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Dissolved Carbon Dioxide for Scale Removal in Reverse Osmosis

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DISSOLVED CARBON DIOXIDE FOR SCALE
REMOVAL IN REVERSE OSMOSIS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
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by
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Accepted by:
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Abstract

Membrane fouling is a major operational issue in reverse osmosis (RO) desalination plants. In particular, plants treating brackish groundwater can encounter troublesome inorganic scales, including carbonates, sulfates, and silicates. A novel cleaning method is proposed to remove inorganic scales from fouled RO membranes using dissolved CO₂. As CO₂ molecules encounter membrane foulants, the surfaces serve as nucleation sites for small bubbles to form and shear off foulants. Dissolved CO₂ solutions were prepared by bubbling CO₂ gas into water held in a pressure vessel. Gas dissolution was confirmed by enhanced exit velocities for water containing CO₂, due to the increase in volume from exsolution, when compared to water containing less soluble N₂.

A dissolved CO₂ solution was effective in removing scale from RO membranes through bubble nucleation. Membranes scaled with CaCO₃ were cleaned for 10 minutes with a once-through dissolved CO₂ solution of approximately pH 4.5, achieving an average 80% flux recovery. Controls were performed with other cleaning regimes to isolate effects from pH and air scouring present in CO₂ cleaning. An HCl solution at pH 3 provided an average flux recovery of 79% after circulating through the system for 30 minutes, while an HCl solution at pH 4 only gave an average 20% flux recovery. Trials using N₂ gas in place of CO₂ only produced a 6% flux recovery on average. Lowering the pH of the N₂ solution to pH 4 with HCl boosted cleaning slightly to an average 8% flux recovery. Thus, the low pH of the CO₂ solution at pH 4.5 and bulk phase air scouring are minor mechanisms in scale removal. In addition, membranes scaled with calcium silicates were not cleaned using dissolved CO₂ – only NaOH at pH 12 plus sodium dodecyl sulfate provided significant cleaning. Future work should be done with additional scale types to narrow in on the mechanism for cleaning by dissolved CO₂.

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1. Background: Brackish Water Desalination using Reverse Osmosis

Reverse osmosis (RO) is commonly used for the production of drinking water. The process involves passing water over a selectively permeable membrane at high pressure; the smallest molecules pass through the fastest and others more slowly. RO membranes are the most selective – typically only monovalent ions are measurable in the product water (American Water Works Association 2007). Brackish water desalination makes larger use of RO than seawater desalination, for which multistage flash distillation is the most common. Considering all desalinated waters world-wide, RO makes up about 44% (Wangnick 2002). Compared to seawater, brackish groundwater tends to contain more calcium, carbonate, and sulfate ions, and less sodium and chloride. Additionally, while seawater RO is more prone to fouling by colloidal particulates and organic matter, brackish water RO is primarily fouled by precipitation of inorganic salts. Membrane fouling can occur when concentrations exceed solubility limits and causes both reversible and irreversible fouling. (Brady et al. 2005; Greenlee et al. 2009).

Brackish water requires lower applied pressure than seawater and can be done with low pressure RO membranes or nanofiltration membranes, while seawater requires high pressure membranes (Crittenden et al. 2005). High pressure RO membranes are typically considered to be nonporous while low pressure RO membranes (pores less than 0.5 nm) and nanofiltration membranes (pores from 0.5 to 2 nm) are considered porous (Van Der Bruggen et al. 2004).

1.1 Issues with Inland Groundwater RO

Groundwater encounters different obstacles compared to seawater. Where fouling from organics and particulates is more common in seawater desalination, the majority of groundwater RO plants have problems with fouling from inorganic scales. For example, a survey of brackish water desalination plants in Texas found that about a third noted inorganic scaling as a major fouling issue, the most of any foulant (Shirazi and Arroyo 2011). In addition, inland desalination has the added difficulty of limited options for concentrate disposal. Some practices, such as discharging to municipal sewers or saline ditches, put strains on other systems. Others are costly and impose an economical hindrance on desalination (Brady et al. 2005; Greenlee et al. 2009).

1.1.1 Scaling

Scaling refers to the precipitation of salts onto the membrane surface which results in reduced permeate flow. Polyvalent ions in the source water, though below solubility limits, can precipitate onto the membrane surface due to enhanced concentration of solutes very near the membrane surface, a phenomenon known as concentration polarization. Scales fall under the categories of alkaline, non-alkaline, and silica based, with non-alkaline scales more difficult to remove than alkaline scales. The most common non-alkaline scale is calcium sulfate, and is typically prevented by maintaining unsaturated conditions. Another common scalant, calcium phosphate, is most effectively treated by acidification of the feedwater. Silica scale can be prevented by either pre-treatment or acidification. Silica scaling can be a limiting factor for brackish water RO since, unlike calcium carbonate and sulfate scale, antiscalants are not effective at preventing silica scales (Antony et al. 2011; Brady et al. 2005; Fritzmann et al. 2007;

Greenlee et al. 2009). The review by Antony et al. (2011) on scaling in high pressure membrane systems is summarized in Table 1 below.

Table 1: Summary of common scales in high pressure membrane systems and their formation and treatment (Antony et al. 2011)

Name	Formula	Scale Type	Formation Notes	Prevention/Removal Techniques
Calcium carbonate	CaCO_3	Alkaline	Common, but predictable and controllable.	Flushing procedures during shutdown
Calcium sulfate	$\text{CaSO}_4 \cdot x\text{H}_2\text{O}$	Non-alkaline	Common	Pretreatment to bring concentration below saturation
Calcium phosphate	Ca_3PO_4	Non-alkaline	Problematic in wastewater streams	pH adjustment to 6.4 (no suitable antiscalants), pretreatment to reduce $\text{PO}_4/\text{Ca}/\text{Al}/\text{Fe}/\text{F}$, or dispersants if present as nanoparticles
Barium sulfate	BaSO_4	Non-alkaline	Rarely seen in RO scaling	Antiscalants effective
Strontium sulfate	SrSO_4	Non-alkaline	Rarely seen in RO scaling	Antiscalants effective
Silicates	$x^*(\text{SiO}_2^-)_n$	Silicate	Below neutral pH, scales as a colloid. Above neutral pH, forms silicates when metals are present.	Pretreatment to lower metal concentrations, pretreatment to remove colloidal silica, and acidification of feed water

1.1.2 Concentrate Disposal

When disposal to a very large body of water, such as the ocean, is unavailable, other means of concentrate disposal are necessary. Inland desalination plants have few options for treatment and disposal of their brine streams. One method that avoids loading of surface waters is deep well injection wherein the brine is pumped underground. This method was chosen by the EPA as the most environmentally friendly – the EPA has also set up regulations for all underground disposal wells (Clark et al. 2005; Environmental Protection Agency 2012). However, the costs of deep wells may be limiting. Zero Liquid Discharge (ZLD) and similar ideas intend to maximize recovery and reduce the volume of waste which reduces the costs and impacts of disposal (Brady et al. 2005; Fritzmann et al. 2007; Greenlee et al. 2009; Lawler and Texas Water Development Board 2010).

This study does not focus on concentrate management but it is an important component to keep in mind when considering the proposed CO₂ scaling treatment.

1.2 Scale Treatment Techniques

1.2.1 Scale Prevention

Prevention techniques typically include feed water pretreatment or addition of antiscalants to the feed water. Often, scale prevention is the preferred solution since a fouled membrane can be very difficult to clean, whether it has membrane scaling or viscous particulate fouling. However, the cost of treating the entire volume of source water can also be limiting. For brackish water sources, surface waters tend to foul more easily than groundwater and pretreatment is often performed. Additionally, if biofouling is known to be a problem, disinfection using non-chlorine oxidants can be used. One last aspect that can be evaluated is changes in operation; for example changes in flow rate have been shown to be effective in mitigating scale in some cases (Antony et al. 2011;

Greenlee et al. 2009). There are additionally many novel designs for scaling prevention; air sparging is covered below as it relates best to the proposed research. Other designs include promotion of flow vortices, such as rotating the membrane module or using helical flow spacers, and pressure pulsing, a method which has been shown to be effective in RO applications (Al-Bastaki and Abbas 2001).

1.2.1.1 Pre-treatment

Pre-treatment is a useful method when the problematic compounds can be removed and is conventionally performed with coagulation/flocculation followed by granular media filtration and/or cartridge filtration. Acid is added before coagulation to solubilize existing precipitates, which reduces the load on the pretreatment system. Feedwater acidification is only useful for some scales; calcium carbonate is easily controlled through pH adjustment but other scales, such as calcium sulfate and barium sulfate, have weaker pH dependence and therefore are not controlled as effectively with acid feeding (Rahardianto et al. 2006).

One issue with pretreatment, aside from costs, is that any additions, including chemical coagulants and antiscalants, have the potential to interact with other molecules in the source water and cause scaling problems. This is true in particular with silica since aluminosilicates can form from the alum added as a coagulant (Antony et al. 2011; Greenlee et al. 2009).

1.2.1.2 Antiscalants

Antiscalants are typically polyelectrolytes with various functional groups to target different scaling problems. They function to disrupt crystallization and may do so through several mechanisms: as a crystal modifier to produce a less adherent precipitate,

attaching to precipitates to prevent crystal growth, increasing the effective solubility limit, or acting as a chelating agent to form soluble complexes. The choice and dosage of antiscalants is highly dependant on the source water characteristics. Additionally, there are some drawbacks to antiscalant use, especially with improper dosing or feed water characterization, since antiscalants can act as foulants or enhance fouling in a number of situations (Antony et al. 2011).

The summary in Table 1 shows barium and sulfate and strontium sulfate as very responsive to antiscalants while the others have other preferred prevention methods (Antony et al. 2011). The three main categories of antiscalants include polyphosphates and phosphonates – antiscalants for prevention of metal scales such as calcium – and the more broadly applied polyphosphates. Another example of an antiscalant is the addition of ferrous iron for calcite inhibition (MacAdam and Parsons 2004). Silica is a notable exception as a prevalent scalant without suitable antiscalants due to highly variable surface characteristics under different formation conditions (Koo et al. 2001).

1.2.1.3 Operational Control

There are several methods of preventing scaling by avoiding conditions that enhance scaling. Limiting product recovery is one method that reduces scaling by reducing the solute concentration at the membrane wall. Another method alternates the location of concentrated feed water by reversing the flow through the system periodically. A third method is to perform demineralization between two stages of an RO plant with the first stage operating under limited recovery. A fourth method is to use centrifugal force to reduce concentration polarization by rotating the membrane module itself (Antony et al. 2011). Silica is an example of a scale that is mitigated through operational control;

plants with silica scaling issues aim to operate under a critical flux level (Lisitsin et al. 2005).

1.2.1.4 Air Sparging

Air sparging is touted less as a fouling prevention method and rather as a flux enhancement procedure. There are several mechanisms behind this phenomenon: disruption of the mass boundary layer or concentration polarization layer, an increase in the effective system pressure or crossflow velocity, and alteration of the cake layer in microfiltration (Cui et al. 2003). The effect of air sparging depends highly on the bubble characteristics – it was found that a bubble diameter of approximately 60% the width of the spacer channel was ideal (Willems et al. 2009). It should be noted that this is primarily done with micro- and ultrafiltration membranes where air sparging has been shown to have significant impacts. However, studies are being done to see if similar benefits are seen in nonporous nanofiltration and RO membranes. Ducom et al. (2002) performed several experiments using vertical, flat sheet, nanofiltration membrane and found mixed results for co-current air sparging based on the foulant to be prevented. Oil-in-water emulsions and solid clay suspensions, which foul by particle deposition, fouled less with air sparging; however, air sparging was not effective at increasing flux for non-scaling salt solutions where osmotic pressure is the limiting factor. It is noted that since air sparging is expected to affect the concentration polarization layer, the air sparging method may work in situations where this is the driving factor behind scale formation (Ducom et al. 2002a; Ducom et al. 2002b; Ducom and Cabassud 2003).

1.2.2 Scale Removal

Membrane plants often perform cleaning after a certain level of flux decline or pressure increase is reached. Different from other filtration systems that call for a cleaning or

backwashing protocol after a set time, RO systems can go for months and years before the flux necessitates a cleaning (Shirazi and Arroyo 2011). Guidelines for operation call for cleaning if there is a 10% reduction in permeate flow, 15% increase in pressure drop, or salt rejection by 10% within 2 days of plant start-up (Fritzmann et al. 2007).

Additionally, common flushing methods such as backwash and reverse flow are not possible due to the nonporous nature of RO membranes. For membranes fouled by inorganic scale cleaning typically consists of acidic or basic chemical solutions and sometimes both are used (Greenlee et al. 2009). Cleaning procedures depend on the specific needs for each plant and thus there is no universal protocol.

1.2.2.1 Chemical Cleaning

In established RO systems with inorganic scaling problems, cleaning is typically carried out with prepared chemical solutions, often produced by adding chemical stocks to permeate water. Fritzmann et al. (2007) looked at the instructions provided by DOW FILMTEC for chemical cleaning. A separate path for flow is used so that the chemical solutions are cycled after draining any remaining feed water/concentrate. The solution is cycled at low pressure and high flow rate, thus flushing out any foulants, and often monitored for both pH and temperature. Membranes can also be soaked in the cleaning solution for up to 15 hours. Finally, all cleaning solution is flushed before plant operation begins again.

The type of chemical and pH used depends on the foulant and degree of fouling.

Additionally, chemicals can be combined or used in series for better cleaning. Cleaners fall into several categories, including acids, bases, metal chelating agents, surfactants, enzymes, and disinfectants (Ang et al. 2006; Mohammadi et al. 2003). Some common cleaners include hydrochloric acid, phosphoric acid, sulfuric acid, sodium hydroxide, the

chelator EDTA, and the surfactant sodium-lauryl-sulphate. DOW recommends acid cleaning for inorganic salts, but recommends caustic for silica scales (Fritzmann et al. 2007).

In general, acids are able to remove inorganic scales through either hydrolysis or solubilization, while alkalines and surfactants are required to remove organic foulants. EDTA is used in experiments as a control for maximum foulant removal. Several studies observed cleaning efficiencies on RO membranes for various membrane foulants:

- A membrane fouled by a natural water source had minimal cleaning with acids, moderate cleaning with caustics, and EDTA combined with caustic and surfactants were able to fully clean the membrane (Madaeni et al. 2001).
- A membrane fouled with wastewater was best cleaned using a two-stage process beginning with surfactant and caustic followed by an acidic solution. This served to remove both organic and inorganic material from the membranes (Madaeni and Samieirad 2010).
- In cleaning a membrane fouled with sodium alginate and natural organic matter (NOM), an exploration of dosing and pH found that EDTA combined with sodium dodecyl sulfate (SDS) worked well and could be optimized through parameter control, but cleaning with NaOH was not effective and could not be optimized (Ang et al. 2006).
- Commercial membrane cleaners were used to remove silica fouling. The generic cleaner for inorganic foulant gave moderate flux regeneration, while the cleaner specifically for silica and other inorganic foulants was successful at full regeneration given sufficient dosage. It should be noted that the latter cleaner has a pH of 4 (Koo et al. 2001).

1.2.2.2 Gas Sparging

A method known as air sparging or two-phase gas-liquid flow was mentioned above as a technique used for flux enhancement, primarily in micro- and ultrafiltration membranes. The same procedures can also be used in cleaning only scenarios. Some techniques are patented, such as Airflush, where two-phase feed side flushing is used intermittently, or gas blow back, where air is forced through the membrane from the permeate side. Gas sparging has also been shown as an effective add on to conventional backwashing techniques (Cui et al. 2003).

Nanofiltration and reverse osmosis membranes cannot be backwashed like micro- and ultrafiltration membranes due to their nonporous nature. However, feed side gas sparging is possible and has been found to be useful in removing biofilms. An examination of air/water cleaning effects on a vertically oriented nanofiltration flat sheet membrane found a daily cleaning routine of less than 5 minutes was sufficient to remove biofilms, with enhanced biofouling control when used with copper sulfate as a biocide (Cornelissen et al. 2007). In micro- and ultrafiltration applications, vertical membrane orientations produced the best results, whether for hollow fiber or flat sheet membranes (Cui et al. 2003).

One very novel approach to membrane cleaning with a gas flow is the idea of forming gas bubbles at the membrane itself, thus providing shear stress at exactly the point of contact. To accomplish this, the gas must be fairly soluble in water, such as is the case for carbon dioxide. One study termed this cleaning method as CO₂ nucleation and successfully used it to remove biofilms from a low-pressure RO membrane and completely restoring the original flux (Ngene et al. 2010). This mechanism for cleaning is tested in this study to examine its use for the removal of inorganic foulants.

2. Proposal: Carbon Dioxide to Treat Scaling

Carbon dioxide is proposed as a green alternative to conventional antiscalants and chemical cleaning solutions. This study evaluates its effectiveness in removing certain inorganic scales from fouled RO membranes. With proven effectiveness, this can lead to further development of a non-toxic cleaning method and/or scale prevention method for RO membranes. If used in conjunction with underground well injection for brine disposal, adding CO₂ to the RO process could even have an added benefit of CO₂ sequestration. One goal in this study is to examine the feasibility of such a combined system.

2.1 Compatibility with RO

CO₂ does not interact much with a membrane – it will not reduce solute rejection but neither will it be rejected by the membrane. As small, uncharged particles, dissolved gases can easily permeate the membrane. A feed with dissolved CO₂ will produce permeate and concentrate with the same concentrations of CO₂ (Milstead et al. 1971). Charged carbonate ions, on the other hand, are easily rejected by the membrane, which leaves permeate with virtually no alkalinity (Crittenden et al. 2005). It is not clear how well carbonic acid permeates or is rejected by RO membranes since it is also an uncharged molecule, however, the formation of carbonic acid from CO₂ and H₂O (Equation 1) is slow relative to its ionization to HCO₃⁻ and H⁺ (Equation 2) thus it is present in relatively small concentrations – the concentration of carbonic acid at equilibrium is approximately 1/1000th the concentration of dissolved CO₂ (Butler 1991). Due to high permeation of CO₂ and high rejection of HCO₃⁻ and CO₃²⁻, the permeate will release H⁺ as H₂CO₃ dissociates to HCO₃⁻ to move towards equilibrium. Thus, the

separation process has a large impact on the final pH. A diagram of carbonate speciation is provided for reference (Figure 1).

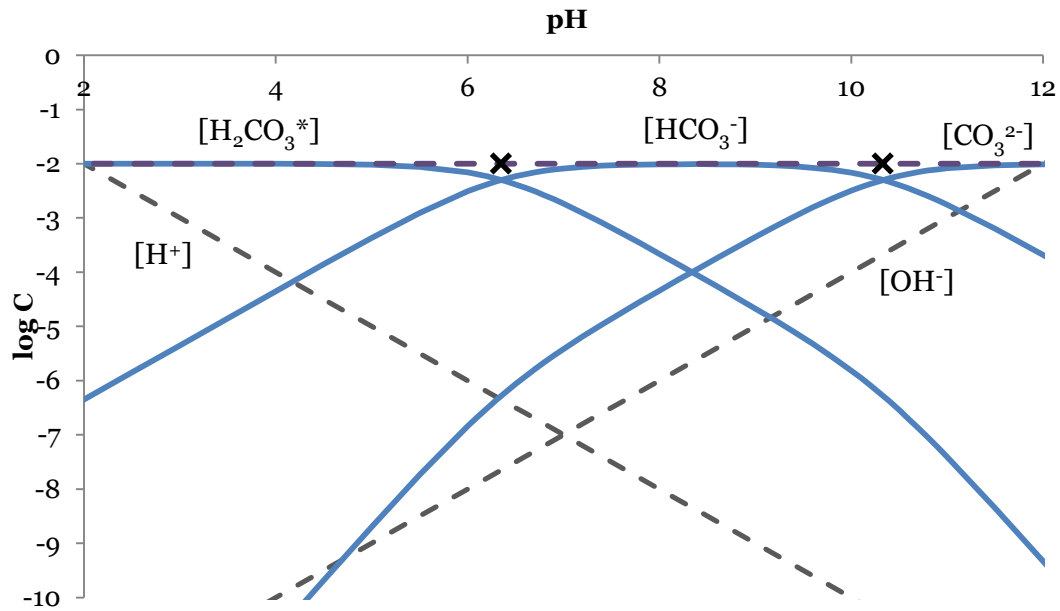


Figure 1: LogC-pH diagram of carbonate chemistry. In this example, the total carbonate concentration is 0.01 M. System points for pKa = 6.35 and pKa = 10.33 are shown as X's.

Many groundwaters have high concentrations of CO₂ – groundwater in Israel has reported concentrations up to 100 mg/L of CO₂ due to a high level of total carbonate species (Oren et al. 2012). The amount of gas in the feed water directly affects the permeate quality due to carbonate equilibration. Some plants may choose to degas or deaerate their feed during pre-treatment using an air-stripping tower. Plants can also degas during post-treatment, since dissolved gas does not affect membrane performance. Post-treatment is required to reintroduce minerals for taste and alkalinity for pH control; brackish feed can be added to the permeate for this purpose with caustic soda

added to raise the pH (Greenlee et al. 2009). Post-treatment that involves degassing includes stripping of excess CO₂, which can cause corrosion, and raising the pH to drinking water standards (United States. Dept. of the Army 1986). Oppositely, some systems add CO₂ during post-treatment in order to achieve recarbonation and/or remineralization through added unit processes such as lime contactors (Withers 2005). In a novel approach, one study achieved post-treatment CO₂ dosing through feed acidification to drive carbonate species to become dissolved gas (Oren et al. 2012).

2.1.1 Saturated CO₂ Solution

In contrast to naturally present carbon dioxide, artificially introducing high concentrations of CO₂ will result in chemical changes to the solution, such as decreased pH. Part of the effectiveness of RO membranes comes from charged interactions that hinder the transport of ions while having no impact on uncharged molecules. Changes in pH alters the surface charge of the membrane which can affect the level of rejection achieved (Childress and Elimelech 1996). For composite polyamide membranes, the rejection stays constant through a broad pH range, however a pH above 8.5 or a pH near the membranes isoelectric point (often around 4-5) can cause a decline in rejection (Cadotte et al. 1980). The pH of a solution can also affect RO performance by changing the chemical composition of the feedwater; a study on defluoridation using RO found a marked decrease in rejection below a pH of 6.5 attributed to the formation of hydrofluoric acid which has a higher solubility in the membrane (Arora et al. 2004).

2.2 Other Considerations

2.2.1 Carbon Sequestration through Deep Well Injection

Where surface water brine disposal is unavailable, deep well injection is an alternative given to options such as evaporation ponds, infiltration basins, and irrigation and it has the environmental benefit of not increasing the salt load of surface waters (Clark et al. 2005; Skehan and Kwiatkowski 2000). About 10% of RO plants in the U.S. use deep wells for disposal, primarily in the state of Florida (Crittenden et al. 2005).

Deep well injection is also used for a variety of other purposes, such as industrial and municipal waste streams and for wastes in the oil and gas industry, and is regulated by the EPA. A new well classification is emerging for long term geological storage of carbon, albeit typically for injection of CO₂ in its supercritical phase (Brady et al. 2005; Environmental Protection Agency 2012). It is conceivable that disposal of CO₂-saturated brine in underground geological formations could have the benefit of carbon sequestration. Experimental results indicate that CO₂ in water may be more stable than CO₂ injected in a supercritical form, though may also cause unintended issues such as rock dissolution or plugging of the rock formation (Canal et al. 2012; Saripalli et al. 2000). A potential configuration for RO combined with CO₂ sequestration is sketched in Figure 2.

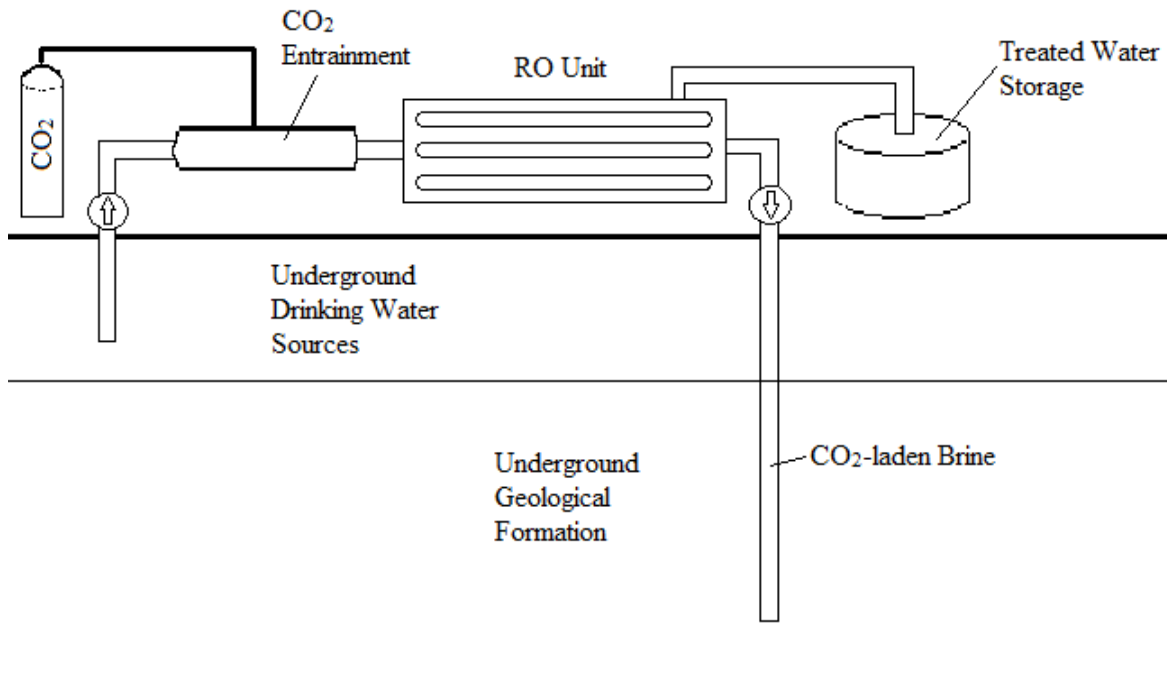


Figure 2: Sketch of a possible configuration for a brackish groundwater reverse osmosis unit with CO₂-entrained feedwater.

