experimental runs (08-04-15). Overall salt rejection taken to be 99.5% (SI values calculated from [248]).
E.3 Flux Decline Data for Membrane Monitoring System Prior to Fresh Water Flush

The following permeate flux data pertain to the triggering of fresh water flush in response to mineral scaling (Sec. 6.3.4).

![Image of permeate flux decline graph](image)

**Figure E-9.** Permeate flux decline in the membrane monitor after mineral scale detection at 78% equivalent recovery with initial dose of 5 ppm AS-1 just prior to fresh water flush to remove detected scale crystal (Run 13).
**Figure E-10.** Permeate flux decline in the membrane monitor after early mineral scale detection at 78% equivalent recovery with 5 ppm AS-1 just prior to fresh water flush to remove detected scale crystals (Run 8).

**Figure E-11.** Membrane monitoring system permeate flux during scale detection at 80% equivalent recovery and AS-2 dosage of 5 ppm, just prior to fresh water flush to remove detected scale crystals (Run 19).
E.4 Potential for Membrane Integrity Loss due to Mineral Scaling

Throughout the course in a field study for optimization of water recovery, it should be recognized that mineral scale can, at times, grow in areas that are not regularly monitored. Although scale typically develops first in areas of highest CP (e.g., channel entrance, exit, and side edges), if left unchecked, can cause increased salt passage (Fig. E-12). Even when removed with fresh water flush, the observed salt rejection may not rebound, suggesting that the damage can be permanent. Optical images of a flushed membrane surface revealed impressions in the same location where extensive mineral scale was located (Fig. E-13). Given the small thickness of the active separation layer for RO membranes, such a layer can eventually be perforated by segments of the growing mineral scale crystals. Thus, early detection of the onset of scaling and removal are critical for effective RO operation.

![Figure E-12](image-url)  
**Figure E-12.** Impairment of observed salt rejection during unchecked mineral scale growth in the membrane monitoring system, corresponding to the mineral scaling depicted in Fig. E-13.
Figure E-13. Images of large mineral scale crystals near the outlet of the membrane monitor channel (i.e., where CP is highest) 6 days before fresh water flush (FWF) (A), just before FWF (B), during FWF (C), and remaining impression after complete removal by FWF (D). Dates correspond to Fig. E-12.

E.5 Mineral Scaling Kinetics in Single-Pass versus Total Recycle Mode

In typical laboratory membrane fouling studies, synthetic batch solutions are recirculated through the membrane module(s) while fouling is monitored either in-situ or with ex-situ measurements. Given the stochastic nature of mineral scaling, convective residence time in the membrane module, and antiscalant use, may both play a factor in affecting the observed onset of mineral scaling. In practice, large RO plants typically operate as once-through steady state processes, as opposed to operation with concentrate recycle mode in laboratory studies. An
illustration of the difference in the impact of the two RO operational modes on mineral scaling is illustrated in Figure E-14. Clearly, laboratory recycle mode operation results in a shorter scaling induction time.

![Figure E-14](image-url)

**Figure E-14.** Comparison of surface scale evolution for single-pass and total recycle operation using RO concentrate at 78% equivalent recovery with 5 ppm AS-1 in the RO feed, obtained from analysis of images in Fig. E-15. The SIMS RO was operated at 68% recovery (SI\(_g\)~2.9–3.1 in the RO concentrate) and at the monitored membrane surface, SI\(_{g,m}\)~4.1–4.4.

It is noted that both of the test cases utilized RO concentrate produced by the RO plant operating at water recovery of 68% and further concentrated to a level equivalent to 78% recovery in the CP layer in the monitored membrane flow channel (see Fig. E-2). In total recycle mode operation, the RO concentrate (~20 L) was produced just prior (~2 minutes) to the beginning of the experiment in order to minimize bulk precipitation or settling that may take place over long storage periods. It was observed that the onset of mineral scaling (as gypsum rods) occurred several hours (~6 h) earlier when the RO concentrate was recycled rather than
passed through the system once and discharged (Figs. E-14, E-15). Recycling of the solution most likely provided sufficient convective residence time for mineral crystals to nucleate either in the bulk or at the surface. However, antiscalant may have also been exhausted, as discussed in [112], due to adsorption onto crystals or nuclei surfaces, whereas in single-pass mode the antiscalant was continuously maintained. Further study is recommended for cases without antiscalant in order to isolate the root cause of this behavior.

**Figure E-15.** Real-time membrane surface images taken during mineral scaling in the membrane monitoring system operating with RO concentrate at 78% equivalent recovery and 5 ppm AS-I in the RO feed (Left column: single-pass, Right column: total recycle).
E.6 Additional SEM Analysis of Mineral Scale Crystals

Membrane samples, from the membrane monitoring system, scaled with salt crystals during AD water desalination were analyzed via scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Sec. 6.3.2). EDS spectra exhibited significant peaks for calcium and sulfur, suggesting that the mineral scale crystals are calcium sulfate (gypsum). It is noted that trace amounts of silicon (Si) were also detected in the EDS analysis, suggesting silica may have precipitated with gypsum to a degree.

Additional SEM micrographs revealed morphologies for the gypsum crystals that resembled flattened or deformed gypsum rosettes (Figs. E-16–E-18), and appeared much different than the typically observed rosette structures, consistent with previous work [236], in which multiple rod structures extend away from a central core. It is hypothesized that the presence of antiscalants, given that they may interact with crystal surfaces to hinder growth, may have modified the crystal structures and thus altered the exhibited morphologies to more two-dimensional flattened structures (Figs. E-16–E-18). This may have occurred by reducing the available surface area for crystal growth in the presence of AS, and thus fewer rods were able to grow from the crystals in the presence of antiscalant.
Figure E-16. SEM micrographs of mineral scale crystals at 250X mag. (left) and 1000X mag. (right).

Figure E-17. SEM images of mineral scale crystals formed on the membrane monitoring system membrane during RO desalination of AD water: mineral crystals resembling "flattened" gypsum rosettes (A-C), and high mag. image of a "flattened" crystal rod or arm (D).
Figure E-18. SEM images of mineral scale crystals formed on membrane monitoring system membrane during RO desalination of AD water: horizontal (A-B), and vertical (C-D) "flattened" mineral crystals.
References


34. *Nitto Denko to provide membranes for Israel's Sorek desal plant*, Filtration & Separation, **48** (2011) 8.


40. *Carlsbad plant helps California to meet its water needs*, Membrane Technology, **2016** (2016) 8.


54. Orange County Water District, Groundwater Replenishment System (website), www.ocwd.com/gwrs/


93. Alawadhi, A. A., Pretreatment plant design—Key to a successful reverse osmosis desalination plant, Desalination, 110 (1997) 1-10.


217. Han, Y., Lin, Q., Effects of inorganics on RO membrane initial biofouling formation, iCBBE, Beijing, 2009.


317. Miller, G. W., *(Integrated concepts in water reuse managing global water needs, Desalination, 187 (2006).)*


319. *(Upgraded Effluent Standards, Inbar Committee, Ministry of Environmental Protection, Israel, 2004.)*


