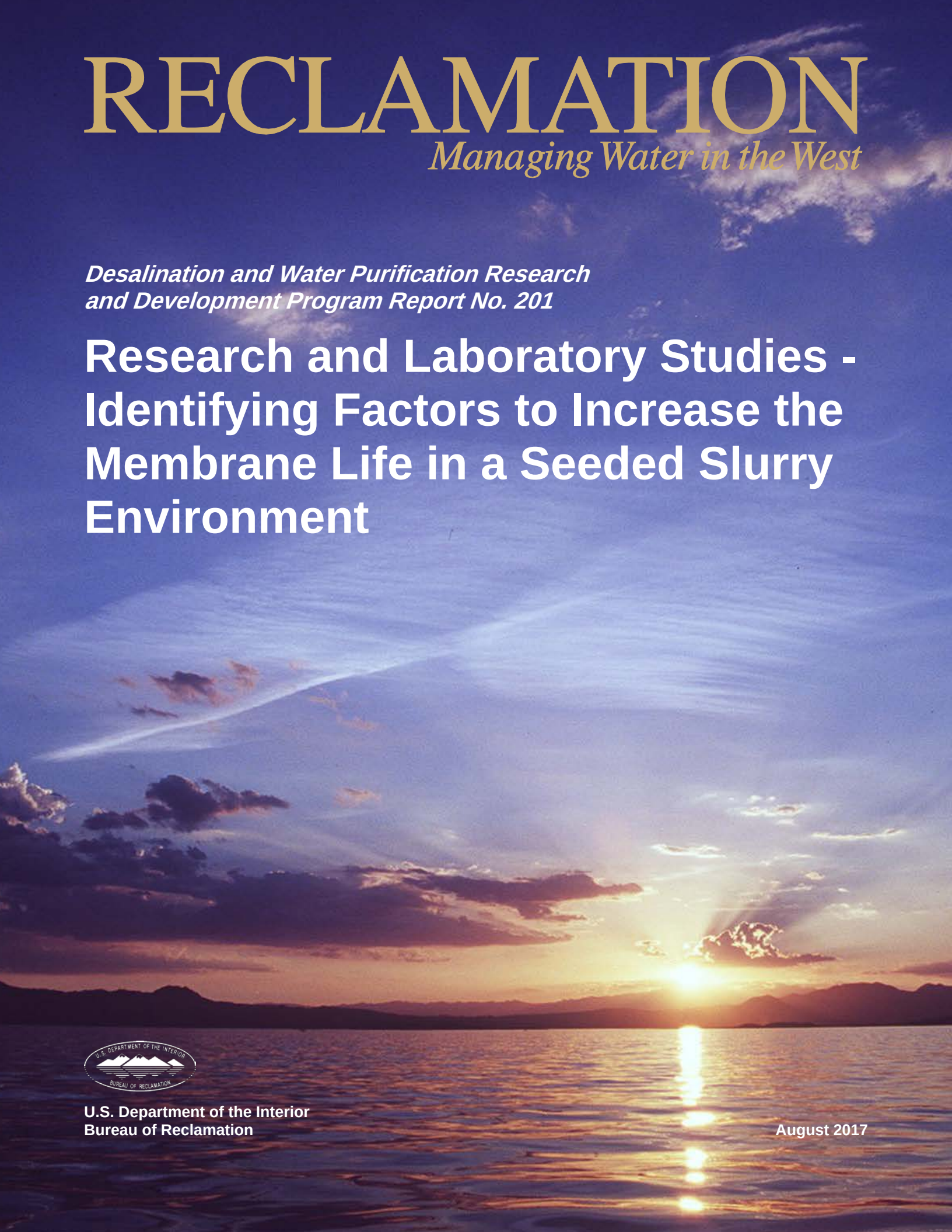

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Managing Water in the West

Desalination and Water Purification Research and Development Program Report No. 201

Research and Laboratory Studies - Identifying Factors to Increase the Membrane Life in a Seeded Slurry Environment