2.3 Bench-scale Work

Fundamental examination of dissolved CO₂ in an RO system provides information regarding the feasibility and/or practicality of this application. To determine efficacy, a solution of CO₂ dissolved in water is characterized and used to clean RO membranes scaled with various inorganic foulants. Comparison of flux recovery with other cleaning methods allows for an evaluation of dissolved CO₂ as well as a determination of the cleaning mechanism. The work is divided into two objectives.

Objective 1. Develop methods for bench-scale carbonation and testing of dissolved CO₂ solutions. Characterize differences between concentrate and permeate flows including visual differences and impacts on flux and rejection.

Objective 2. Develop a method for bench-scale membrane scaling. Determine flux recovery after cleaning scaled membranes with dissolved CO₂. Compare with flux recoveries achieved through other cleaning methods.

Hypothesis. If flux is recovered after cleaning with dissolved CO₂, this method is an effective cleaning regime. Differing levels of scale removal for various scale types indicate mechanistic differences in cleaning. Comparison of dissolved CO₂ cleaning to other cleaning methods narrows in on the cleaning mechanism.

3. Materials and Methods

3.1 Bench-Scale Apparatus

The bench-scale test setup (Figure 3) was adapted from a system used previously (Ladner et al. 2010). A plunger pump cycled water through a GE Osmonics SEPA II membrane cell which held the RO membrane coupon. The membrane cell was clamped with 1200 psi of pressure using a hydraulic hand pump before beginning RO operation. The concentrate flow from the membrane cell was diverted either to the feed tank during for recycle or to waste. Permeate flow passed through a flow buffer cell for a conductivity reading and then dispensed to a beaker on top of a balance for continuous mass readings. Not shown in Figure 3 are various temperature control methods for preventing the water from heating up over time including a coiled section of concentrate line tubing that passes through water from a cooling tank and a fan for convective cooling of the pump.

A vertically installed cylindrical pressure vessel was outfitted with ball valves for optional flow patterns: bypassing the vessel (valve 3 open, all others closed), only into the vessel (valve 1 open, all others closed), only out of the vessel (valve 4 open, all others closed), or through the vessel (valves 1 and 4 open, all others closed). Gas was filled into the pressure vessel through valve 2. The port for valve 4 is located in the endcap of the pressure vessel, the port for valve 1 is located 4 inches above the bottom, and the port for gas through valve 2 is located 12 inches above the bottom.

A LabView program provided an interface for both manual and automated control of the pump speed and valve actuator. Control of the actuator served as system pressure control through control of a needle valve situated after the membrane cell. Adjusting the

voltage sent to the actuator would adjust the needle valve opening and thus the pressure of the system between the pump and the needle valve.

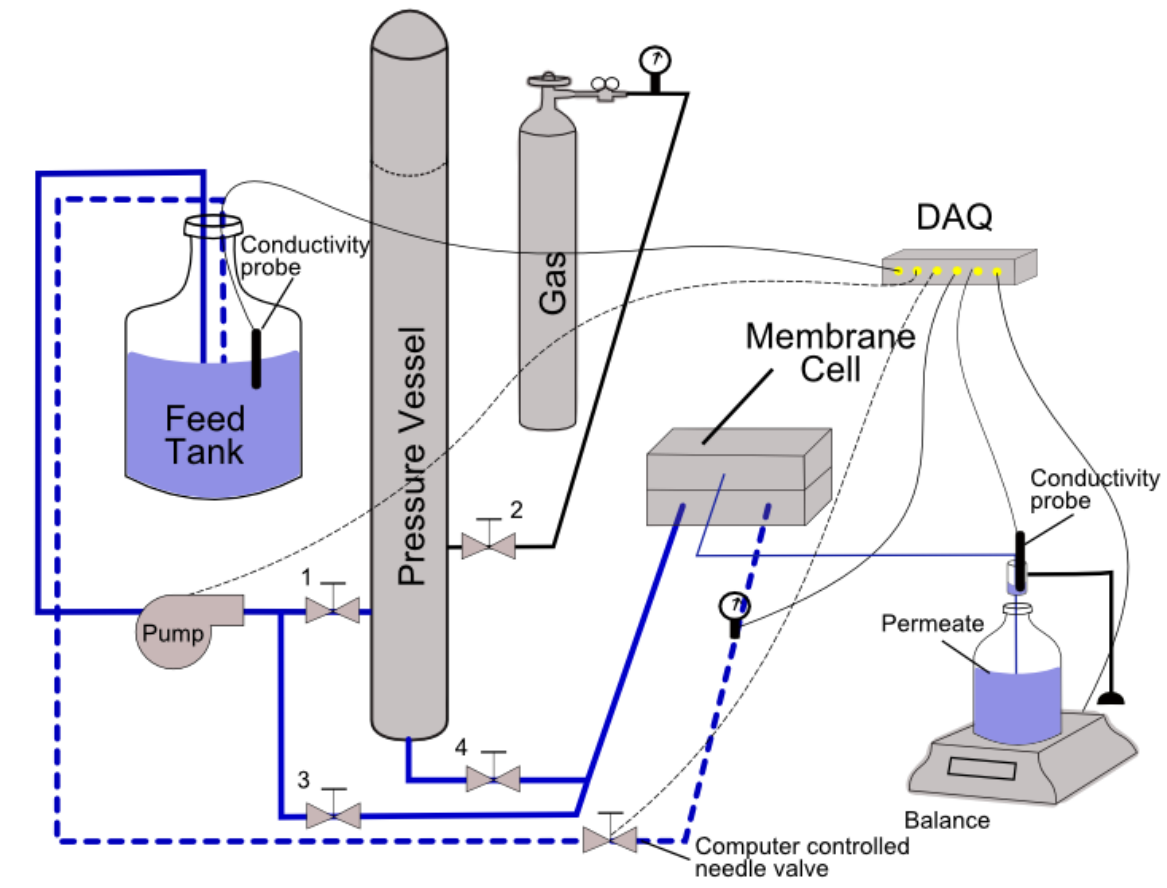


Figure 3: Left-to-right fluid flow in bench-scale apparatus. A series of valves allows for flow either through the pressure vessel or directly to the membrane. From the membrane, flows split into permeate (thin blue line) and concentrate (dotted blue line). The concentrate is returned to the feed tank for continuous operation. In total recycle mode, the permeate is manually returned to the feed tank to maintain feed concentration. Dashed lines from DAQ represent computer control of pump speed and needle valve opening; solid lines represent data input to DAQ from conductivity probes and balance.

3.1.1 RO Membrane

A CPA2 Hydranautics brackish water membrane was used. The CPA2 membrane has the following characteristics: composite polyamide membrane material, pH range 2-10, 45°C maximum temperature, and 600 psig maximum pressure. Membrane coupons were cut from a larger membrane sample and maintained in a refrigerator in an aqueous solution of 0.02% sodium azide. Baseline tests performed on this membrane produced the results in Figure 4. The cross-flow velocity was kept a constant 800 mL/min and the pressure was controlled by the actuator-driven needle valve.

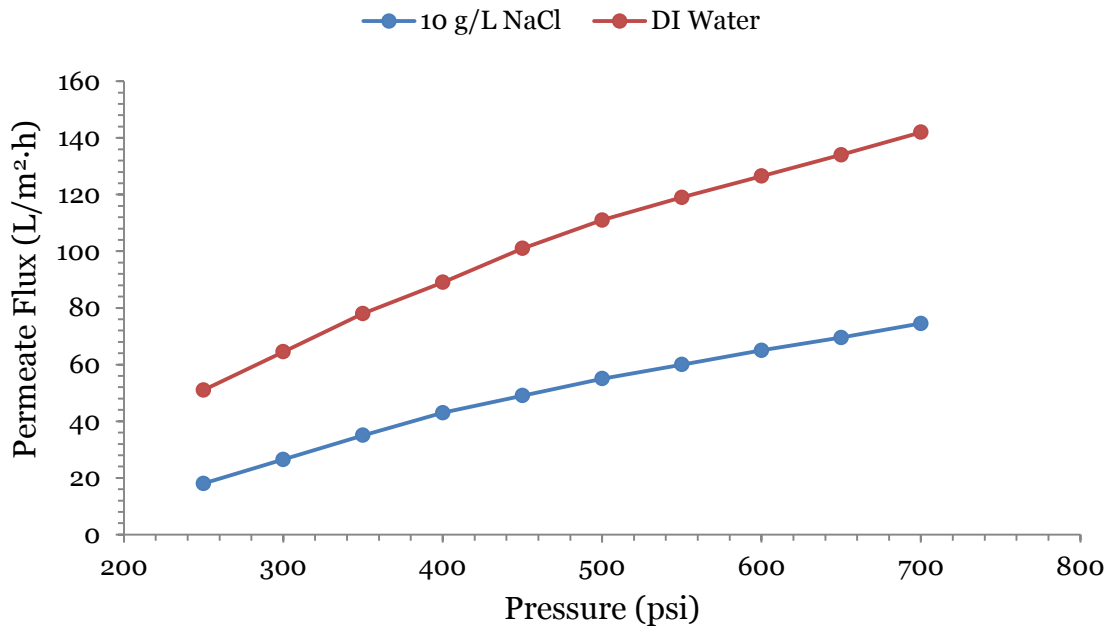


Figure 4: Flux measurements as a function of pressure for distilled (DI) water and 10 g/L NaCl through the CPA2 membrane. A constant cross-flow velocity of 800 mL/min was used.

3.2 Analytical Methods

3.2.1 RO System Monitoring

A LabView program was used to monitor data continuously and convert mass readings into flux readings. The DAQ collected data for from the permeate balance, pressure

gauge, and two conductivity probes – one to measure feed concentration and one for permeate concentration. A LabView interface was used to graphically monitor system parameters including pressure, permeate and feed conductivity, permeate flux, and rejection. Measurement of permeate mass, m_w , every 100 seconds (the timestep Δt), along with a known membrane area, A_m , was used for calculation of permeate flux, J (Equation 3). The density of water, ρ_w , is used to convert to standard units of L/m²·h. The ratio of permeate conductivity, K_p , to feed conductivity, K_f , was used to calculate rejection, R (Equation 4).

$$J = \frac{\frac{\Delta m_w}{\rho_w}}{A_m \Delta t} \quad (3)$$

$$R = \left(1 - \frac{K_p}{K_f}\right) \cdot 100\% \quad (4)$$

To obtain accurate rejection readings, a background ionic content of 10 g/L NaCl was used in all runs. This is due to the very low concentrations of salts used to form scales which are below detection by the conductivity probes. With 10 g/L NaCl, the initial conductivity was 18 mS/cm and increased over time with the concentrating solution to around 30 mS/cm. The permeate conductivity increased from an initial 0.6 mS/cm to around 1.2 mS/cm.

3.2.2 Water Measurements

Measurements were taken of feed solutions and cleaning solutions both after preparation and during operation. pH measurements were taken using an Orion pH meter with a waterproof Ag/AgCl pH electrode (Thermo Scientific Orion, 9157BNMD). Alkalinity was measured by titration with 0.02 N H₂SO₄ using the indicator bromocresol for total alkalinity measurement. The feed solutions were checked for analytical composition

before application to ensure it matched the target characteristics. The cleaning solutions were monitored during operation and the solutions amended with additional acid/base stock if pH values increased more than a few tenths of a pH point.

3.2.3 Carbon Dioxide Quantification

In the carbonated soft drink industry, filled cans are tested for carbonation by capturing escaped gases upon piercing. First, the container is pierced without agitation to release excess gas in the headspace. Then, the container is connected to a gas regulator and shaken to release all dissolved gas. The volume of captured gas is compared to the volume of the sample to determine the degree of entrainment (Steen and Ashurst 2006).

A measurement method following similar principles was used here. During operation of the bench-scale apparatus, all lines exiting the membrane are returned to atmospheric pressure. Thus CO₂ will tend to leave solution. Measurements of the gas that leaves solution were made by taking enclosed samples in capped syringes from the permeate line. The syringe was attached to the permeate line to capture both gas and water, and the syringe plunger was pushed back by the flow of gas from the membrane cell. The total volume was read from the markings on the syringe, and the mass of water weighed on a microbalance. The volume of gas was calculated as the difference between the volume of water, found using the density of water, and the total volume. This gives a measurement of the volumes of CO₂ dissolved and is a good real time representation of changes in concentration between samples taken from the same point in the system. Measurement of the concentrate line could not be performed in real time due to the higher flow rate and more turbulent depressurization. Instead, characterization of CO₂ concentration in the concentrate line was done in a separate run. Water and gas from the concentrate line were diverted into a filled beaker inverted in a tub of water. The

displaced water equaled the volume of gas present and the increase in water equaled the corresponding volume of water. These two methods – capped syringe samples and inverted filled beakers - allowed for measurement of the amount of CO₂ that was either dissolved or entrained.

3.3 Objective 1 – CO₂ Entrainment

To use CO₂ for cleaning, it was first necessary to develop a method for achieving a high degree of CO₂ entrainment within the context of a reverse osmosis system.

3.3.1 Method 1 – Gas Phase Entrainment

The pressure vessel in the RO setup served as a holding tank for water under a CO₂ headspace. When water is passed through the vessel, it entered at a side port and exited through the bottom port. A third port, above the water entry, was connected to a gas cylinder and used for pressurization.

Solubility and Diffusivity

Transport of CO₂ from a headspace into a liquid is determined by its solubility and diffusivity within that liquid. At the interface, the concentration of CO₂ is governed by the solubility and can be calculated using Henry's Law. Equation 5 shows Henry's Law for dissolved CO₂ in water expressed in molar units and CO₂ gas expressed in atmospheres.

$$[CO_2] = k_H P_{CO_2} = \left(0.033 \frac{mol}{L \cdot atm}\right) P_{CO_2} \quad (5)$$

The Henry's Law coefficient, k_H , is equal to 0.033 for standard conditions, but the coefficient will vary with pressure, temperature, and pH. Additionally, this coefficient is only valid for dilute solutions. To check whether the brackish solutions used significantly change CO₂ solubility, an empirical correlation is used to calculate solubility based on the amount of dissolved ions. The correlation (Equation 6) uses total dissolved solids (TDS) on a weight basis as the correlating parameter to find the solubility in brine, w_{brine} , based on the solubility in pure water, w_{pure} (Enick and Klara 1990).

$$w_{brine} = w_{pure} (1.0 - 4.89 * 10^{-2}(TDS) + 0.13 * 10^{-2}(TDS)^2 - 0.19 * 10^{-4}(TDS)^3) \quad (6)$$

In Table 2, CO₂ solubility coefficients are calculated using this correlation for three solutions of interest – distilled (DI) water, typical brackish water concentration of 10 g/L, and typical seawater concentration of 35 g/L. A temperature of 25 °C was used. As evident in Table 2, at the pressures and concentrations of interest for RO desalination, deviation from the standard coefficient is negligible. 10 g/L represents the TDS in a typical brackish water while 35 g/L represents a typical seawater concentration. Pressures up to 1000 psi are used for seawater desalination, but for brackish water, pressures below 600 psi are used.

Table 2: Solubility of CO₂ in three solutions calculated as a function of TDS at 25 °C using a correlation by Enick and Klara (1990). Calculations made from 0-900 psi since these are in the range relevant to reverse osmosis operation.

Pressure (psig)	C _{eq} (mol/L)		
	0 g/L	10 g/L	35 g/L
0	0.033	0.033	0.033
100	0.258	0.257	0.257
200	0.482	0.482	0.481
300	0.707	0.706	0.705
400	0.931	0.931	0.930
500	1.156	1.155	1.154
600	1.380	1.380	1.378
700	1.605	1.604	1.602
800	1.830	1.829	1.826
900	2.054	2.053	2.051

Another consideration is the role of CO₂ in the carbonate system. Due to the formation and ionization of H₂CO₃, the standard form of Henry's law is not always applicable. Expansion on the Krichevsky-Kasarnovsky equation observes non-linear solubility relationships with high CO₂ mole fractions at high temperatures and pressures; fortunately, RO operating temperatures are maximally around 45 °C, where the relationship between pressure and solubility is sufficiently linear (Carroll and Mather 1992).

Beyond the gas-liquid interface, movement of CO₂ is dictated by its diffusivity in the solution. CO₂ has a diffusivity of 1600 μm²/s. Figure 5 was generated using unsteady state penetration theory to model the penetration depth of CO₂ in pure water over time. Equation 7 shows the equation of change for unsteady diffusion in one dimension (Bird et al. 2007). The concentration C at depth x and time t is predicted by the Gaussian error function of the depth over the diffusion length, where D_a is the diffusivity. The model shows that diffusion alone is a very slow process since transport of CO₂ has only reached

4 cm past the gas-water interface after 24 hours. The penetration depth depends only on time and not on the interface concentration – with a different interface concentration the amplitude of the curve changes but not its shape. Therefore, regardless of the pressure of CO₂ in the pressure vessel headspace, completely non-agitated diffusion will not produce a significant level of entrainment.

$$C(x, t) = C_{int} \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right) \quad (7)$$

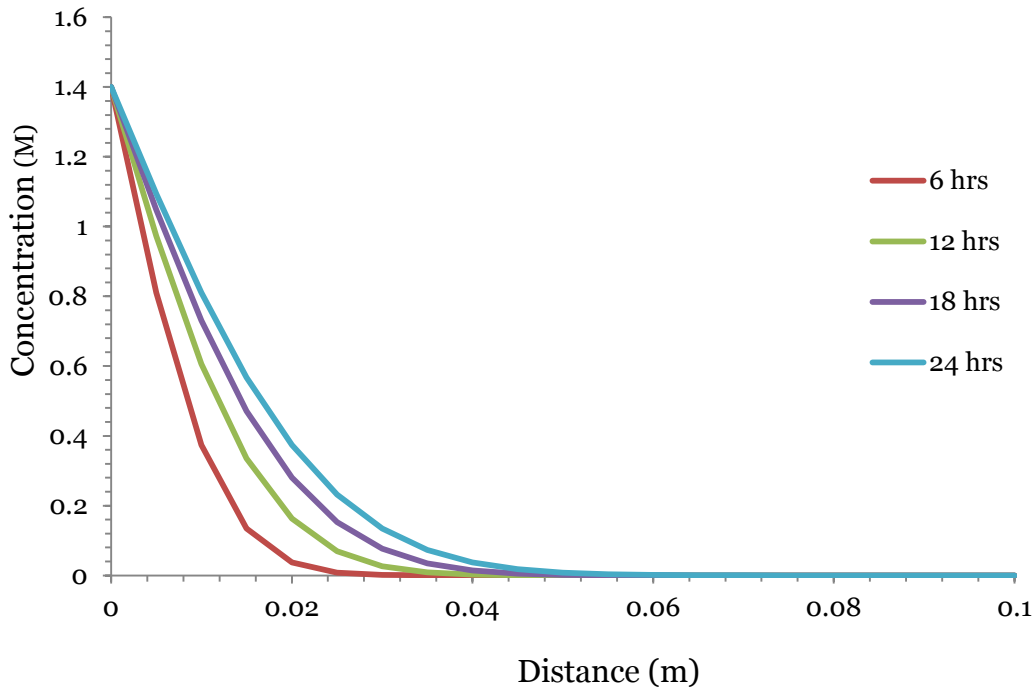


Figure 5: Diffusion distance into pure water with a pure CO₂-filled headspace at a pressure of 600 psi. With 24 hours to equilibrate, the carbon dioxide has only diffused 4 cm below the surface.

Agitated Entrainment

Typical agitated entrainment methods at an industrial level include spraying water into the headspace or mixing with paddles or similar mixers (Wheeler 1973). One bench scale study dissolved CO₂ by first micronizing the CO₂ at a pressure of 0.5 MPa before

pressurizing the headspace to 4 MPa (~580 psi), but one week was still required to ensure saturation (Canal et al. 2012).

A common method used in soda production is inline carbonation. This process applies pressurized CO₂, often around 100 psi to produce around 40 psi in the finished product, to a flowing fluid line, often through a diffusing stone or membrane (Steen and Ashurst 2006). This method of entrainment is likely to be very effective, but was discarded due to the high price of inline carbonators. A similar method used in laboratories for introduction of gasses is through a sparge. Since a gas sparge could not be easily introduced to the pressurized system, it was mimicked by very slightly opening the valve from the pressurized gas line to bubble gas into a column of water.

3.3.2 Method 2 – Artificial Generation

Carbon dioxide can be generated through chemical reactions as well. One study succeeded in saturating the feedwater by first adding a carbonate species and then adjusting the pH through the addition of acid to shift the dominant species to H₂CO₃ (Oren et al. 2012). While this method is effective for increasing the concentration of CO₂ in the feedwater, it undermines the benefits of this coupling – acidification without toxic chemicals and utilization of waste CO₂ gas for possible sequestration. However, it may be a sufficient method of CO₂ entrainment for experimental purposes in lieu of an apparatus for pressurized carbonation.

3.3.3 Method Development

Both carbonation methods were tested for application to the pressure vessel system and in both continuous and batch modes. First, non-agitated dissolution was tested in a continuous mode. This was done by circulating water through the pressure vessel to the

membrane while the pressure vessel on average contained 4 liters of water so that flow through the vessel caused minimal agitation in the water column. Samples taken from the permeate line showed a volumetric gas to liquid ratio, or volumes of CO₂, of approximately 0.07. Samples from the concentrate line had even less measured gas, though it is expected that not all of the gas left solution at that point. Next, a test was performed with agitated dissolution using only 1 liter of water in the pressure vessel so that flowing water would cause a high level of mixing at the gas-water interface. Samples taken from the permeate line in this experiment had a final measurement of 0.14 volumes of CO₂ after almost 8 hours of operation. Figure 6 presents data collected from the continuous entrainment experiments. The initial concentrations measured in the non-agitated experiment are higher than the agitated experiment as expected since gas passed through the water column when filling the pressure vessel during the non-agitated experiment. In the agitated case, the water line is below the gas port and did not receive any effects from bubbling.

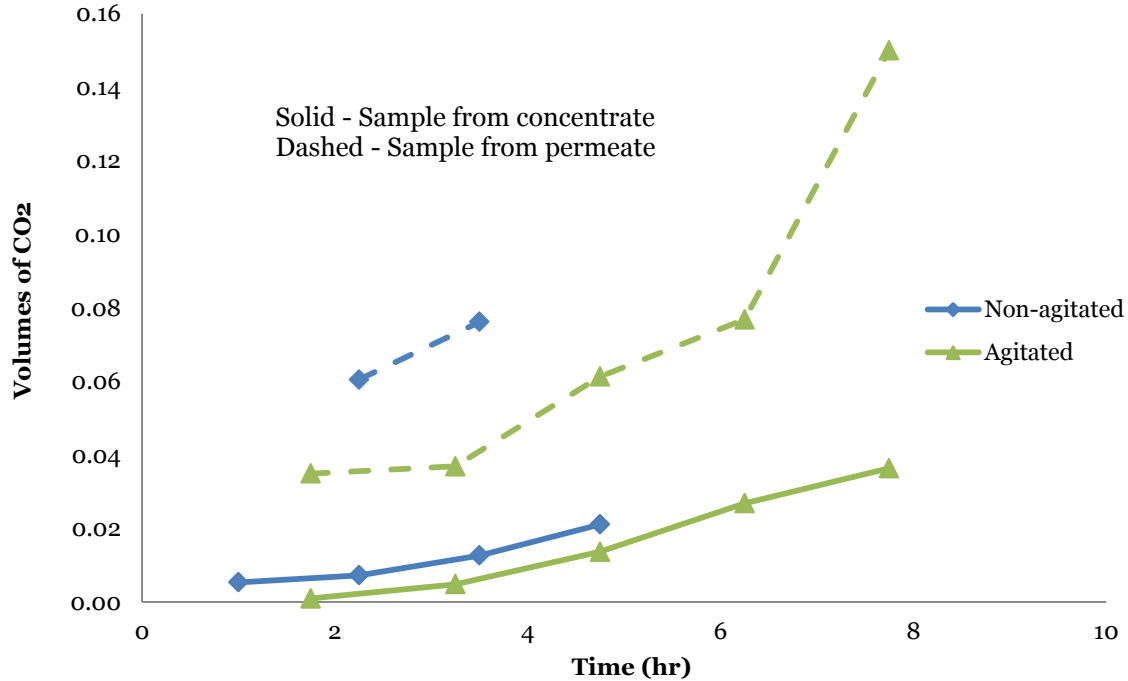


Figure 6: Continuous CO₂ entrainment using pure CO₂ headspace in the pressure vessel. Non-agitated entrainment started with 4 liters in the pressure vessel; agitated entrainment started with 1 liter. Concentration increases with continued flow but overall entrainment is low.

However, both of these experiments demonstrated a flaw. Despite the low levels of dissolution observed, the continuous operation meant that water with excess CO₂ was passing through the pump which caused gas to be released from solution. Over time, the gas accumulated to the point where the entire feed line was filled with gas. Additionally, the gas released caused the pump to perform poorly and required some amount of effort for the gas to be removed. This phenomenon was confirmed with a third test in which commercially available seltzer water was used as feed to examine the effect of the system on the retention of CO₂ in solution. In a matter of minutes after beginning pump operation, the feed line filled with gas and the pump displayed erratic behavior. A similar result occurred with artificial generation of CO₂ using a pH-adjusted sodium bicarbonate solution to release CO₂, thus negating the feasibility of Method 2. The system was not

able to handle continuous flow with excess dissolved gas due to depressurization to atmospheric pressure in the feed tank and turbulence within the pump. It is possible that by using a pump that can withstand high pressures, the system can be unbroken in terms of pressurization and continuous operation would be possible. However, for the purpose of this study, only batch operations, and thus cleaning of scale instead of scale prevention, could be examined.

Further testing was conducted to determine the extent of dissolution possible in batch operation. Based on the theoretical rate of diffusion through the water column (see Figure 5), it was concluded that relying on the headspace for entrainment was not an option. A batch test was performed using only the pressure vessel. After filling the pressure vessel with 4.5 liters of water, CO₂ was leaked in slowly to fill the vessel to 500 psi. Gas was collected upon release of water from the pressure vessel by directing the outflow from the pressure vessel into a 4 L container filled with water that was inverted in a basin filled with water. The difference in total water volume after the beaker was fully filled with gas was measured and the gas to volume ratio calculated by dividing 4 L of gas by the measured water volume. An estimated 12 volumes of CO₂ were dissolved in the batch experiment. Thus, bubbling is effective at initial entrainment, but its effects cannot be observed in continuous operation.

3.3.4 Selected Method

The method of entrainment to be used in this study is bubbling CO₂ into a pressure vessel pre-filled with water. A water volume between half to three-quarters of the total capacity is optimal to avoid rapid pressurization – a volume of 7.5 liters was chosen. Bubbling is achieved by slowly leaking CO₂ into the pressure vessel until the headspace reaches the target pressure of 500 psi. This is similar to the use of air spargers for

increasing dissolved oxygen. After reaching 500 psi, the valve between the pressure vessel and the line to the gas cylinder is closed to ensure no leakage of gas into or out of the pressure vessel; remaining CO₂ in the gas line is released through the needle valve for safety reasons before operating the RO system.

3.4 Objective 2 – CO₂ for Scale Removal

CO₂ permeation through pressure-driven membranes is little studied. According to the results of Milstead (1971), it is expected that CO₂ will pass easily through the membrane and thus the concentrations will not be affected by membrane filtration. The goal is to determine whether passing CO₂-laden water through the system is effective at removing various types of inorganic scale and if so, whether the effect is in some way different from conventional cleaning regimes.

3.4.1 Scaling Solutions

The feed water is designed to mimic brackish groundwater as this source of drinking water commonly encounters scaling issues. Brackish water is that with a total dissolved solids content between 1000 and 10,000 mg/L. For this study, a background concentration of 10 g/L NaCl is used to generate brackish TDS since sodium and chloride will not react with other components to form sparingly soluble salts that could contribute to membrane fouling.

Experimental solutions were generated from laboratory grade reagents to create scaling conditions for select scales. The scales of interest are calcium and silica based scales – common scales formed in groundwater treatment. Particular attention is paid to silica scales since these are not effectively treated with known antiscalants but rather can be treated with acidification (Antony et al. 2011). Calcium scales are very common but

typically manageable. For this study, calcium carbonate scale is chosen to represent common alkaline scale and calcium silicates are used for silica scales. Reagents were laboratory grade calcium chloride dihydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (EMD Chemicals), anhydrous sodium carbonate, Na_2CO_3 (VWR), and sodium meta-silicate 9 hydrate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (J. T. Baker). Each solution contained only the components for a particular chosen scale, in addition to background sodium chloride (VWR), and was not meant to represent real groundwaters but rather serve to heavily scale the membrane within several hours.

Recipes were determined based on the visual observance of precipitation. Reagents were added to 10 g/L NaCl dissolved in 1 L of DI water in 3.5 mL increments. After each addition, the solution was stirred and observed for precipitate formation. The final recipe was chosen as the total reagent added before precipitates were observed. The recipe was further refined after a full scale trial which determined if the solution could be concentrated over the course the scaling experiment without crossing the saturation threshold. If precipitates were observed, the concentration of scale forming elements was reduced.

Solutions were prepared in four liter batches from stock solutions of each scaling reagent at 15 g/L. Thus, to generate a CaCO_3 scaling solution, after adding 40 g of NaCl to 4 L of DI water, 45 mL each of CaCl_2 stock and Na_2CO_3 stock was added and the pH checked. To prepare silicate scaling solution, 40 g of NaCl was added to 3 L of DI water. Then 160 mL of Na_2SiO_3 stock was added and the pH checked. Using 0.1 M HCl, the pH was lowered to 8 in acid dose increments of 50 mL, checking the pH after each addition and adding approximately 400 mL in total. Lastly, 100 mL of CaCl_2 stock was added and the pH checked. The volumes and masses of reagents added in each recipe are summarized in Table 3.

Table 3: Recipes for calcium carbonate and calcium silicate scaling solutions in terms of prepared reagent stock solutions.

Reagent	Calcium Carbonate Solution	Calcium Silicate Solution
NaCl, crystals	40 g	40 g
15 g/L CaCl ₂	45 mL	100 mL
15 g/L Na ₂ CO ₃	45 mL	--
15 g/L Na ₂ SiO ₃	--	160 mL
0.1 M HCl	--	400 mL

The final recipes in molar units are found in Table 4. CaCO₃ scaling solution was comprised of CaCl₂ and Na₂CO₃ at 2 mM, or 170 mg/L each, with no pH adjustment (final pH around 10). Silicate scaling solution was comprised of Na₂SiO₃ at 5 mM, or 600 mg/L, with CaCl₂ at 3.5 mM, or 375 mg/L, with addition of HCl to reduce pH from 12 to approximately 8 which required approximately 10 mM of HCl. For comparison, a study on silica scaling used a fouling recipe containing 250 mg/L SiO₂, 750 mg/L Ca²⁺ and 500 mg/L Mg²⁺ (Koo et al. 2001).

3.4.2 Cleaning Solutions

To understand the mechanism by which dissolved CO₂ in water is able to clean scaled membranes, several other cleaning runs were performed, including low pH cleaning solutions, dissolved nitrogen gas, and DI water. A pH 3 HCl solution was used to approximate solutions used for membrane cleaning in industry. Preliminary trials of preparing a dissolved CO₂ solution showed a resulting pH around 4.5. Thus, trials with a pH 4 HCl cleaning solution were used to examine pH effect contributions to CO₂ cleaning. The nitrogen gas trial performed the opposite control, looking at gas effects with no pH changes. A third combination, lowering the pH of the dissolved N₂ solution isolated effects due to carbonate chemistry. For silicate scale, there is no known cleaning procedure to remove most of the scale; both acidic and basic solutions have shown to be

somewhat effective. CO₂ cleaning of silicates was compared to low pH cleaning at pH 3 and high pH cleaning at pH 12 combined with sodium dodecyl sulfate, C₁₂H₂₅NaO₄S (Sigma-Aldrich), as a surfactant. The cleaning regimes applied to each scale type are summarized in Table 4. Cleaning solutions were prepared in eight liter batches to minimize pH changes due to dissolution of scale within the membrane system over the duration of the cleaning cycle.

Table 4: Matrix of feed solutions and cleaning regimes used for scaling experiments. Each solution has a background ion content of 10 g/L NaCl. CO₂ and N₂ cleanings use the gas cleaning procedure; all other cleanings use the chemical cleaning procedure.

Purpose	Feed Solution					Cleaning Procedures
	NaCl	Na ₂ CO ₃	CaCl ₂	Na ₂ SiO ₃	HCl	
DI Control NaCl control	10 g/L					none
CaCO ₃	10 g/L	2 mM	2 mM			CO ₂ , pH 3, pH 4, N ₂ , N ₂ /acid, DI
Silicates	10 g/L		3.5 mM	5 mM	10 mM	CO ₂ , pH 3, pH 12 + SDS, DI

3.4.3 Scaling Procedure

A pressure of 500 psi, applicable for CPA2 membrane, and a crossflow velocity of 800 mL/min was used for all flux experiments. A new membrane coupon, obtained from a set of wet-stored cut coupons, was used for each scaling run. Before each membrane installation, the new coupon and membrane cell components were rinsed in distilled water. With the membrane cell connected, the system was flushed to remove all stagnant water and replaced with fresh DI water. Then, the system was pressurized to 500 psi and DI circulated for one hour to compact the membrane. The first 10-15 minutes typically had significant flux decline on the order of 10-15 lmh due to membrane compaction and slight decline on the order of 5 lmh over the remaining time period. Compaction at this

low rate of flux decline is expected to continue over the duration that the membrane is in use; therefore, a standard one hour compaction period before beginning membrane scaling was applied to each membrane.

After membrane compaction, a salt only flux decline experiment was performed on a few membranes to determine a profile for flux decline due to a concentrating salt solution that did not cause membrane scale. As expected by membrane theory, this flux declined linearly with increased concentration. The transport of water through the membrane is governed by the difference between the applied transmembrane pressure, ΔP , and the transmembrane osmotic pressure, $\Delta\pi_m$ (Equation 8). Multiplying by the membrane area, A_w , gives the permeate flux, J_w .

$$J_w = A_w(\Delta P - \Delta\pi_m) \quad (8)$$

To scale the membranes, the feed was switched to a prepared solution. Measurements of pH, alkalinity, and conductivity on the scaling solution were taken before each scaling run. To expedite scaling, scaling runs were operated in recycle to allow concentration of the feed and increase the propensity of scale formation. Osmotic pressure increases with an increased salt concentration, but no change was made in the applied pressure, thus the water flux driving force must decrease with increasing feed concentration. Figure 7 shows how a scaling solution is observed through flux decline as a function of feed conductivity due to the concentrating effect of recycling. Since the salt does not form scales, flux declines linearly with the concentrating feed. The scale causes additional flux decline over that expected from the increased osmotic pressure.

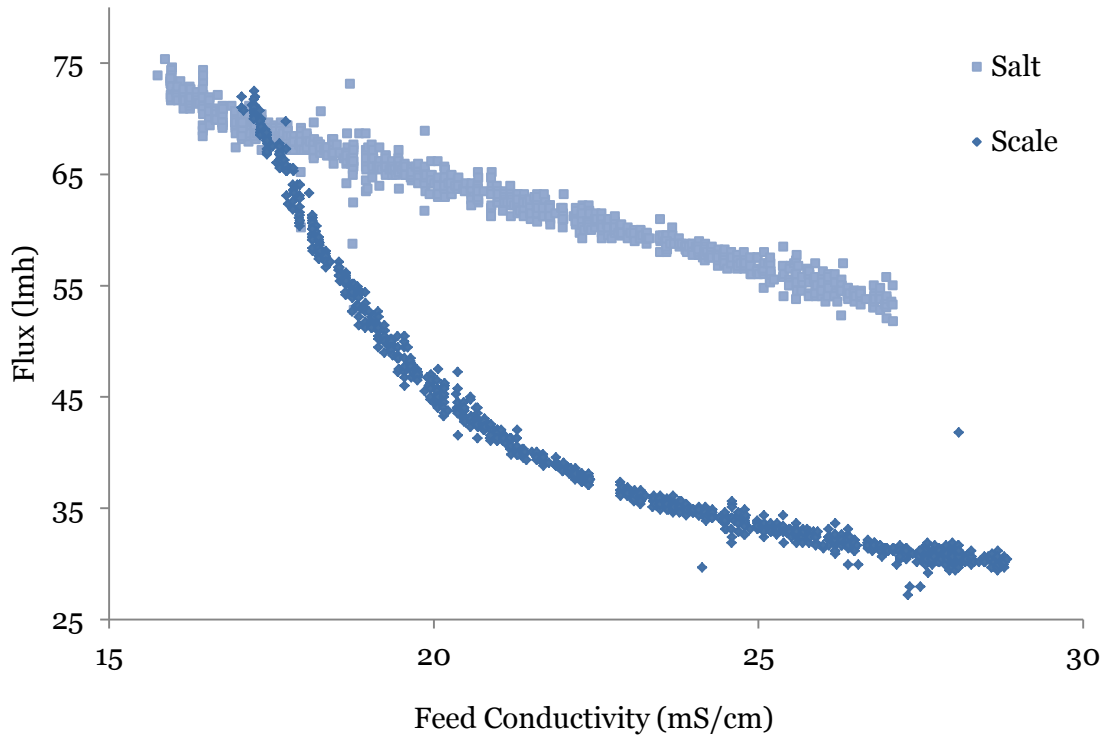


Figure 7: Examples of flux decline due to a salt solution, which is only a function of concentration, and due to a scaling solution, which is a result of particle build-up on the membrane. Both solutions had 10 g/L NaCl and were allowed to concentrate by recycling.

The feed solution was visually monitored over the course of each experiment to ensure that no precipitates had formed, which would have caused flux decline due to cake formation of colloids and not due to scaling as a result of crystal formation at the membrane surface. If precipitates formed, the experiment was restarted with a fresh membrane and feed solution. Flux was monitored to confirm additional flux decline over the expected amount due to the concentrating background salt.

3.4.4 Cleaning Procedure

Dissolved Gas Cleaning

To generate a dissolved gas solution, the pressure vessel was first filled with DI water – 7.5 liters filled into the 9.7 L space. For pH-adjusted N₂ cleaning, the pressure vessel was filled with water acidified with HCl instead of DI water. Then gas from a gas cylinder, either CO₂ or N₂, was released through a slightly opened ball valve to slowly pass through the water column and fill the headspace, thus acting like a sparge. The headspace was filled to 500 psi with approximately 0.5 moles of gas. After reaching the target pressure, cleaning was performed by releasing the held water through the membrane cell. Since the pump was not used for cleaning, the water was only propelled through the system under pressure from the headspace; the final pressure in the vessel after all water had left was 180 psi. The majority of the water was diverted to a waste tank; only 50-100 mL passed to the permeate side of the membrane.

Samples were taken from the concentrate and permeate and measured for pH and alkalinity. For CO₂ trials, three samples from the permeate were taken to measure the volumes of gas dissolved; samples were taken when the pressure vessel headspace was at 400 psi, 300 psi, and 200 psi. No gas was observed in the permeate during N₂ trials.

After the pressure vessel was emptied of water, the remaining gas in the pressure vessel was vented through the bottom port, thus did not pass the membrane cell. The vessel had to be emptied before the membrane system could be operated in circulation again in order to prevent accidental pressure build-up in the pressure vessel due to water leaking through the valves. A clean water flux was performed immediately after cleaning to determine the extent of flux recovery.

Chemical Cleaning

Trials without dissolved gas did not utilize the pressure vessel. The procedure for chemical cleaning is based on industry convention for membrane cleaning, which circulates a cleaning solution through the RO system without added pressure (Fritzmann et al. 2007). For this study, a circulation time of 30 minutes was used. Cleaning was performed with all valves fully open and at a crossflow rate of 800 mL/min; under these parameters, the pressure in the system is approximately 140 psi. For the acid cleaning trials, the pH was measured every two to five minutes to ensure a consistent pH throughout the cleaning cycle. Cleaning solutions were prepared to be within 0.1 pH unit of the target pH. Early trials used small volumes of cleaning solution, about 2 liters. Since the cleaning solutions were unbuffered, these volumes were too small to maintain a constant pH. Later trials were performed with cleaning solution volumes between 5 liters and 8 liters. For an increase in the measured pH above 0.3 pH points, 10 mL of 0.1 M HCl was added to the feed. More acid addition was needed for the calcium carbonate scaled membranes in comparison with the calcium silicate scaled membranes. It was found that for 5 L of a pH 3 solution, an average of 40 mL of an 0.1 M HCl solution needed to be added to maintain the pH over the course of the half hour cleaning run for calcium carbonate scale. Almost no acid was needed for the calcium silicate scale. After cleaning, the system was flushed and a clean water flux measurement was taken to evaluate the flux recovery.

4. Results and Discussion

4.1 Flux Recovery

Flux values were compared from three different points: after membrane compaction for one hour, after scaling, and after cleaning. Flux readings were taken using DI water at 500 psi. To compare between runs, scaled and cleaned flux readings were normalized to the initial reading of the coupon. comparison between runs is accomplished by examining the percent of flux recovery, which is calculated as the difference between the clean water flux values after scaling, J_s , and after cleaning, J_c , divided by the difference between the initial clean water flux, J_i , and the clean water flux after scaling, J_s (Equation 9). In other words, the flux recovery is the flux regained by cleaning relative to the flux lost due to scale and is presented as a percentage of the lost flux.

$$FR = \frac{J_c - J_s}{J_i - J_s} \quad (9)$$

Tests with calcium carbonate were performed in triplicate while tests with calcium silicate were performed in duplicate. For the triplicate samples, statistical analysis was performed. Measured values were averaged to give an overall flux recovery value representative of the scaling and cleaning combination. Even in the same membrane material, variability in initial flux is expected between coupons either due to the membrane itself or because of slight differences in membrane preparation and installation; observed initial flux ranged from 120-140 lmh after one hour of membrane compaction using DI at 500 psi. Additionally, each run varied in the extent of scaling. This was a result of any slight differences in the scaling solution and changes in the system over time, such as scale build-up within the pipes and tubes.

4.2 Calcium Carbonate Scale

Membranes scaled with a solution containing CaCl_2 and Na_2CO_3 produced two crystal morphologies as revealed by scanning electron microscope (SEM) imaging at 1000x magnification. The SEM image shown in Figure 8 is of a scaled membrane cleaned with a pH 4 cleaning solution. The rectangular structure in (a) appears to be a calcite crystal; the hexagonal structure in (b) appears to be a vaterite crystal. These crystals are expected; in precipitation experiments, vaterite and calcite were formed at temperatures below 30 °C while aragonite, a third form of calcium carbonate present in aqueous systems, was only observed at temperatures above 40 °C (Ogino et al. 1987). Additionally, vaterite is metastable and, given enough time, will transform to calcite at low temperatures. In natural water systems, vaterite is not common as it does not form well in the presence of magnesium (Antony et al. 2011). Energy-dispersive X-ray spectroscopy (EDX) performed as an area analysis of the two different morphologies revealed calcium, oxygen, and carbon in addition to platinum from the sample coating and sulfur from the membrane backing material (Figure 8). Notably, sodium and chlorine were absent though they were components of the feed. This supports the hypothesis that both samples are calcium carbonate crystals. Comparative EDX point analysis of membranes cleaned with CO_2 gas and pH 3 to a scaled and uncleaned membrane show the same compounds but calcium is absent from the pH 3 cleaned membrane where scale was almost completely removed (Figure 9). Similar results were produced by Mitrouli et al. (2012) on CPA2 membranes lightly scaled with calcium carbonate from a synthetic brackish feed solution very similar to the one applied in this study. SEM images from their study, also taken at 1000x magnification, showed distributed crystals of both calcite and vaterite forms.

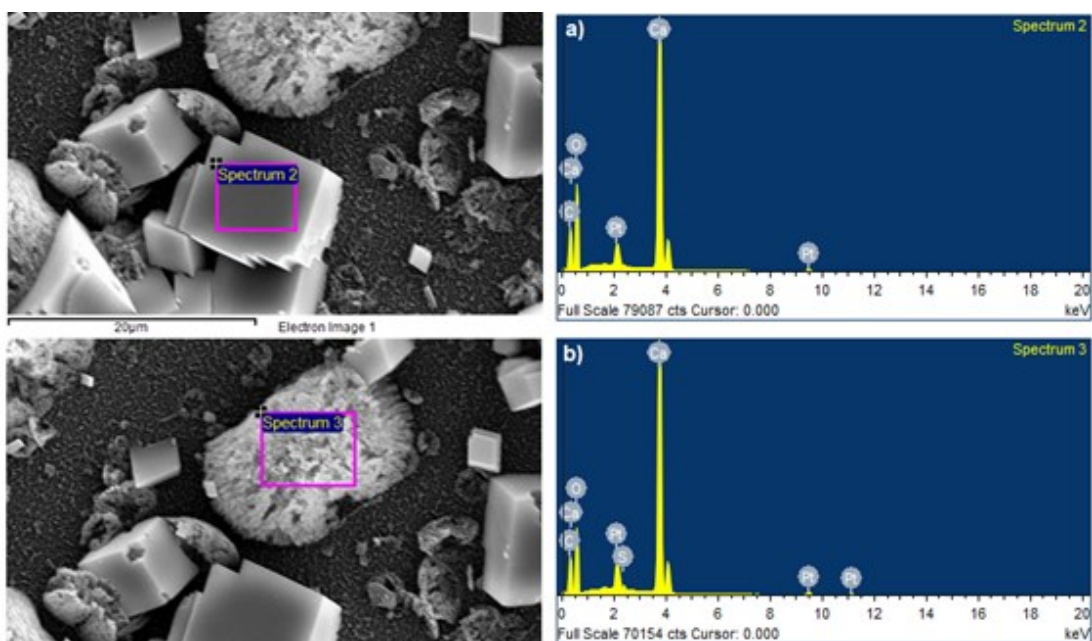


Figure 8: EDX analysis (left) and SEM imaging (right) of two CaCO_3 crystal structures on a pH 4 cleaned membrane. SEM reveals a) a rectangular crystal structure and b) a hexagonal crystal structure.

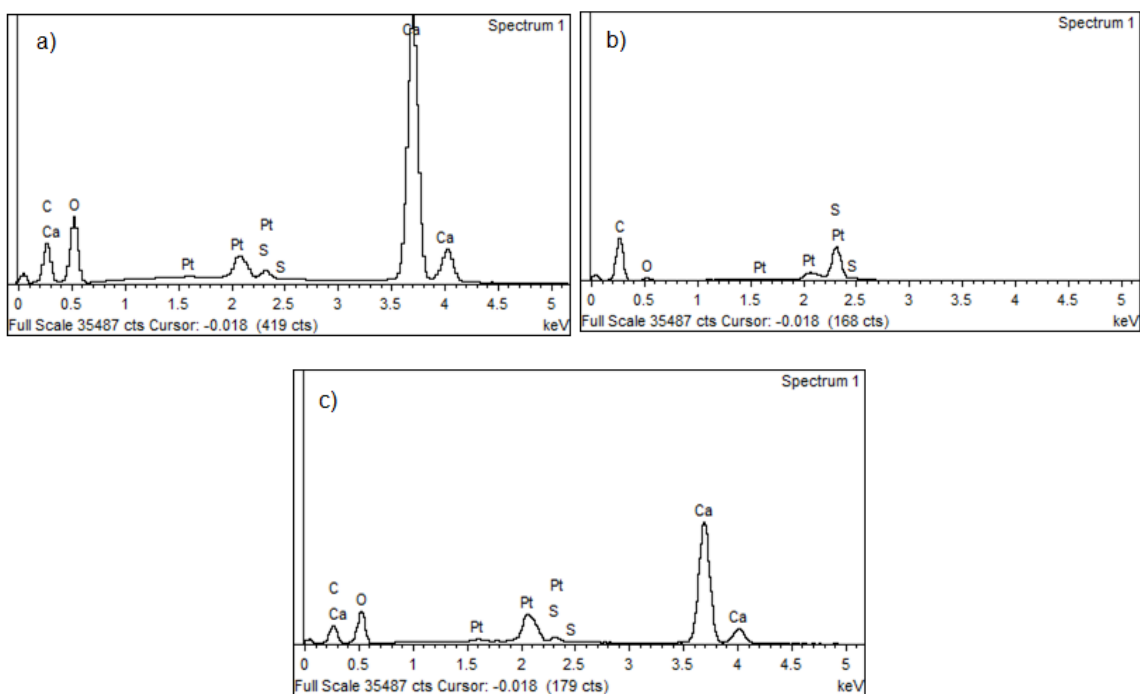


Figure 9: EDX analysis at one point of a) a membrane scaled with CaCO_3 , b) a scaled membrane cleaned with a pH 3 solution and, c) a scaled membrane cleaned with a dissolved CO_2 solution. Platinum signals are due to the coating used in SEM imagine. Sulfur signals are due to the polysulfone membrane support layer.

Six cleaning regimes were applied to membranes scaled with calcium carbonate: CO₂ gas, N₂ gas, pH-adjusted N₂ gas, pH 3 HCl solution, pH 4 HCl solution, and DI water. The first three experiments used the gas cleaning procedure while the last three experiments used the chemical cleaning procedure. The normalized clean water flux measurements of the unscaled, scaled, and cleaned membranes are shown in Figure 10 as white, dark grey, and light grey, respectively, where the values are normalized to the clean water flux of each membrane coupon after one hour of compaction. High variability in the degree of scaling between runs results in variability of flux recovered since each cleaning regime was performed identically. Average flux recoveries with standard deviations from each set of triplicates are tabulated in Table 5. For reference, SEM images of each cleaned membrane are compared to images of a virgin membrane compacted with DI water and a scaled but uncleaned membrane (Figure 11).

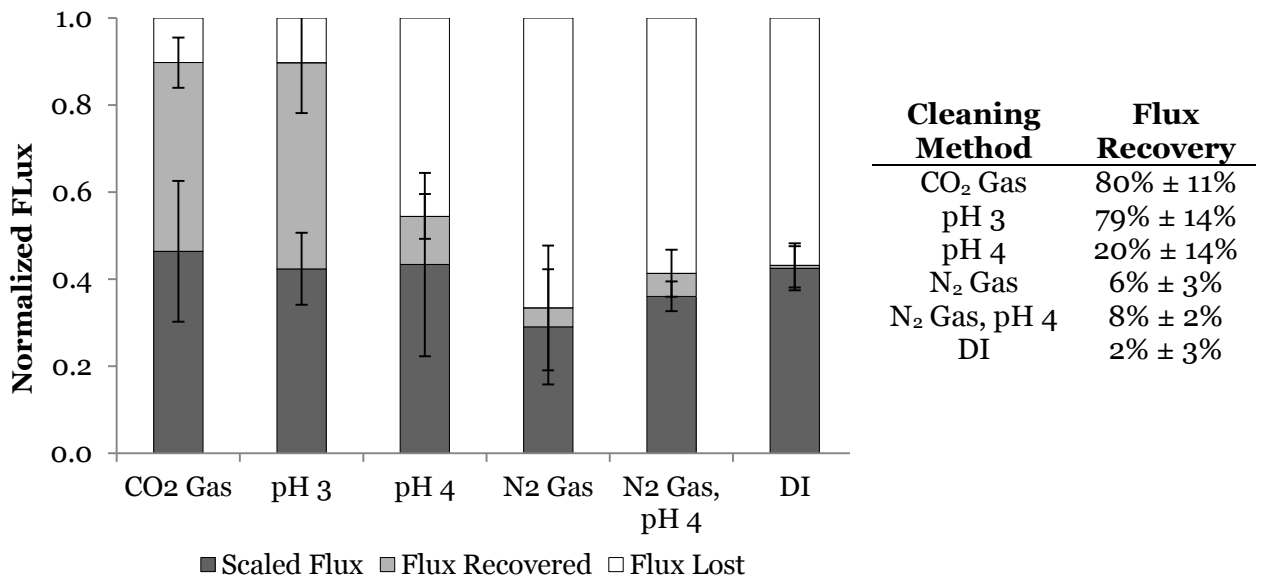


Figure 10: Averages of trials performed with calcium carbonate scale shown. Error bars represent the high and low values within each set.

Table 5: Average flux recovery value and standard deviation corresponding to each set of trials shown in Figure 10.

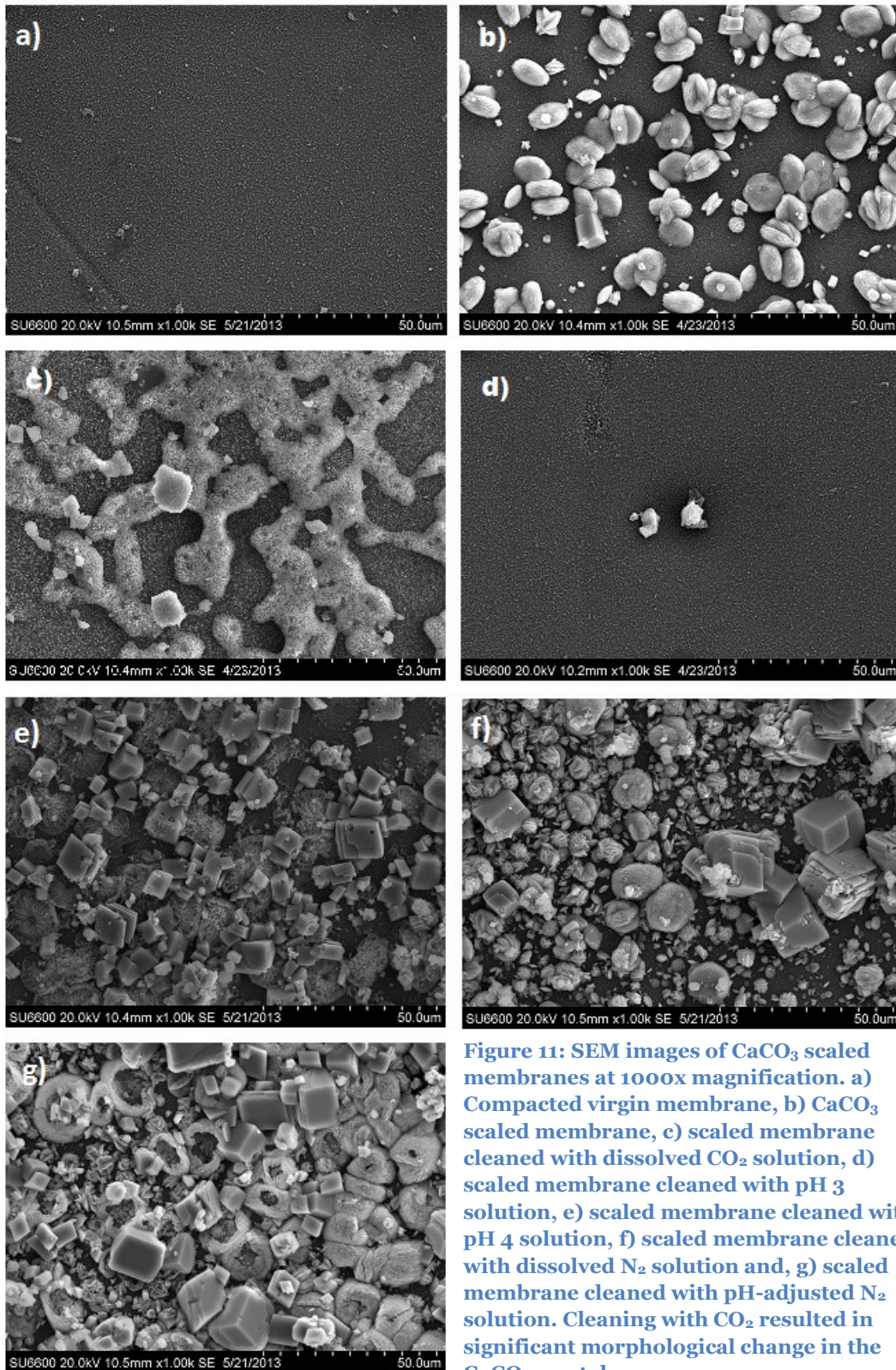


Figure 11: SEM images of CaCO_3 scaled membranes at 1000x magnification. a) Compacted virgin membrane, b) CaCO_3 scaled membrane, c) scaled membrane cleaned with dissolved CO_2 solution, d) scaled membrane cleaned with pH 3 solution, e) scaled membrane cleaned with pH 4 solution, f) scaled membrane cleaned with dissolved N_2 solution and, g) scaled membrane cleaned with pH-adjusted N_2 solution. Cleaning with CO_2 resulted in significant morphological change in the CaCO_3 crystals.

4.2.1 Dissolved CO₂ Cleaning

Scaled membranes were effectively cleaned with a dissolved CO₂ solution. The average flux recovery among four trials was 81% with a standard deviation of 14%, showing a consistently high recovery among four trials (Figure 10). Results from individual trials and SEM imaging of the cleaned membrane at 1000x magnification are shown in Figure 12 below. The highest flux recovery was 95% while the lowest was 67%. Notice that the degree of scaling as shown by a smaller dark grey bar did not affect the level of flux recovery. The SEM image revealed an altered crystal formation after cleaning that appears more amorphous when compared to the crystal appearance before cleaning (Figure 11, panel b). The masses that appear in the foreground were originally calcite crystals while the conglomerated mass against the membrane was originally distinct vaterite crystals. When looking at the membrane through SEM, the CO₂ cleaned membrane had large areas without scales, which is consistent with the level of flux recovery observed, dotted with stretches of the transformed crystals.

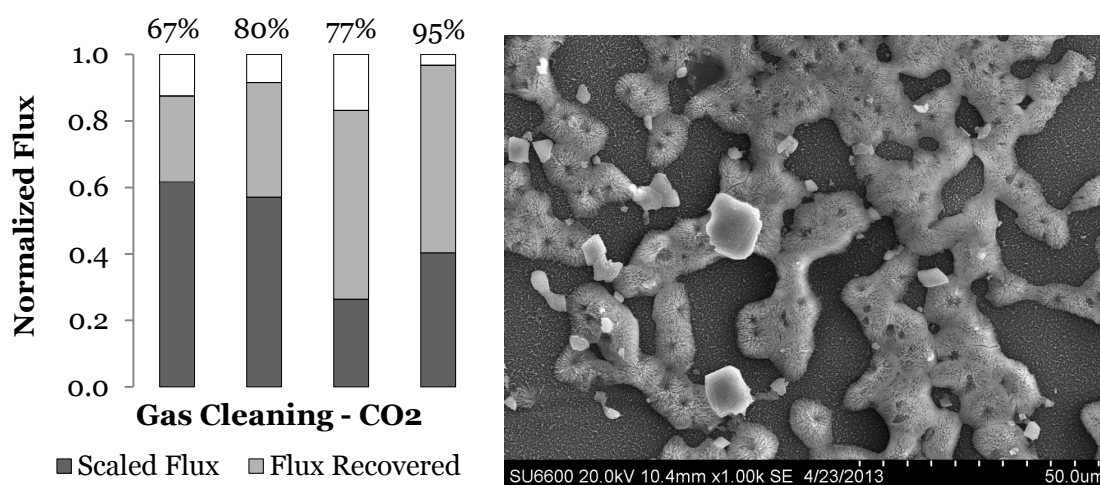


Figure 12: Left: Flux values for individual cleaning trials of a calcium carbonate scaled membrane cleaned with a dissolved CO₂ solution. Flux recovery values are shown above each trial. Right: An SEM image of a cleaned membrane that shows altered calcium carbonate crystal forms.

During the CO₂ cleaning, water in the concentrate line from the membrane cell exited rapidly. Bubbles were observed in the permeate line after approximately 30 seconds, enough time for non-carbonated water to be flushed out of the system. Samples were taken of the gas to water ratio in the permeate line using the syringe method. An initial reading at 400 psi showed on average 20 volumes of CO₂ while readings at 300 psi and 200 psi showed on average 8 volumes of CO₂. The drop from 500 psi to 300 psi occurred within two minutes. The total run time from 500 psi to the final pressure of 180 psi in the pressure vessel was 7.5 minutes. The waste stream was tested for pH and alkalinity. In each case, the pH of the water after carbonation and passing through the system was approximately 4.5. The change in alkalinity after carbonation and cleaning was always positive though so small as to be negligible.

4.2.2 pH Effects

Most of the flux was regained when a pH 3 HCl solution was used for cleaning. The average flux recovery was 79% with a standard deviation of 14%, nearly identical to the CO₂ cleaning results (Figure 10). Figure 13 shows the results from the individual trials and a representative SEM image of a cleaned membrane. The three trials were very close in flux recovery despite very different levels of scaling. SEM imaging confirms the absence of scale after cleaning – only two particles are observed in the image, the rest of the image matches the image of the virgin membrane. This is expected as low pH solutions are the conventional cleaning solution for inorganically scaled membranes.

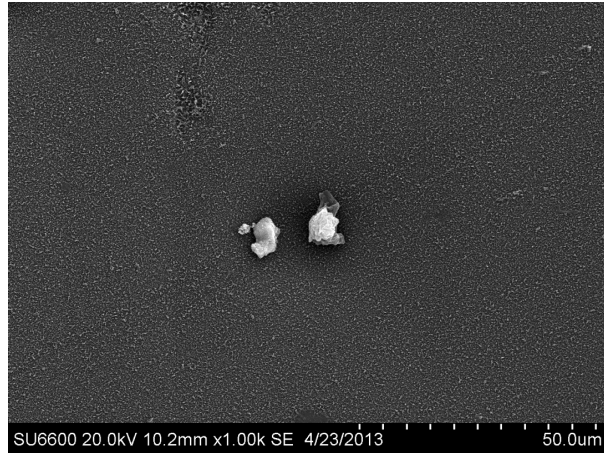
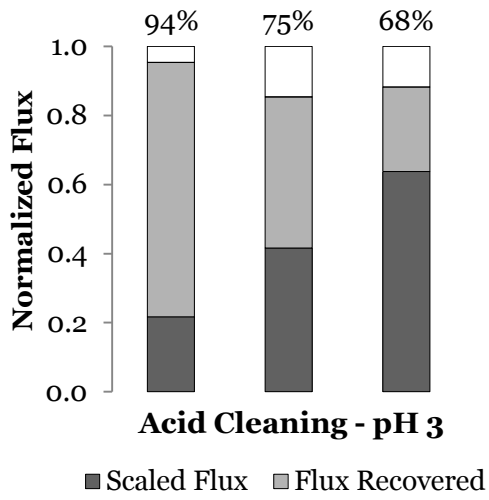


Figure 13: Left: Flux values for individual cleaning trials of a calcium carbonate scaled membrane cleaned with a pH 3 HCl solution. Flux recovery values are shown above each trial. Right: An SEM image of a cleaned membrane that shows a nearly clean membrane.

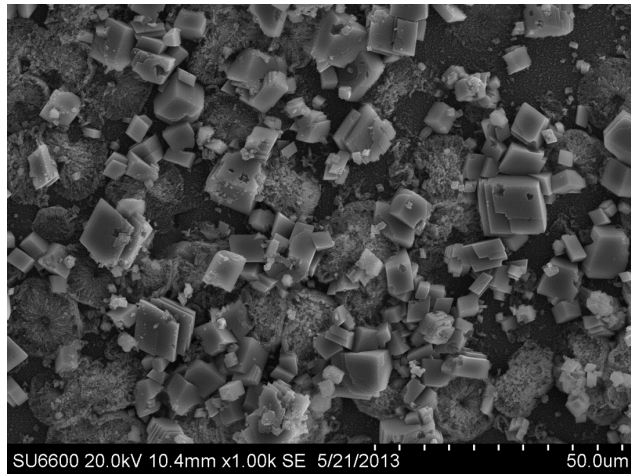
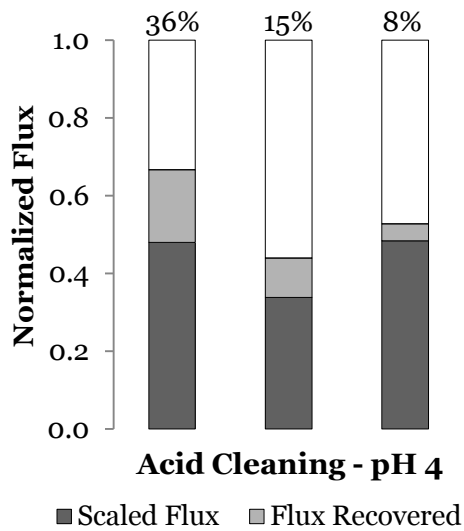


Figure 14: Left: Flux values for individual cleaning trials of a calcium carbonate scaled membrane cleaned with a pH 4 HCl solution. Flux recovery values are shown above each trial. Right: An SEM image of a cleaned membrane that shows some morphological change in the crystal structure.

Very little flux recovery was achieved using a pH 4 cleaning solution; the average flux recovery was 20% with a standard deviation of 14% (Figure 10). The relatively wide spread of flux recoveries occurred despite similar degrees of scaling, with the lowest value at 8% and the highest at 36% (Figure 14). The highest recovery value was still far below those of the CO₂ cleaning and pH 3 cleaning values. This low cleaning ability of the pH 4 solution demonstrates that the final pH of 4.5 observed with the dissolved CO₂ solution is not a major factor in the cleaning mechanism. Some morphological change in crystal structure was observed in the SEM image of the pH 4 cleaned membrane, which corroborates the mild cleaning effect observed in the flux results (Figure 14).

4.2.3 Dissolved Gas Effects

Trials were performed using N₂ gas in place of CO₂ gas to investigate non-carbonate bubbling effects. The dissolved N₂ was prepared using the same method as the dissolved CO₂ solution – by bubbling N₂ gas into the vertical pressure vessel. Trials were also run with the water adjusted to a pH of 4 before adding N₂ through bubbling. This trial served to isolate bubbling effects from the low pH observed in the final CO₂ solution. The average flux recovery from N₂ dissolved in DI was 6% with a standard deviation of 3%, while the average flux recovery of N₂ dissolved in solution adjusted to pH 4 was 8% with a standard deviation of 2% (Figure 10). Figure 15 and Figure 16 show the individual trials; all runs had similar degrees of scaling and resulted in a very small range of flux recoveries. The lower pH slightly enhanced cleaning with a high of 9% and low of 6%, though all the trials showed only limited cleaning of the calcium carbonate scale.

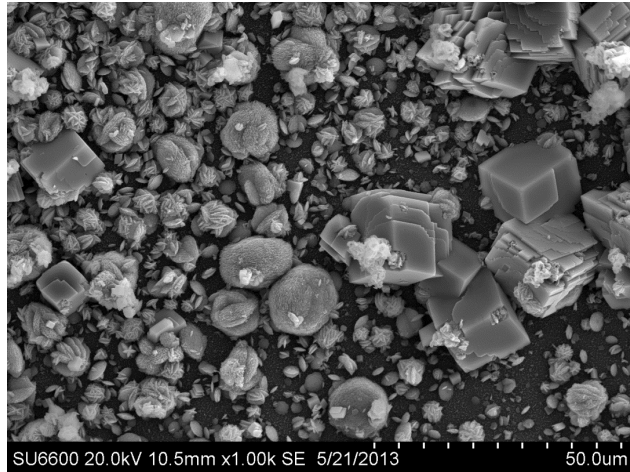
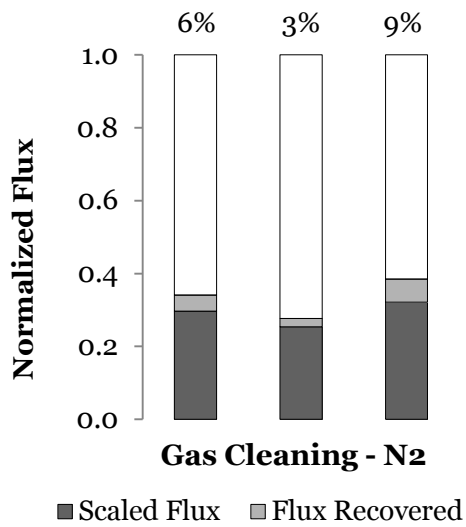


Figure 15: Left: Flux values for individual cleaning trials of a calcium carbonate scaled membrane cleaned with an N₂ gas solution. Flux recovery values are shown above each trial. Right: An SEM image of a cleaned membrane that shows no morphological change in the crystals.

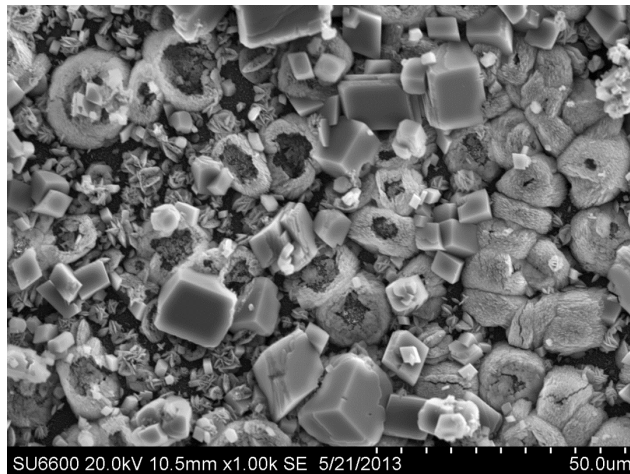
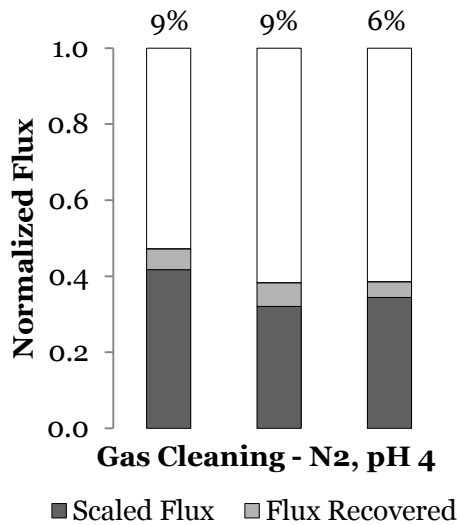


Figure 16: Left: Flux values for individual cleaning trials of a calcium carbonate scaled membrane cleaned with an N₂ gas solution at pH 4. Flux recovery values are shown above each trial. Right: An SEM image of a cleaned membrane that shows morphological change beginning in the center of the hexagonal crystal structures.

SEM images of the membranes at 1000x magnification showed no difference between the N₂ cleaned membrane and the uncleaned membrane in Figure 11 panel b. However, the membrane cleaned with N₂ in a pH 4 solution displayed an interesting result; the vaterite crystals were not morphed as with the pH 4 chemical cleaning (Figure 16). Instead, the crystal spherulites appeared to be hollowed out, perhaps in some intermediate state between the original state and the morphed state. The calcite structures did not show much change from the uncleaned scales. Thus, it appears that the vaterite structure is more susceptible to removal than calcite. This correlates with the fact that vaterite is an unstable structure of calcium carbonate that eventually shifts to form calcite.

Cleaning experiments with N₂ gas acted differently from experiments with CO₂ gas. Under the same pressure conditions and within the same timeframe, water with N₂ bubbled through it exited very calmly from the concentrate line while water with CO₂ bubbled through it exited very rapidly and in short bursts. This leads to the conclusion that there was an increase in volume with the CO₂ test, possibly from the exsolution of gas as dissolved CO₂ molecules left the solution while returning to atmospheric pressure. The agitation arises from the valve that the concentrate passes through, causing rapid release of gas from solution. Additionally, bubbles were not observed in the permeate line until the pressure reached 210 psi while bubbles were observed almost immediately in the CO₂ cleaning trials. These observations support the hypothesis that more gas is dissolved in the CO₂ solutions compared to the N₂ solutions due to the higher solubility.

4.2.4 Mechanism of CO₂ Cleaning

To summarize the experimental results, the dissolved CO₂ solution cleaned the scaled membranes in under 10 minutes as well as the pH 3 solution cleaned the scaled membranes in half an hour while N₂ gas tests and pH 4 cleaning resulted in minimal flux recovery. Two conclusions can be drawn from these results. One, the pH of 4.5 of the carbonated solution plays a small role in membrane cleaning. Two, bulk phase bubbling as simulated with N₂ plays an even smaller role in membrane cleaning with no change as a result of N₂ alone.

One explanation for membrane cleaning with CO₂ is attributed to the higher solubility of CO₂ where scales are removed by shear force applied from CO₂ bubbles that form by nucleation at the membrane surface. This cleaning method, with similar procedures for preparation of the dissolved CO₂ solution, was previously employed successfully to remove biofims from NF and RO membranes (Ngene et al. 2010). Though the opaque membrane cell in this study prevents direct observation of bubble formation, as done in Ngene et al. (2010), the phenomenon of bubble nucleation can be observed through other behavior in the system. First, the rapid exiting characteristics of the CO₂ solution were not seen with the N₂ solution, implying gas exsolution in the former and not the latter. Additionally, the N₂ solution appeared whitish, similar to aerated water, while the CO₂ solution did not have this appearance. This leads to the conclusion that the N₂ solution contained small, entrained bubbles as opposed to dissolved gas molecules. Secondly, bubbles were not observed in the permeate line during N₂ runs until the very end when the headspace pressure is around 210 psi. Conversely, bubbles are observed early in CO₂ runs and in high quantity. This further supports the theory that CO₂ exists

as dissolved molecules which can easily pass through the membrane while N_2 exists as small bubbles which have difficulty permeating the membrane.

The other mechanism that may be employed is a reaction occurring between the CO_2 molecules and the calcium carbonate scale. This was not accounted for in any of the trials and should be considered in future experiments. For example, performing cleaning trials on calcium sulfate or calcium phosphate crystals may provide insight on any reaction-based scale removal present with the calcium carbonate crystals.

4.3 Calcium Silicate Scale

In silica experiments, membrane scaling was created with a solution containing Na_2SiO_3 and $CaCl_2$ to create calcium silicate complexes. This was confirmed through area EDX analysis of the scaled membranes which revealed the expected elements of calcium, silica, sodium, and chlorine – platinum is from the sample coating and sulfur is from the membrane backing; all other elements were present in the feed (Figure 17).

SEM imaging of the fouled membranes show an amorphous structure; the texture of the surface could only be discerned at a magnification of 10000x (Figure 17). Amorphous silica may also have contributed to some fouling but this was minimized by controlling the pH to be under 9. The silicate texture is consistent with descriptions of silica precipitates in the presence of a metal (Ning 2003). Similar images were seen with barium silicate scales at 10000x magnification (Sahachaiyunta et al. 2002). During SEM imaging, the scale was observed to crack on the membrane surface and move apart, as seen in the dark thin lines of the image in panel b1 and panel d of Figure 17. This is hypothesized to be a result of the energy used in imaging. Similar surface cracking was observed in iron silicate scale (Sahachaiyunta et al. 2002).

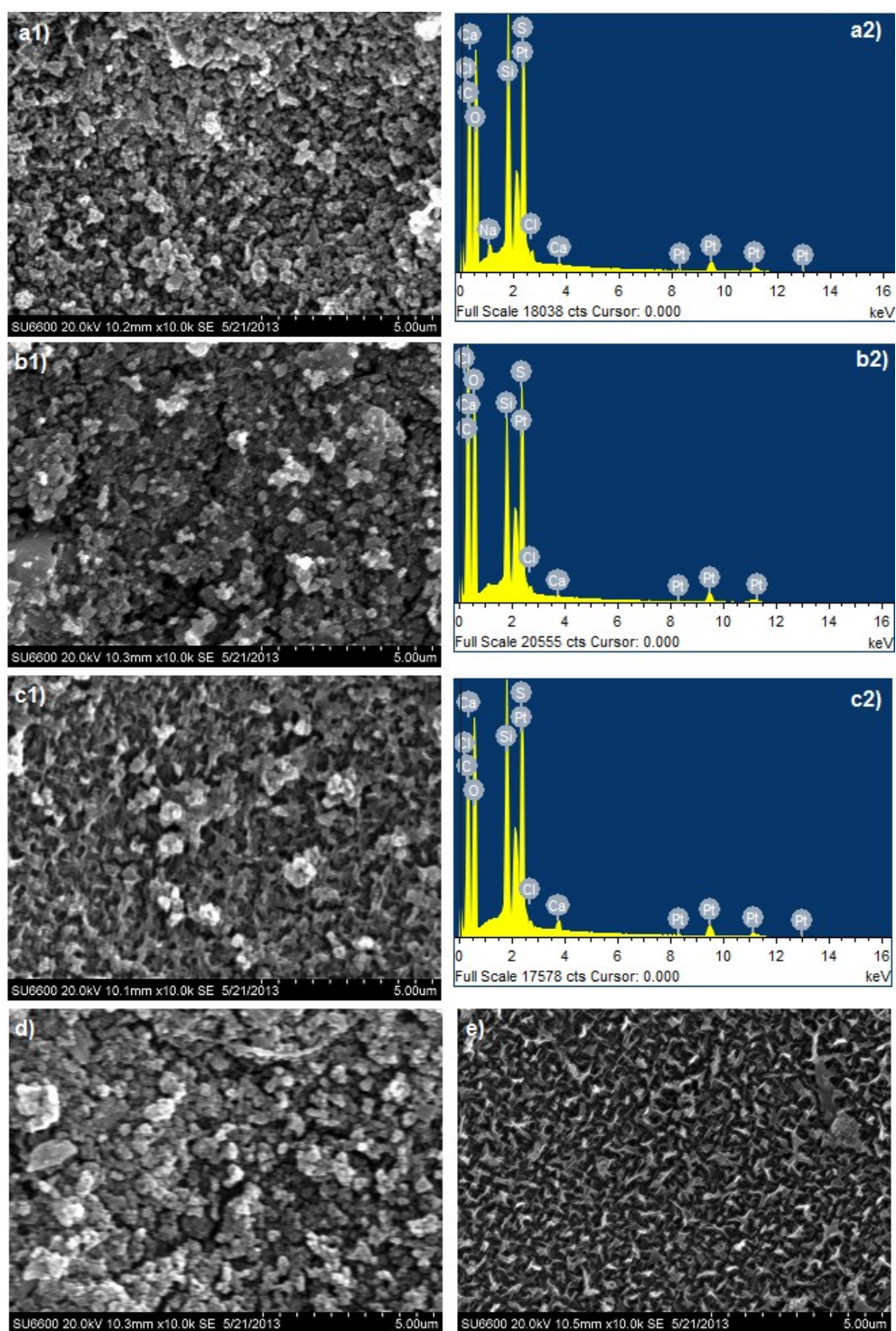


Figure 17: SEM images at 10000x magnification and EDX analysis of membranes scaled with calcium silicates. a) scaled membrane with no cleaning, b) scaled membrane cleaned with dissolved CO₂, c) scaled membrane cleaned with a pH 12 + SDS solution. Also shown d) scaled membrane with pH 3 cleaning and e) compacted virgin membrane at the same magnification.

Cleaning trials for membranes scaled with calcium silicates included CO₂ gas, HCl at pH 3, NaOH at pH 12 with sodium dodecyl sulfate (SDS), and DI water. The CO₂ cleaning experiment followed the same gas cleaning procedure as used for the calcium carbonate scaled membranes, and the other three experiments used the chemical solution cleaning procedure of cycling the solution without pressure for 30 minutes. The normalized clean water flux measurements of the unscaled, scaled, and cleaned membranes are shown in Figure 18 as white, dark grey, and light grey, respectively.

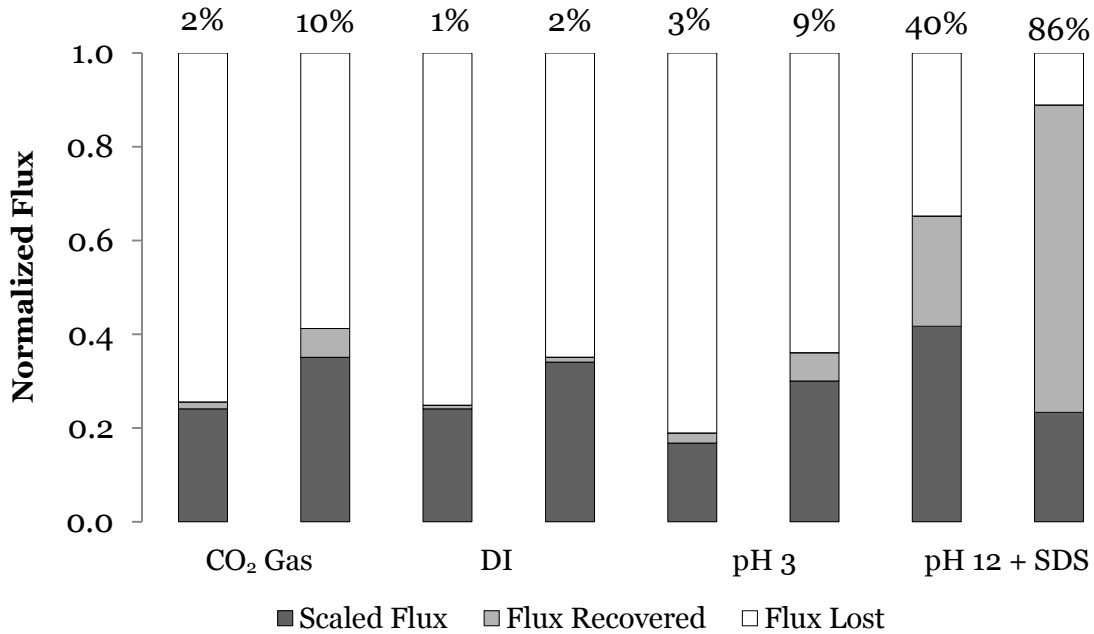


Figure 18: Cleaning results for membrane coupons scaled with calcium silicates. Flux recovery values are shown above each respective trial. CO₂ gas, DI water, and a pH 3 solution all resulted in minimal cleaning to none. The only cleaning regime with significant scale removal was the use of a pH 12 solution with sodium dodecyl sulfate (SDS).

4.3.1 Dissolved CO₂ Cleaning

Dissolved CO₂ cleaning had very little effect on the removal of silicate scale with removals of 2% and 10% over two trials (Figure 18). There were no observed differences in the cleaning operation, thus the mechanism that allows for calcium carbonate removal did not apply to calcium silicates. SEM imaging of the cleaned membrane showed no

discernible difference when compared to the non-cleaned membrane and the EDX analysis is also nearly identical – there is no labeled peak for Na in the CO₂ cleaned membrane but it appears as if a slight peak is present at that location nevertheless (Figure 17). Thus, all analyses show no change as a result of the dissolved CO₂ cleaning solution.

4.3.2 Chemical Cleaning

Two chemical solutions were applied to clean membranes scaled with calcium silicates. The pH 3 solution performed equally poorly as the CO₂ cleaning with very little flux recovery – 3% and 9% over two trials. The only solution that resulted in significant flux recovery was a solution adjusted to pH 12 with NaOH with SDS added, which produced flux recoveries of 40% and 86% over two trials (Figure 18). This moderate flux recovery matches recommendations by DOW Filmtec for silicate scale cleaning regimes which call for high pH for silicate cleaning as opposed to low pH for other inorganic foulants (Fritzmann et al. 2007). The SEM image of the pH 12 cleaned membrane supports this cleaning – detail of the membrane surface can be seen in the background of panel (e) (Figure 17).

5. Conclusions

CO₂ gas, when dissolved in a pressure vessel, was effective at removing calcium carbonate scale from low-pressure RO membranes. The same cleaning regime was not effective at removing calcium silicate scale. The experimental method was validated by obtaining expected results from cleanings modeled after industry standards – pH 3 cleaning for calcium carbonate scale and pH 12 with surfactant for calcium silicate scale.

Two possible mechanisms for CO₂ cleaning were deemed minor – a pH around 4.5 and bulk phase bubbling. One possibility is the nucleation of bubbles at the membrane surface that results in cleaning. This is the mechanism used by Ngene et al. (2012) to remove biofilms from RO membranes. Another possibility is a chemical reaction occurring between CO₂ and the calcium carbonate that results in cleaning. Future experiments should be designed to narrow in on the primary mechanism behind this cleaning.

On the bench-scale system, the dissolved CO₂ cleaning worked quickly and efficiently, removing heavy fouling with a ten minute once-through cleaning. Despite the failure to remove silicate scale, the cleaning ability of CO₂ for calcium carbonate scale is significant and leads to the possibility of future environmentally sustainable and cost-effective applications where calcium carbonate scale is currently treated using antiscalants or acid cleaning regimes. The cost of CO₂ is currently high, but this cleaning method may undergo market driven application as carbon capture installations become more popular.

6. Future Work

Future work should be performed to explore the effectiveness of dissolved CO₂ on different types and combinations of scale. In RO applications, scale is made of multiple constituents and can be compounded by the combination of organic and inorganic foulants. In addition to measuring the cleaning effect on various scales, these experiments will also provide more information on the fundamental mechanism behind the cleaning ability of dissolved CO₂. One starting point will be to examine the ability to clean calcium sulfate scale from membranes. Calcium sulfate is a common and problematic scale that is neither a carbonate nor a silicate, thus it can provide a good comparison for the existing work. Other membrane foulants to consider include non-calcium scales, such as barium sulfate.

Additionally, experiments can be conducted to evaluate CO₂ cleaning ability for scaling from feedwaters other than brackish groundwater, such as seawater and industrial wastewater treatment. Dissolved CO₂ cleaning has been shown to be effective on biofilms and with consideration of the above presented work, there is reason to believe that there will be a benefit in using dissolved CO₂ for cleaning of seawater RO operations.

Future work should also consider an in-line application of dissolved CO₂ to examine any scale prevention benefits. In order to test this, it will be necessary to devise a system for continuous pressurization without breakpoints to atmospheric pressure. Alternatively, this examination would be possible by comparing two membrane modules using the same feedwater, except for the addition of CO₂, to perform this experiment without system recycle under pressure.

Since this study has demonstrated effectiveness for removing calcium carbonate scale using dissolved CO₂, further development of this application would be to test the feedwater of a reverse osmosis plant subject to high levels of calcium carbonate scale. A study would be performed on a membrane module with CO₂ supply and pressure vessel configured to the RO system as a side stream process. The effects from CO₂ would be evaluated on a realistic rate of scale formation, as opposed to the enhanced rate used in laboratory conditions. Multiple tests would be done to compare CO₂ cleaning to existing treatments including acid cleaning regimes and cleaning in conjunction with pre-treatment. Data collected from such a study would give an indication as to the real advantages and disadvantages of using dissolved CO₂ for cleaning, including factors such as cost, ease of use, and sustainability.

APPENDICES

Appendix A: CPA2 Membrane Specifications



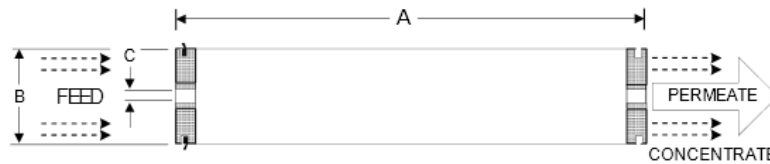
Membrane Element		CPA2
Performance:	Permeate Flow:	10,000 gpd (37.9 m ³ /d)
	Salt Rejection:	99.7 % (99.5 % minimum)
Type	Configuration:	Spiral Wound
	Membrane Polymer:	Composite Polyamide
	Membrane Active Area:	365 ft ² (33.9m ²)
	Feed/Brine Spacer Thickness:	34 mil (0.87 mm)
Application Data*	Maximum Applied Pressure:	600 psig (4.16 MPa)
	Maximum Chlorine Concentration:	< 0.1 PPM
	Maximum Operating Temperature:	113 °F (45 °C)
	pH Range, Continuous (Cleaning):	2-10 (1-12)*
	Maximum Feedwater Turbidity:	1.0 NTU
	Maximum Feedwater SDI (15 mins):	5.0
	Maximum Feed Flow:	75 GPM (17.0 m ³ /h)
	Minimum Ratio of Concentrate to Permeate Flow for any Element:	5:1
Maximum Pressure Drop for Each Element:	10 psi	

* The limitations shown here are for general use. For specific projects, operating at more conservative values may ensure the best performance and longest life of the membrane. See Hydranautics Technical Bulletins for more detail on operation limits, cleaning pH, and cleaning temperatures.

Test Conditions

The stated performance is initial (data taken after 30 minutes of operation), based on the following conditions:

- 1500 PPM NaCl solution
- 225 psi (1.55 MPa) Applied Pressure
- 77 °F (25 °C) Operating Temperature
- 15% Permeate Recovery
- 6.5 - 7.0 pH Range



A, inches (mm)	B, inches (mm)	C, inches (mm)	Weight, lbs. (kg)
40.0 (1016)	7.89 (200)	1.125 (28.6)	36 (16.4)

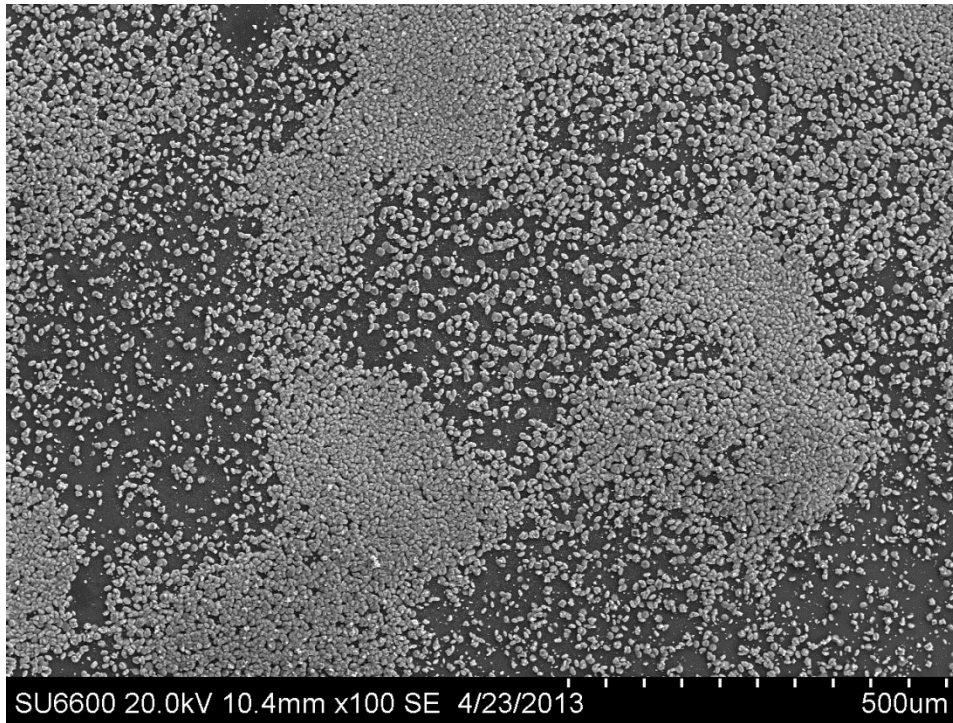
Notice: Permeate flow for individual elements may vary + 25 or - 15 percent. Membrane active area may vary +/-4%. All membrane elements are supplied with a brine seal, interconnector, and o-rings. Elements are enclosed in a sealed polyethylene bag containing less than 1.0% sodium meta-bisulfite solution, and then packaged in a cardboard box.

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Appendix B: SEM Images

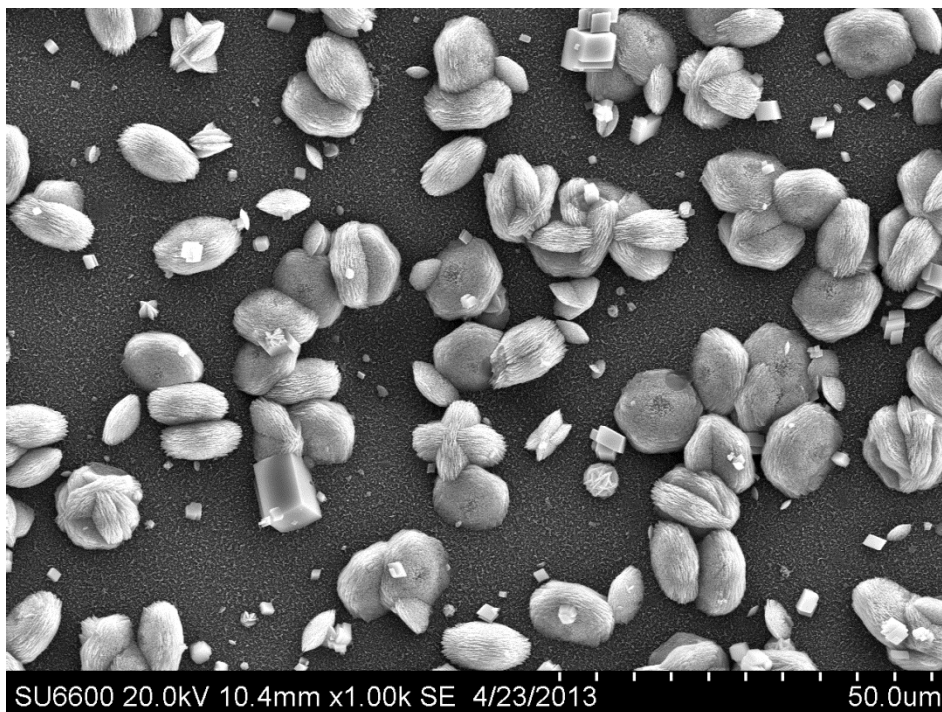
This appendix contains all the SEM images taken of membranes used in this study.



Scale: CaCO₃

Cleaning:
none

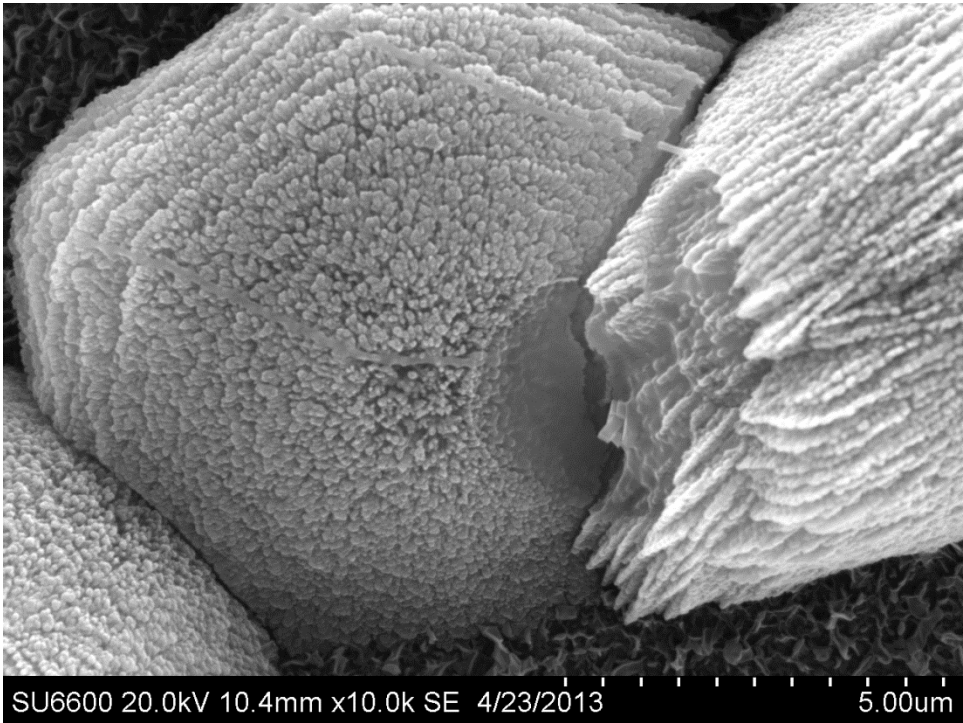
Zoom:
100X



Scale: CaCO₃

Cleaning:
none

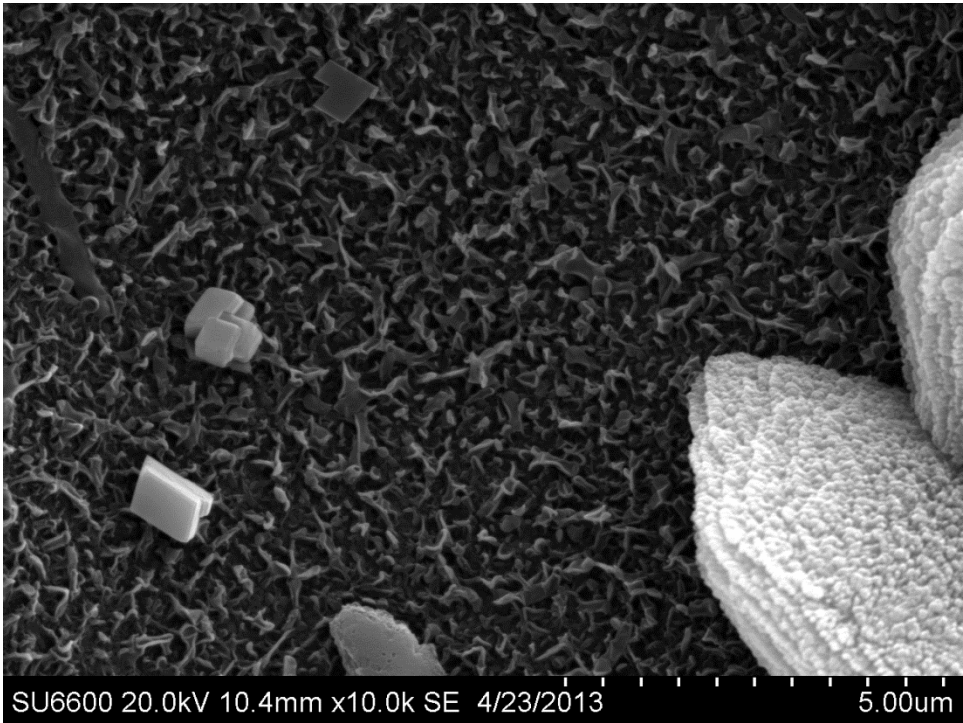
Zoom:
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Scale: CaCO₃

Cleaning:
none

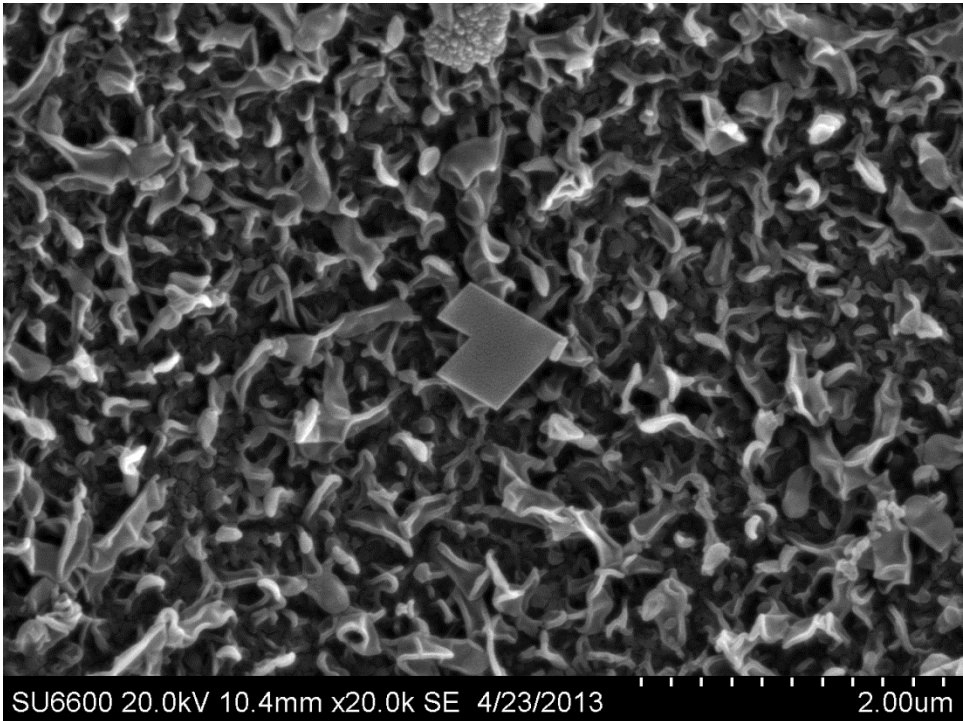
Zoom:
10kX



Scale: CaCO₃

Cleaning:
none

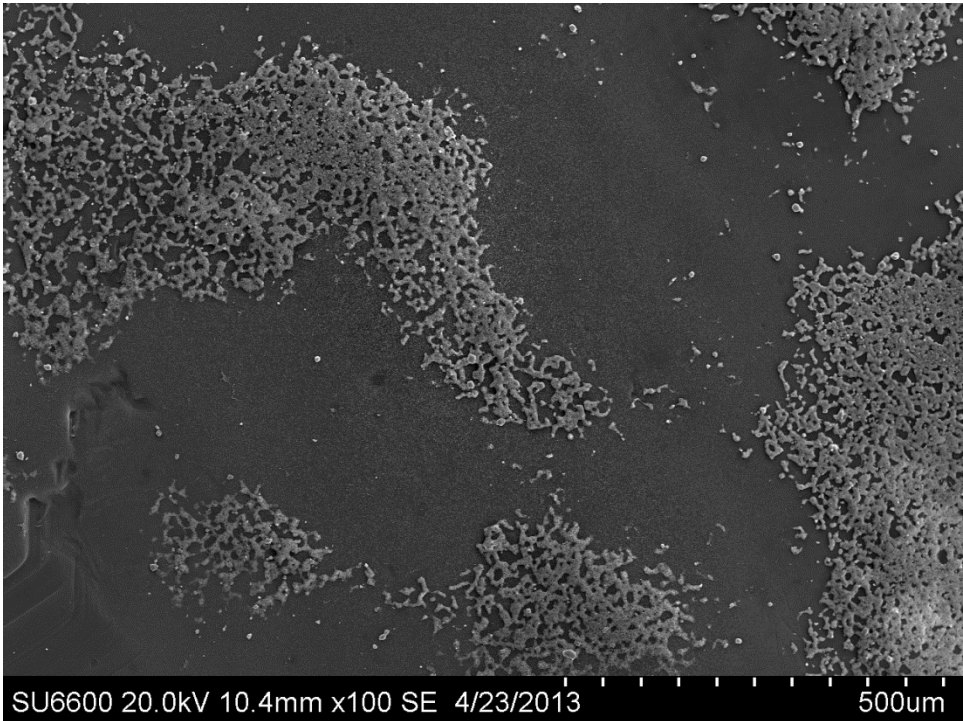
Zoom:
20kX



Scale: CaCO₃

Cleaning:
none

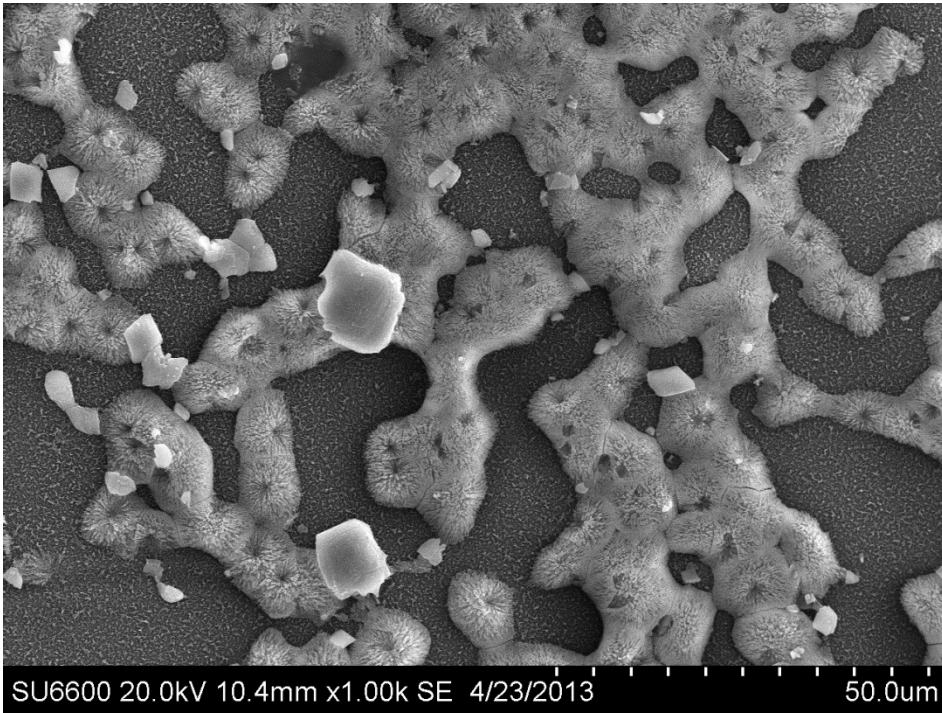
Zoom:
20kX



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample A)

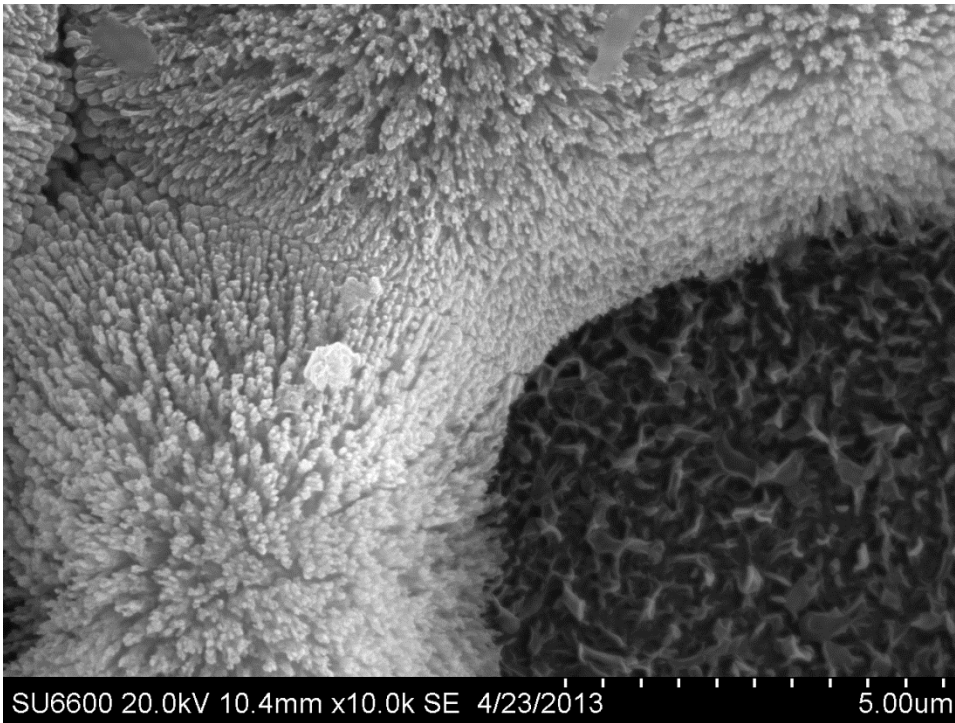
Zoom:
100X



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample A)

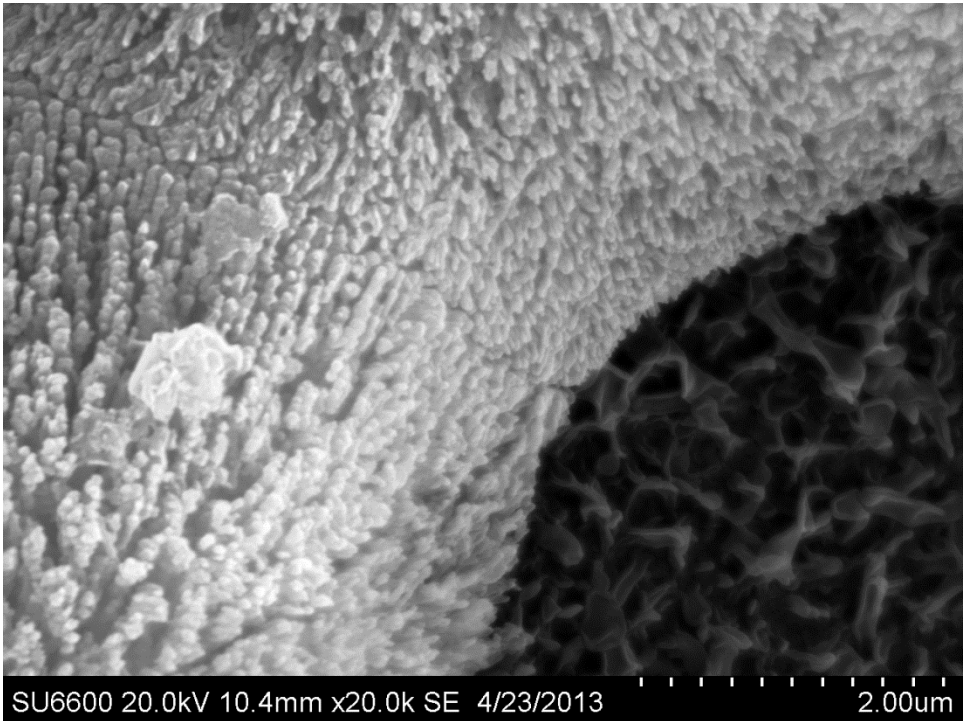
Zoom:
1kX



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample A)

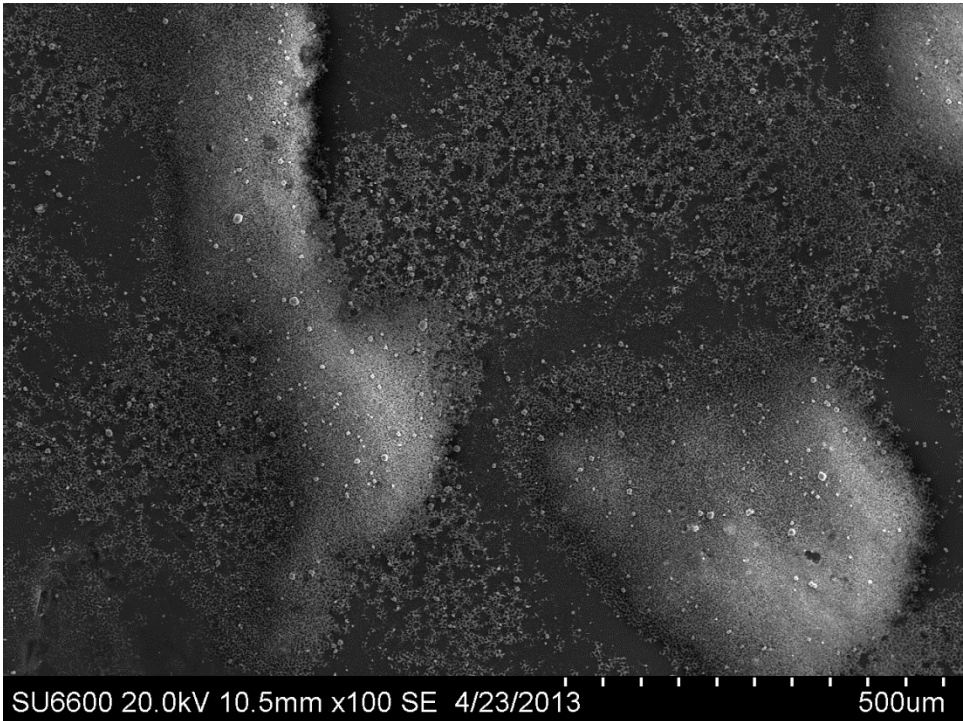
Zoom:
10kX



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample A)

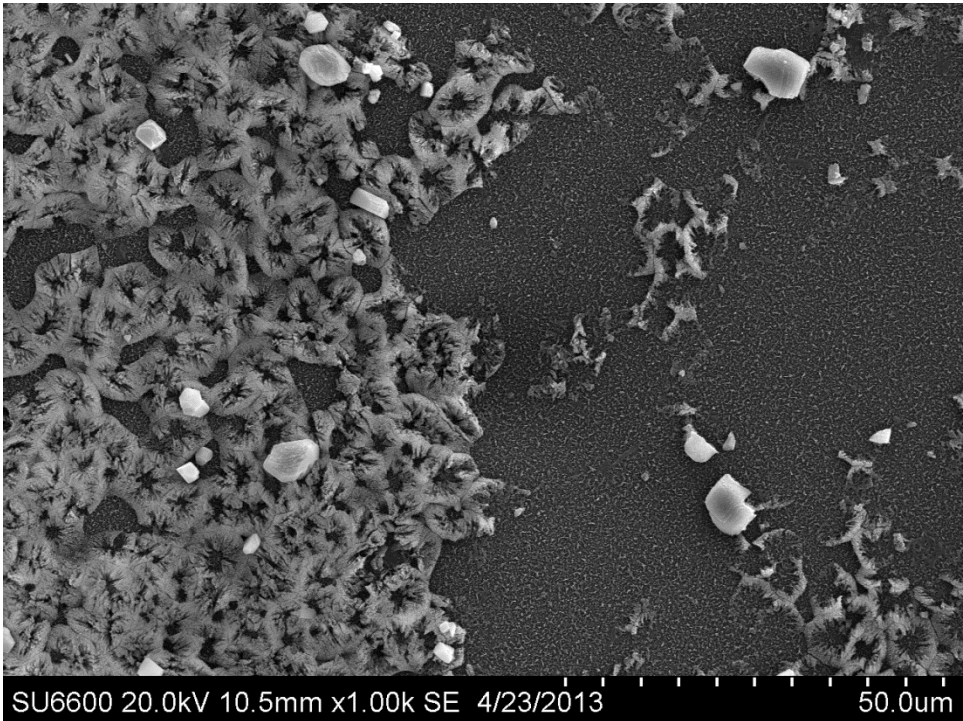
Zoom:
20kX



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample B)

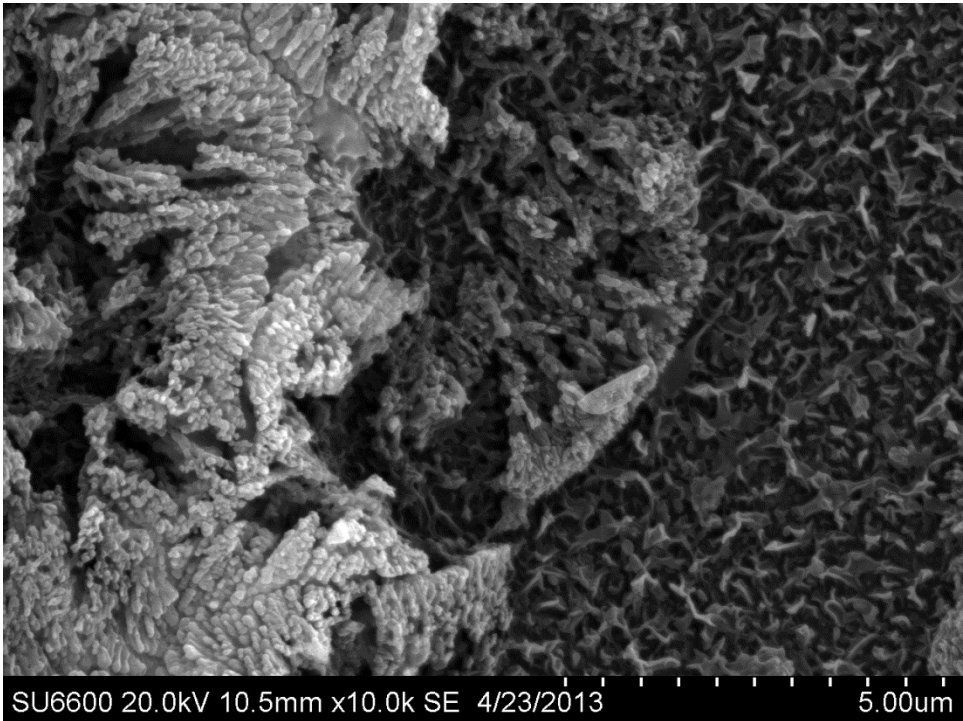
Zoom:
100X



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample B)

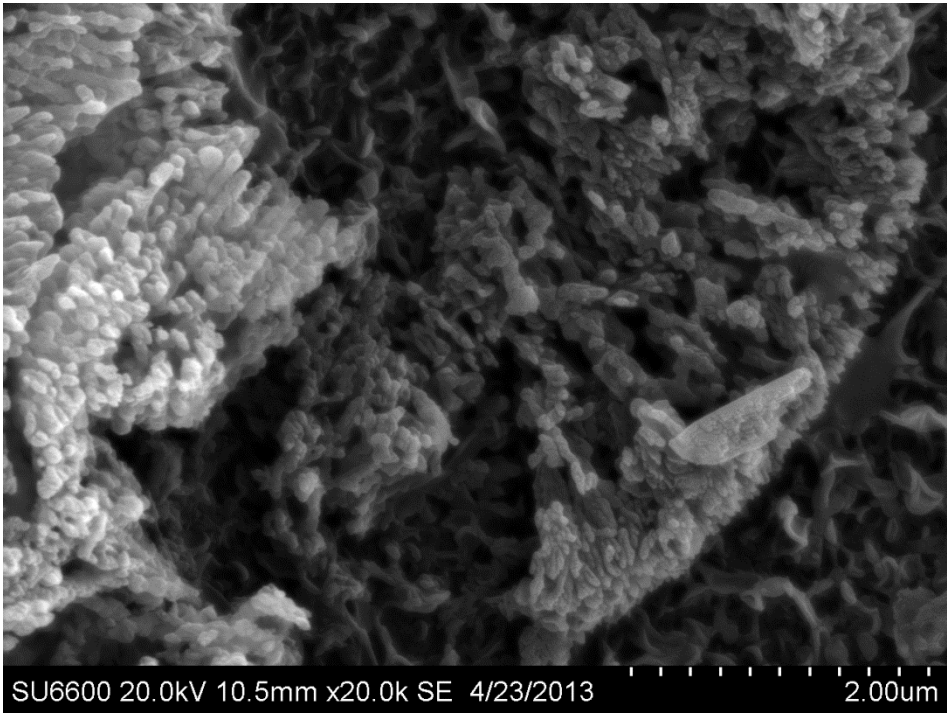
Zoom:
1kX



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample B)

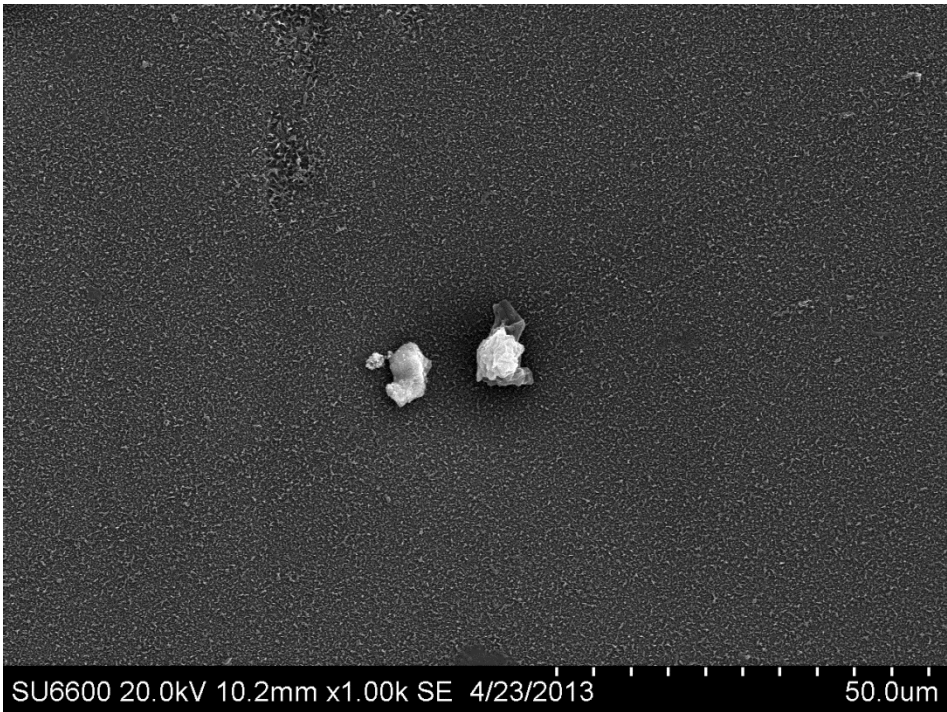
Zoom:
10kX



Scale: CaCO₃

Cleaning:
CO₂ gas
(sample B)

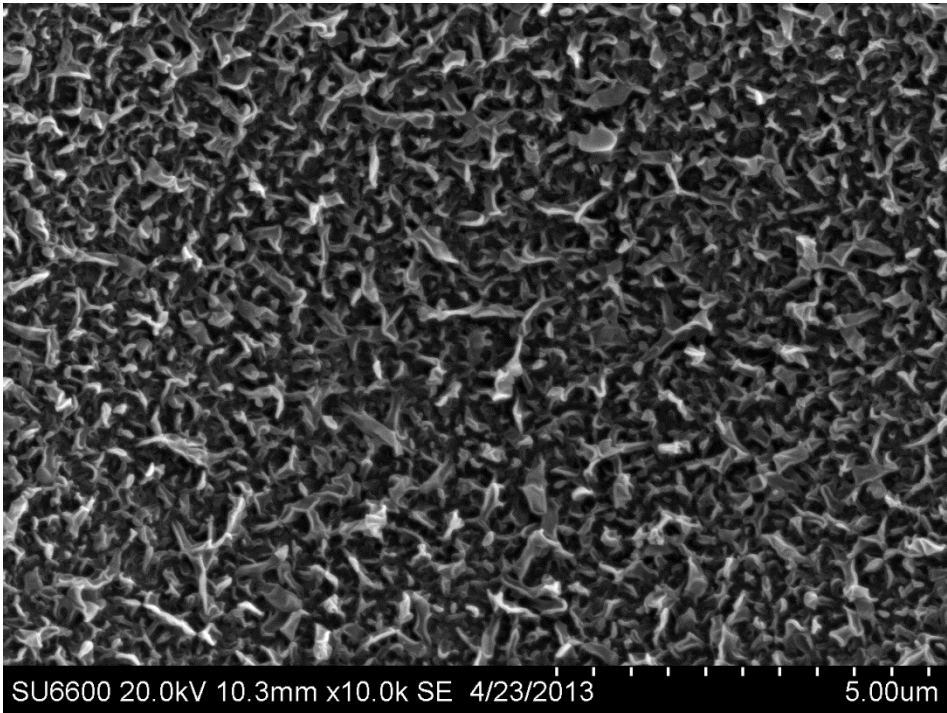
Zoom:
20kX



Scale: CaCO₃

Cleaning:
HCl at pH 3

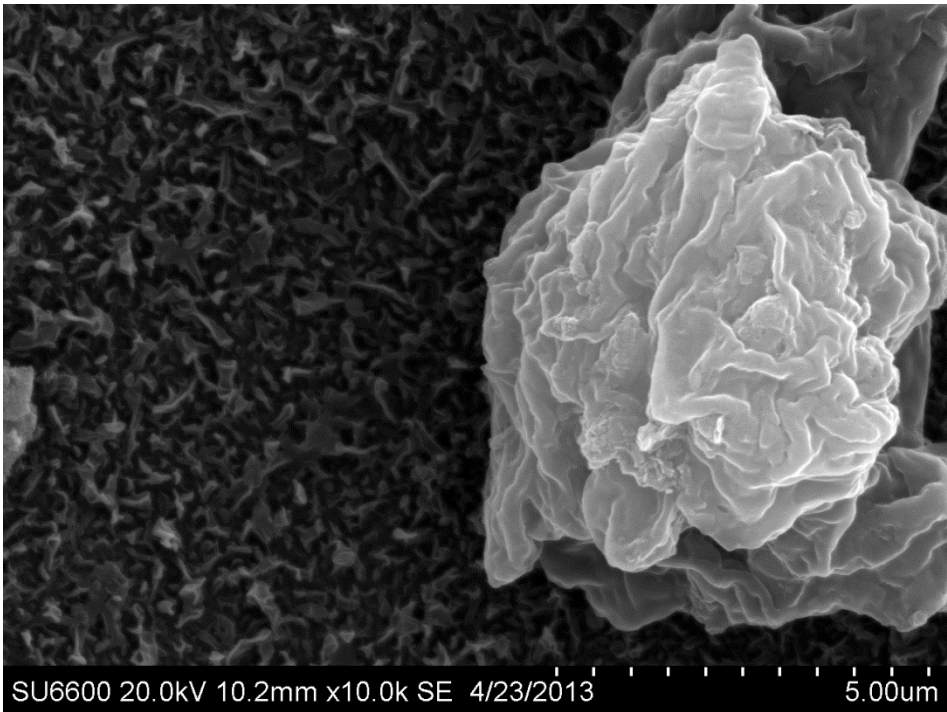
Zoom:
1kX



Scale: CaCO_3

Cleaning:
HCl at pH 3

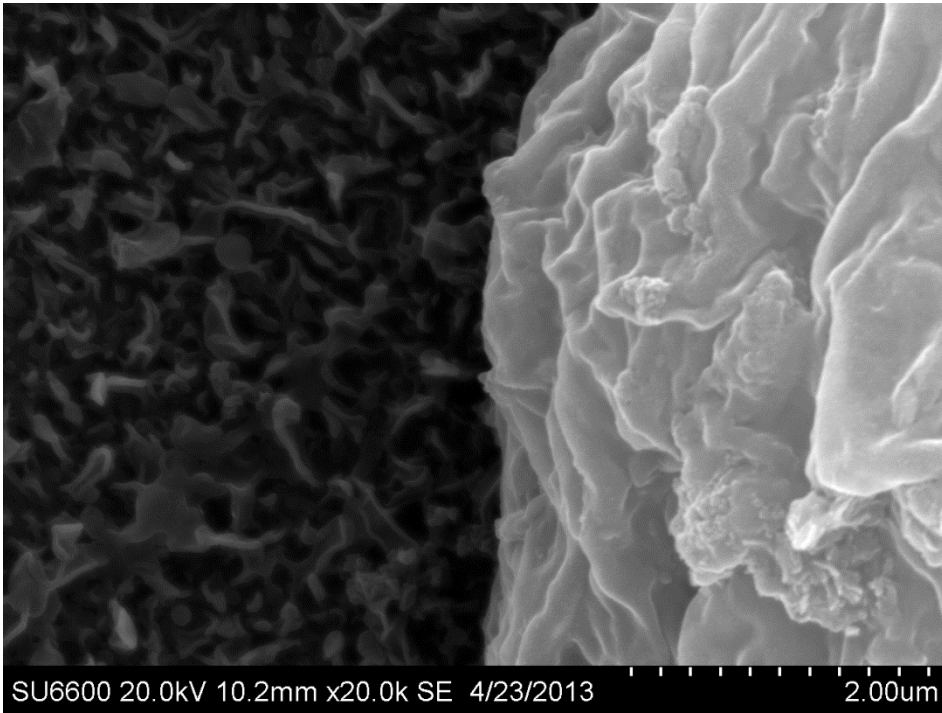
Zoom:
10kX



Scale: CaCO_3

Cleaning:
HCl at pH 3

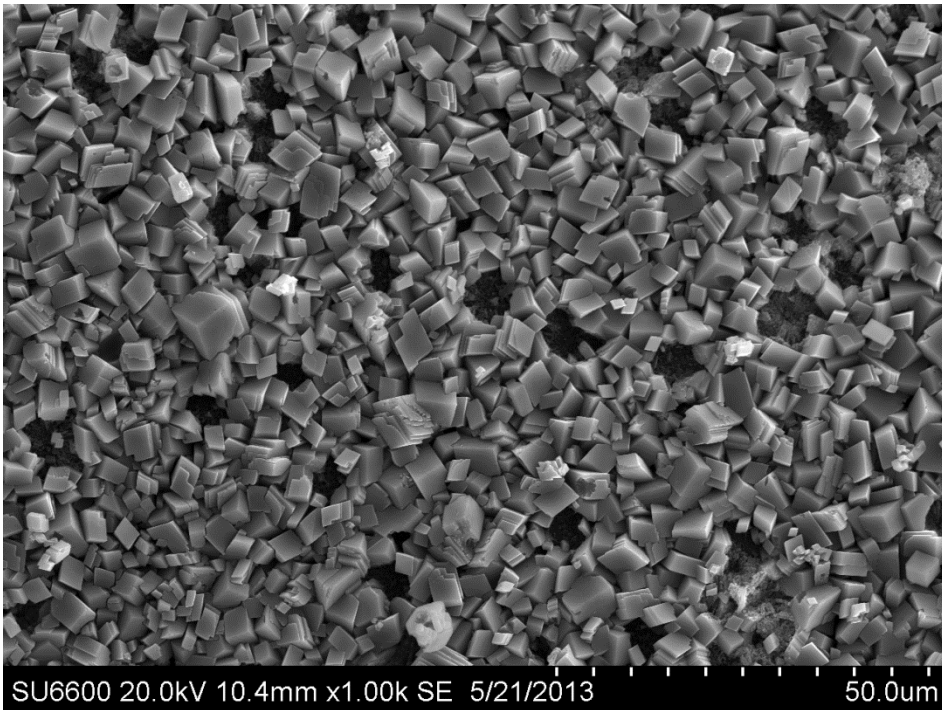
Zoom:
10kX



Scale: CaCO₃

Cleaning:
HCl at pH 3

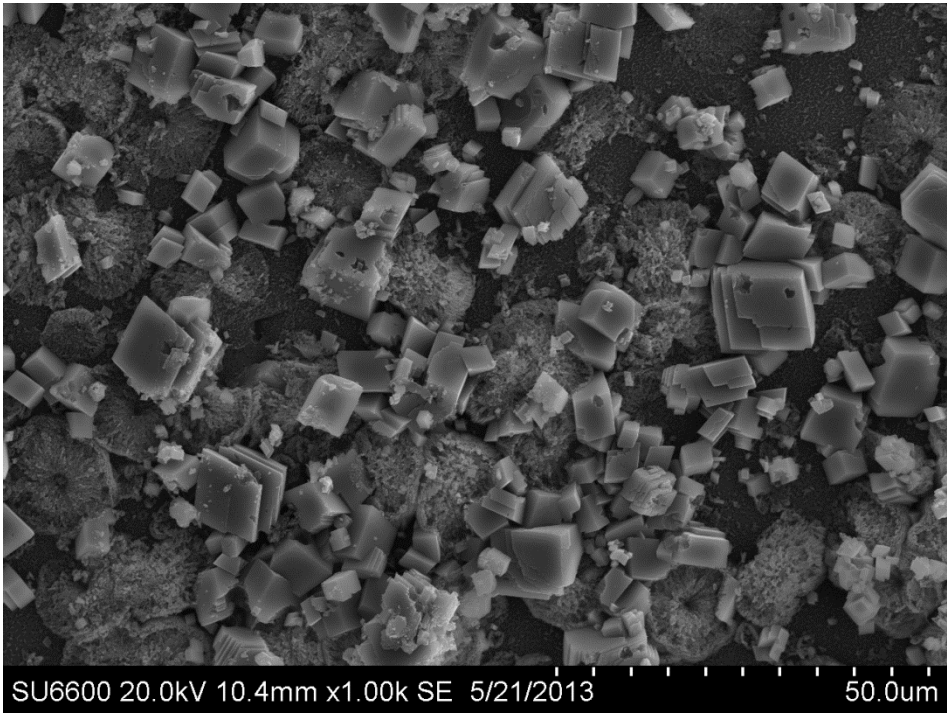
Zoom:
20kX



Scale: CaCO₃

Cleaning:
HCl at pH 4

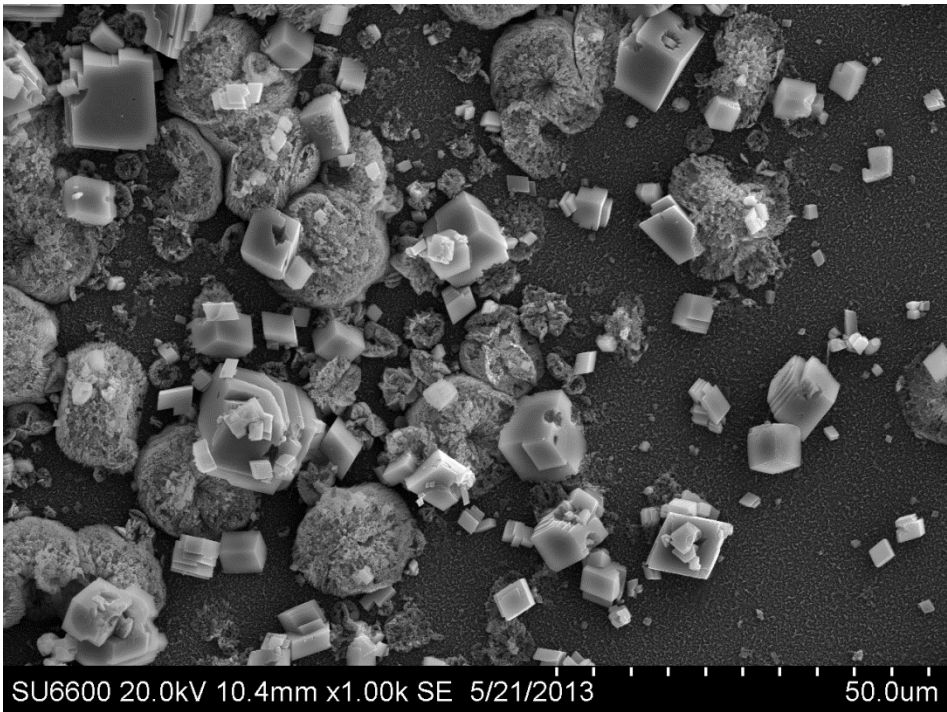
Zoom:
1kX



Scale: CaCO₃

Cleaning:
HCl at pH 4

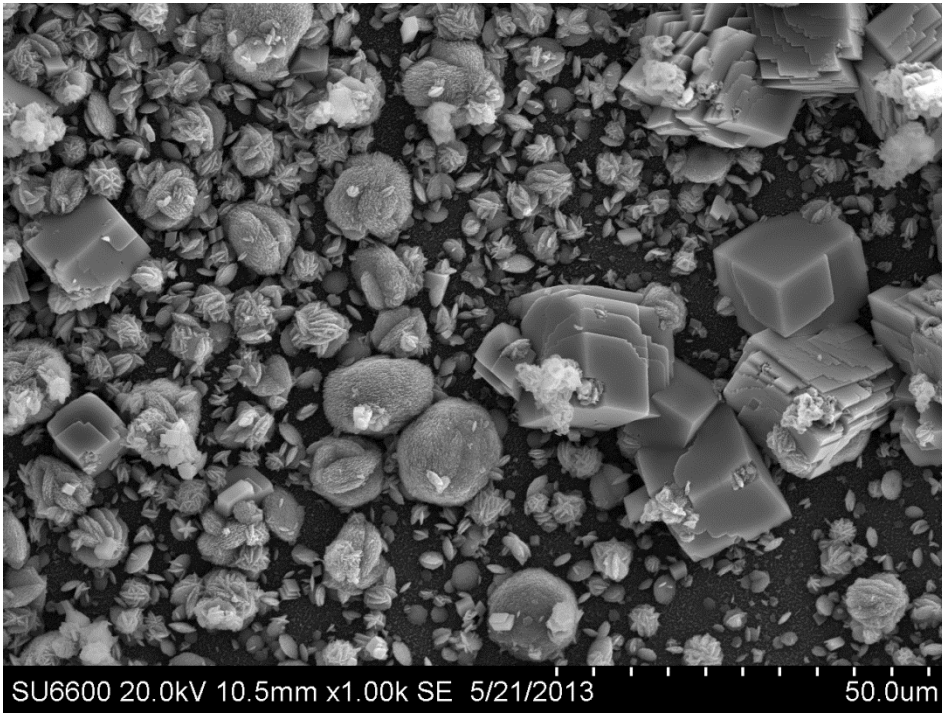
Zoom:
1kX



Scale: CaCO₃

Cleaning:
HCl at pH 4

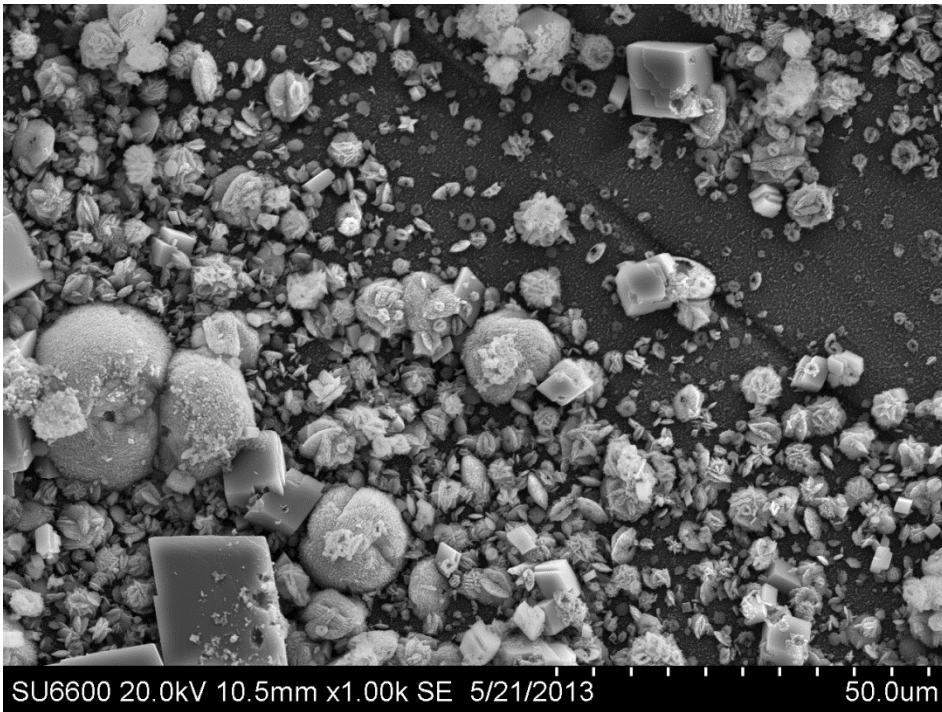
Zoom:
1kX



Scale: CaCO₃

Cleaning:
N₂ gas

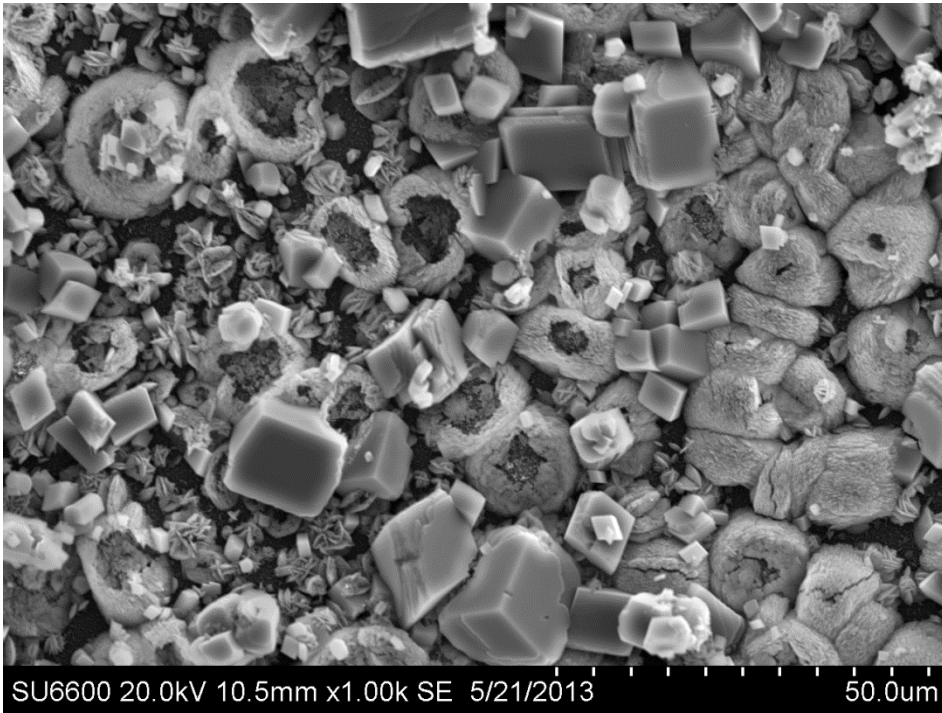
Zoom:
1kX



Scale: CaCO₃

Cleaning:
N₂ gas

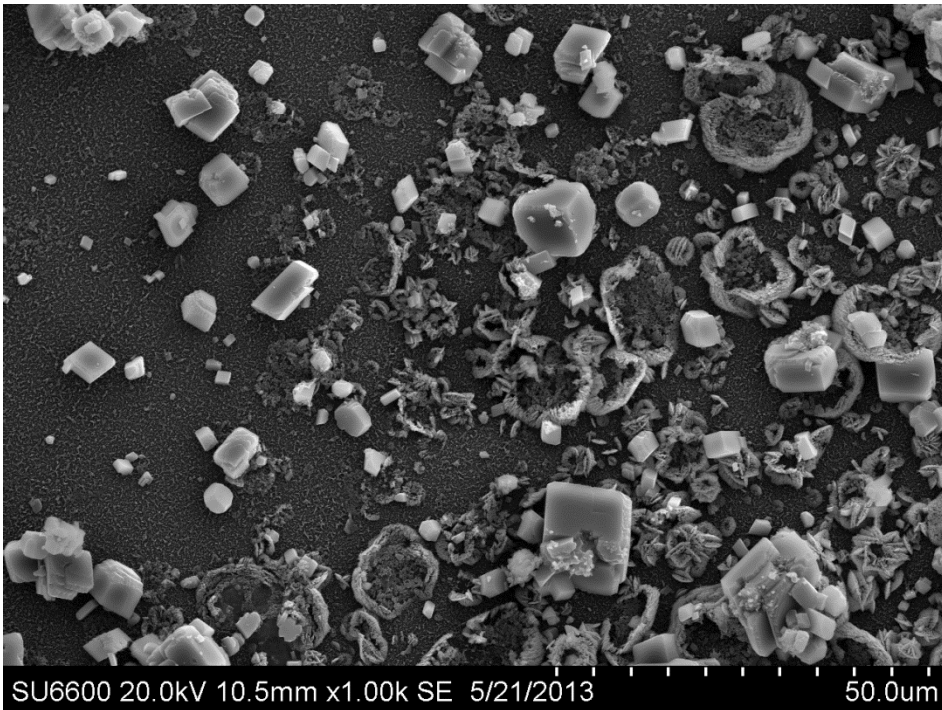
Zoom:
1kX



Scale: CaCO₃

Cleaning:
N₂ gas in
HCl at pH 4

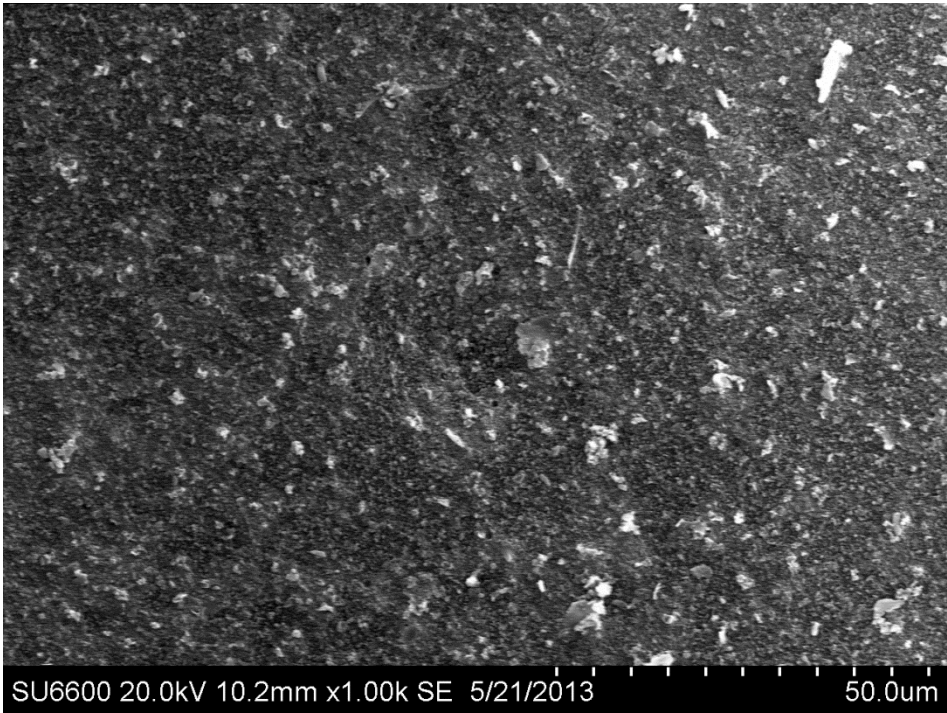
Zoom:
1kX



Scale: CaCO₃

Cleaning:
N₂ gas in
HCl at pH 4

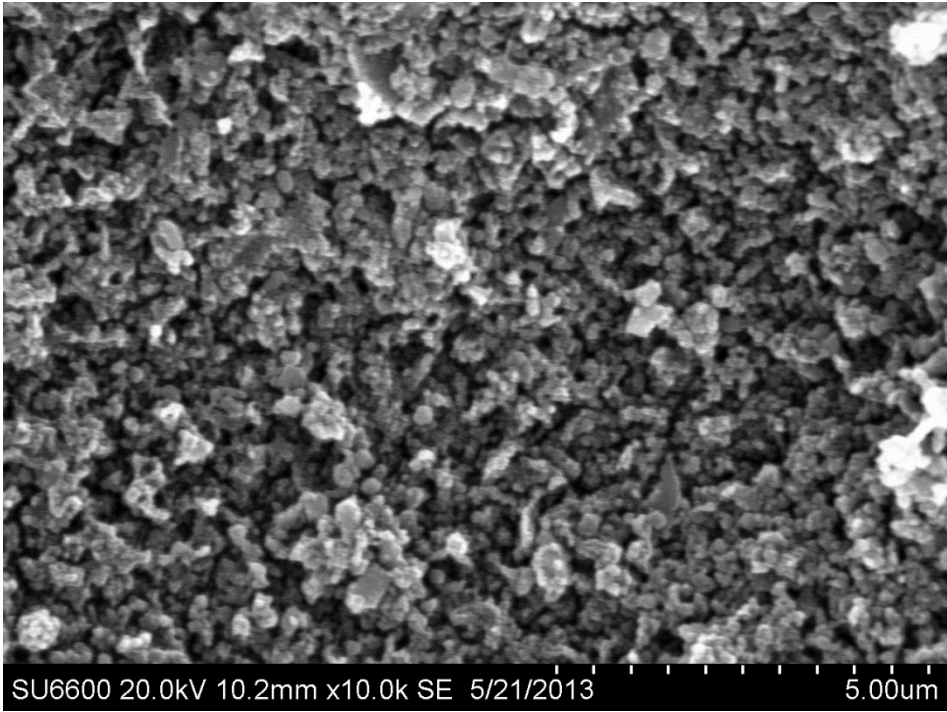
Zoom:
1kX



Scale: Calcium silicate

Cleaning: none

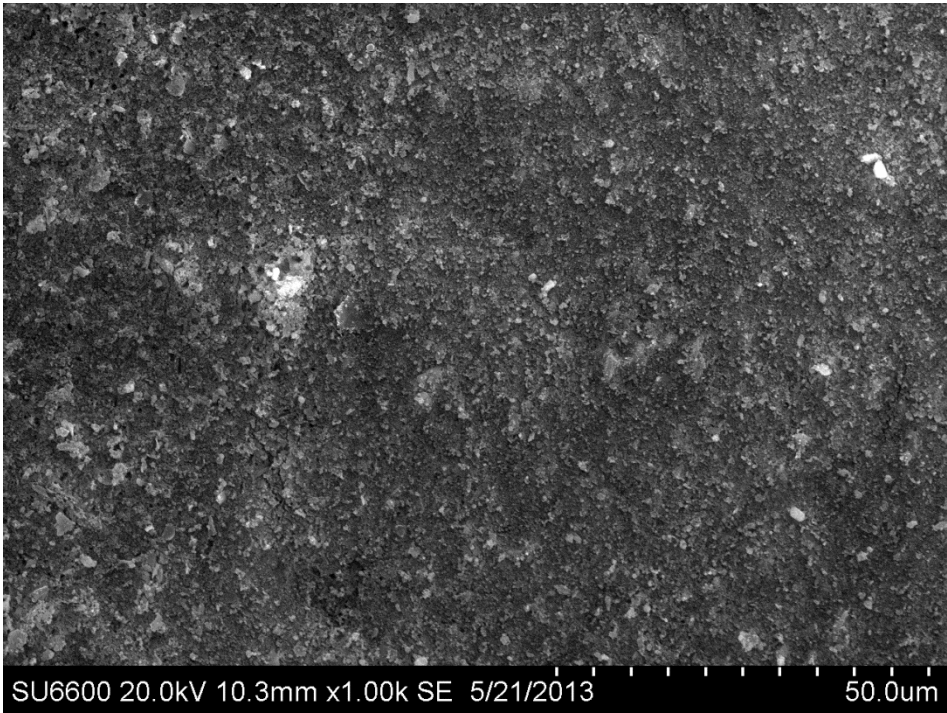
Zoom: 1kX



Scale: Calcium silicate

Cleaning: none

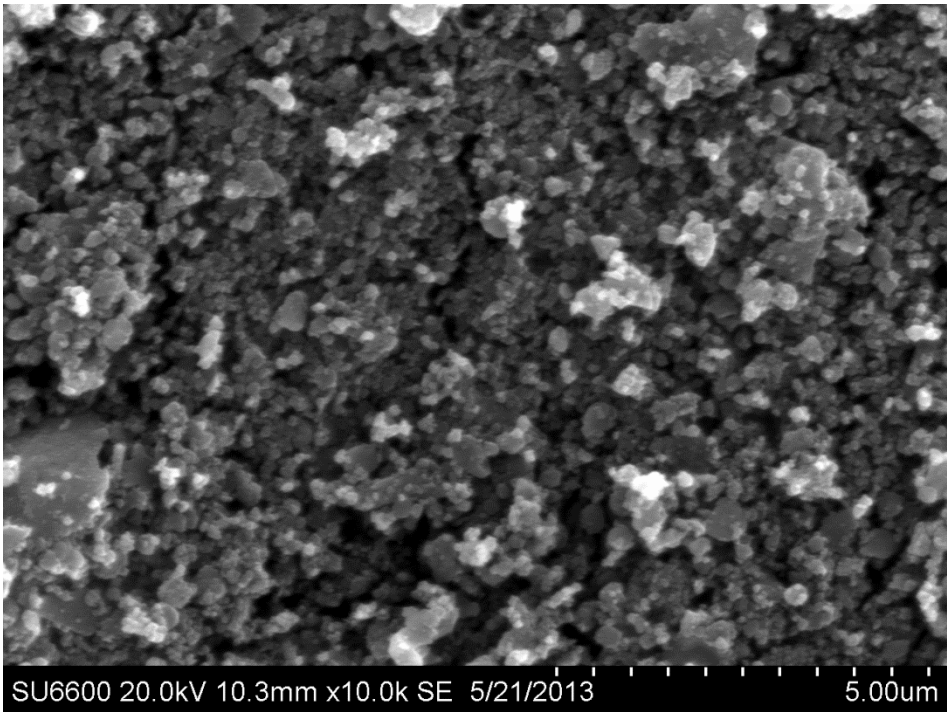
Zoom: 20kX



Scale: Calcium silicate

Cleaning: CO₂ gas

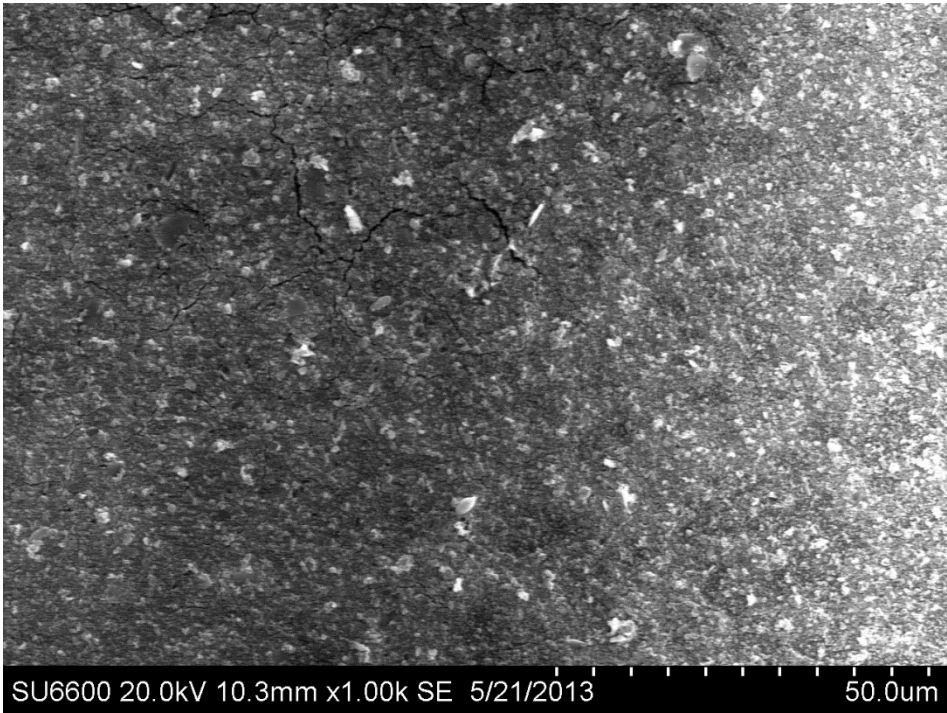
Zoom: 1kX



Scale: Calcium silicate

Cleaning: CO₂ gas

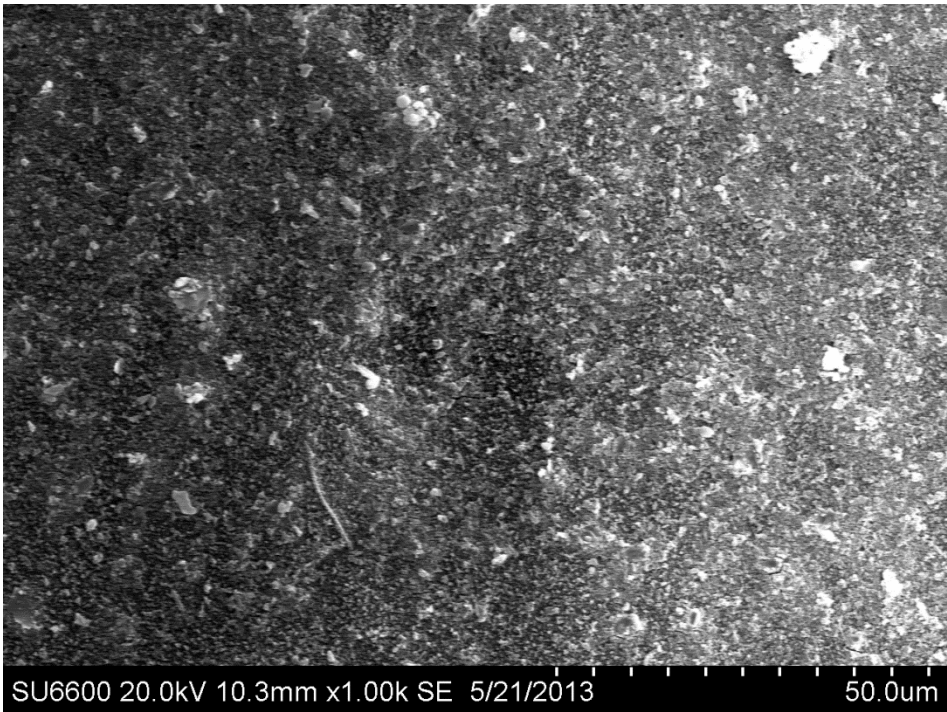
Zoom: 10kX



Scale: Calcium silicate

Cleaning: HCl at pH 3

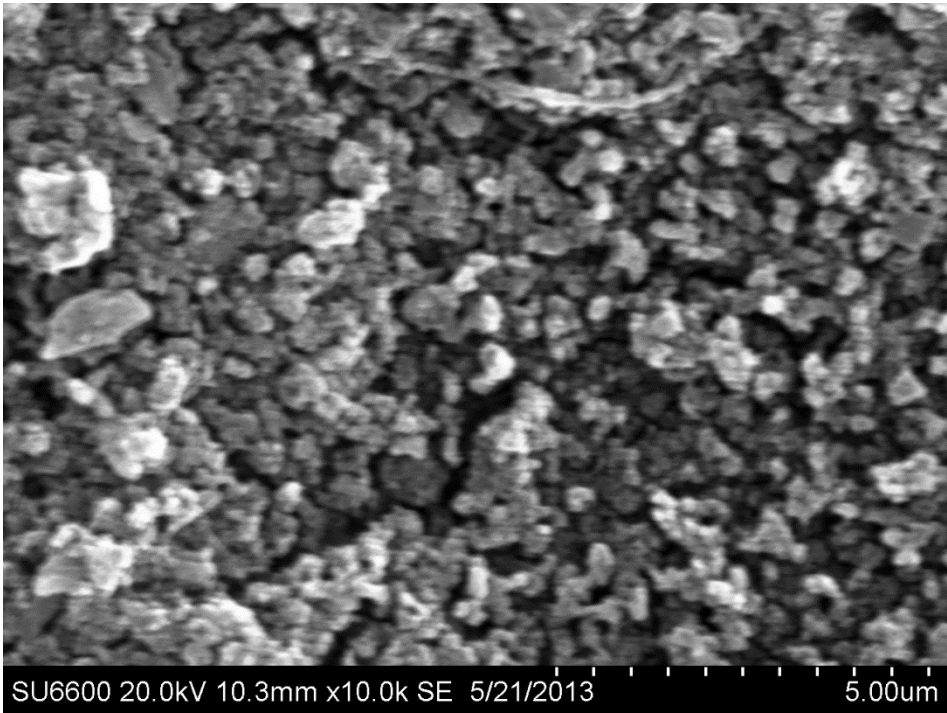
Zoom: 1kX



Scale: Calcium silicate

Cleaning: HCl at pH 3

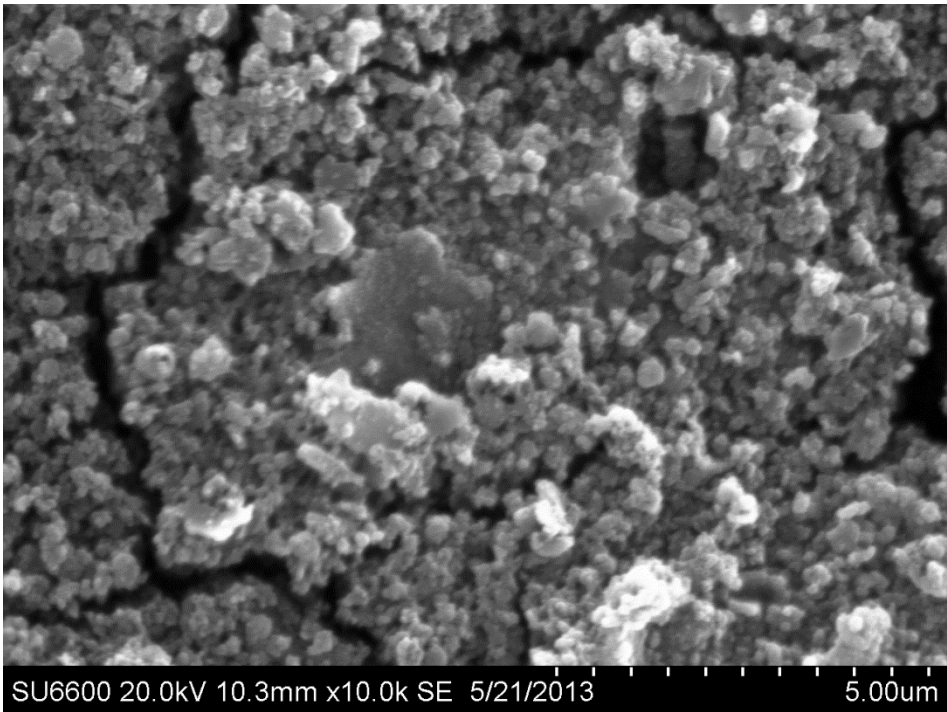
Zoom: 1kX



Scale: Calcium silicate

Cleaning: HCl at pH 3

Zoom: 10kX

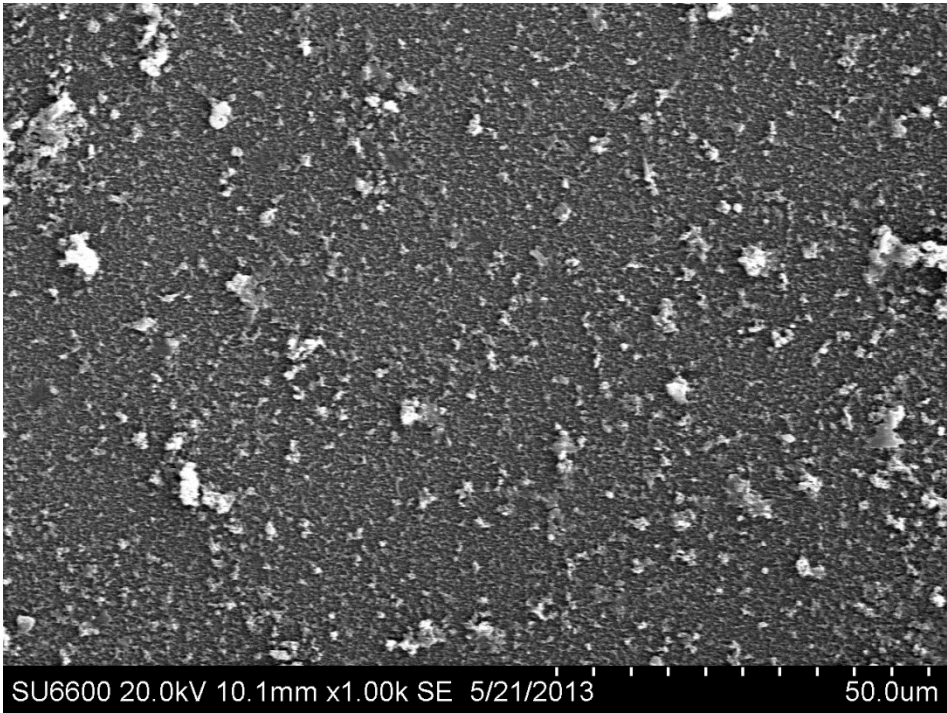


Scale: Calcium silicate

Cleaning: HCl at pH 3

Zoom: 10kX

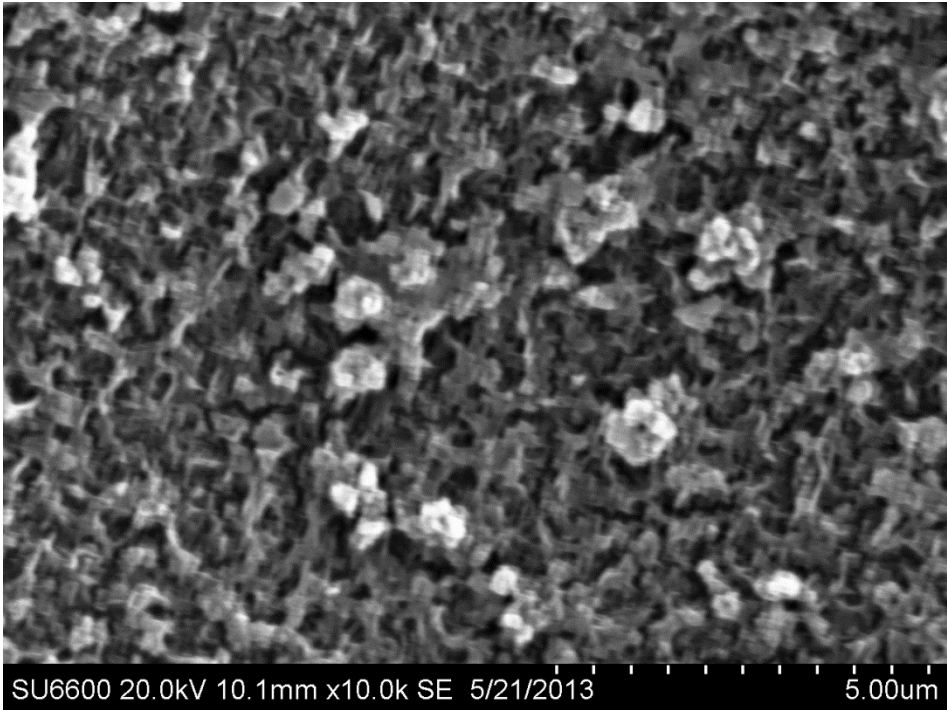
Note: cracks formed in sample during observation under SEM



Scale: Calcium silicate

Cleaning: NaOH at ph 12 and sodium dodecyl sulfate

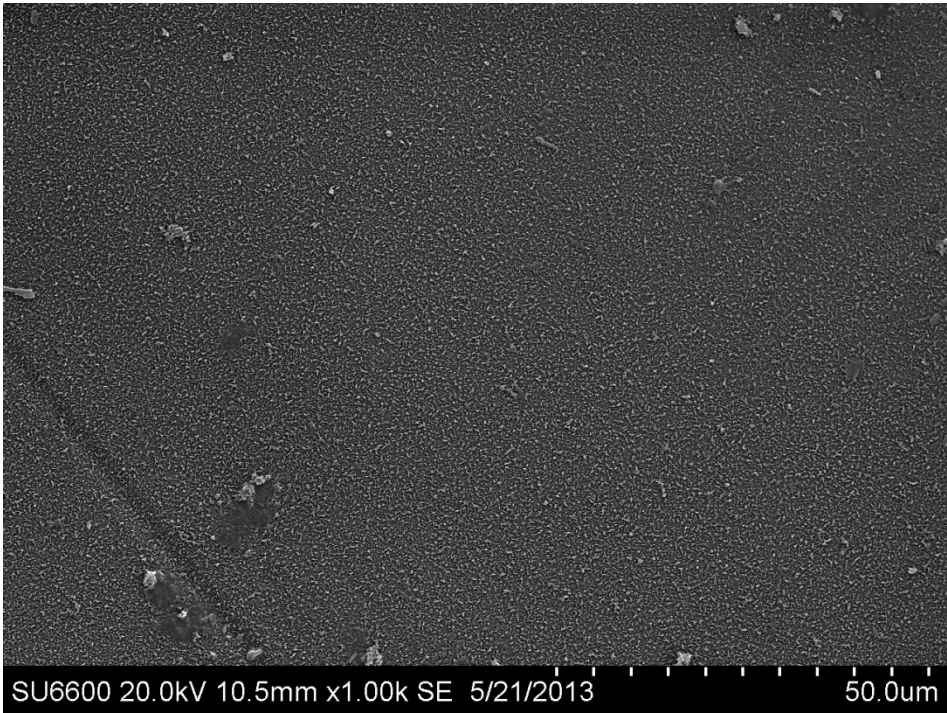
Zoom: 1kX



Scale: Calcium silicate

Cleaning: NaOH at ph 12 and sodium dodecyl sulfate

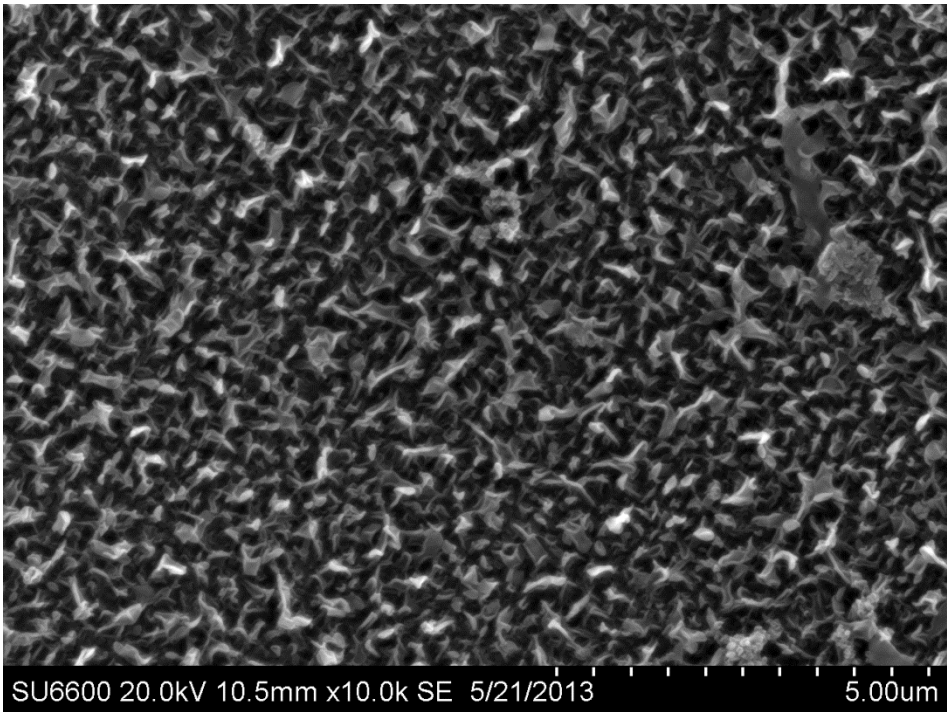
Zoom: 10kX



Scale: none

Cleaning:
compacted
membrane

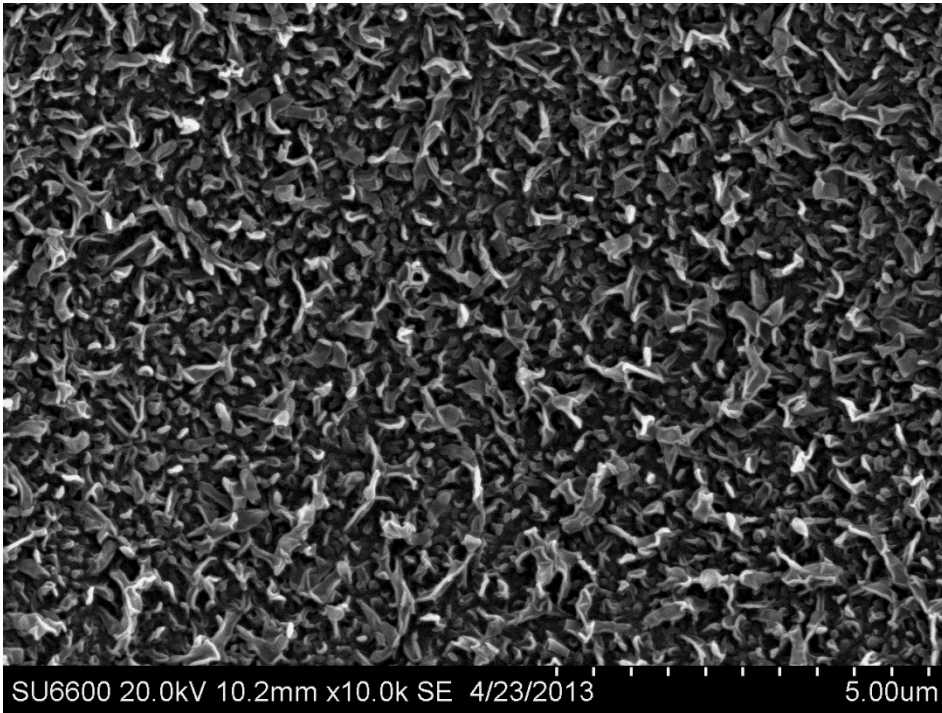
Zoom:
1kX



Scale: none

Cleaning:
compacted
membrane

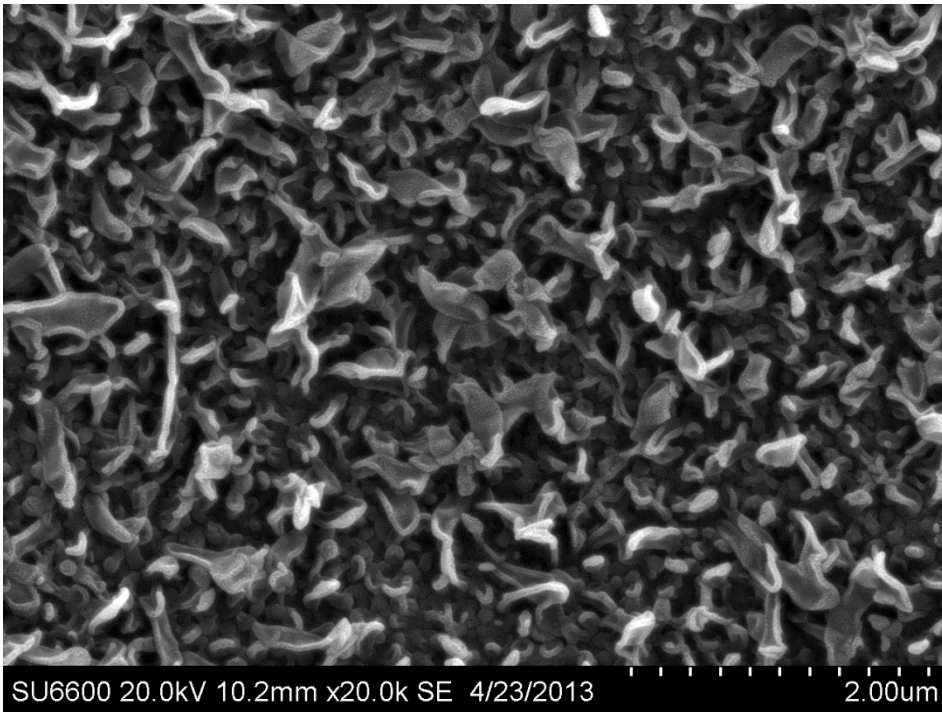
Zoom:
10kX



Scale: none

Cleaning:
none

Zoom:
10kX



Scale: none

Cleaning:
none

Zoom:
20kX

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