U.S. Department of the Interior
Bureau of Reclamation

August 2017

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14. ABSTRACT Carollo Engineers conducted this laboratory study to determine factors to increase membrane life in a seeded-slurry treatment process. In Phase 1, two tubular membranes, a polyamide thin-film composite (TFC) and a cellulose acetate (CA) membrane, were tested concurrently over a six-week period under different feed water seed concentrations and flow velocities. The seed material used during Phase 1 had a rod-like (needle) morphology. Throughout Phase 1, both membranes performed well and there was no significant difference in performance under the various conditions. There was also no evidence of impingement or damage to the membrane surface by the recirculating crystals of calcium sulfate. Phase 2 was set up with two full-scale modules in series (with TFC membranes) to run at a feed water seed-slurry concentration of 15 to 18 g/L and a tube velocity of 1.3 m/s. An error resulted in operating with only 1.9 g/L of seed and consequent failure of the test. Despite this setback, several of the goals of the study were achieved and there were several positive outcomes of this study:. recirculating seed-slurry crystals of calcium sulfate at these test levels for one week does not cause wear and tear of the membrane surface, there was no evidence of any abrasion or damage to the membrane surface due to the recirculation of the rod-like crystal morphology in Phase 1, a seed-slurry concentration of 2.5 g/L appears to be the lower limit for operating this system under the conditions encountered, and gypsum formed during the Phase 2 operation had a purity of approximately 95 percent. Other salts such as barium and silica did not appear to form on the gypsum crystals.

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Prepared for Reclamation Under Agreement No. R15AC00087

by

Principal Investigator: Graham J.G. Juby, Ph.D., P.E.

U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Water and Environmental Services Division
Water Treatment Engineering Research Team
Denver, Colorado

August 2017

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Acronyms and Abbreviations

AWC	American Water Chemicals
CA	cellulose acetate
Carollo	Carollo Engineers, Inc.
CIP	clean-in-place
DWPR	Desalination and Water Purification
DI	distilled water
DWR	Department of Water Resources
EDR	electrodialysis reversal
EDX	energy dispersive x-ray spectroscopy
EMWD	Eastern Municipal Water District
FRP	fiberglass reinforced plastic
HDPE	high-density polyethylene
IWVWD	Indian Wells Valley Water District
LOI	Loss on Ignition
NF	nanofiltration
NPF	normalized permeate flow
NSP	normalized salt passage
NSR	normalized salt rejection
O&M	operation and maintenance
ORP	oxidation reduction potential
PLC	programmable logic controller
PRS	pressure reducing station
PRV	pressure relief valve
PVC	polyvinyl chloride
PV	pressure vessel
Reclamation	Bureau of Reclamation
RO	reverse osmosis
SEI	superimposed elemental imaging
SEM	scanning electron microscopy
SG	specific gravity
SPARRO	Slurry Precipitation and Recycle Reverse Osmosis
SS	stainless steel
S.T.T.	single-tube-testers
TCF	temperature correction factor
TDS	total dissolved solids
TFC	thin film composite
TGA	thermogravimetric
TSS	total suspended solids
UCT	University of Cape Town
WMWD	Western Municipal Water District
XRD	x-ray diffraction
XRF	x-ray fluorescence

Measurements

°C	degrees Celsius
°F	degrees Fahrenheit
°K	degrees Kelvin
ft2	square foot
ft/s	feet per second
g/L	gallon per liter
gfd	gallon per day per square foot
g/min	gram per minute
gpm	gallon per minute
kg	kilogram
kg/h	kilogram per hour
kPA	kilopascal
lb/h	pound per hour
L	liter
L/day	liter per day
L/min	liter per minute
Lb	pound
M	moles per liter
m3/d	cubic meter per day
m/s	meter per second
mg/L	milligram per Liter
m2	square meter
mgd	million gallons per day
mL/15 seconds	milliliters per fifteen seconds
mL/min	milliliters per minute
mm	millimeter
MPA	megapascal
mS/cm	millisiemen per centimeter
NTU	Nephelometric Turbidity Unit
psi	pound per square inch
psig	pounds per square inch gauge
rpm	revolution per minute
µm	micrometer
µS/cm	microsiemen per centimeter

Contents

Page

1.0 Executive Summary 1
2.0 Background 2
2.1 Description of the SPARRO Process 3
2.2 Previous Research 4
2.2.1 SPARRO Pilot Testing 2008 4
2.2.2 EDR/SPARRO Testing 2010 7
2.2.3 EDR/SPARRO Testing 2013 9
2.2.4 Project Goals and Objectives 10
3.0 Technical Approach 11
3.1 Methodology 11
3.1.1 Equipment and Site 11
3.1.2 Repairs and Modifications to SPARRO Pilot Plant 14
3.1.3 Installation, Testing, and Commissioning 17
3.1.4 Source Water for Pilot Testing 21
3.1.5 SPARRO Pilot Unit Description 22
3.2 Laboratory Sampling and Data Collection 27
3.2.1 Water Samples 27
3.2.2 Seed Samples 29
3.2.3 Data Collection 30
3.3 Interpretation of Performance Data 31
4.0 Results and Discussion 34
4.1 SPARRO Performance Results - Phase 1 34
4.1.1 Phase 1 Timeline and Operation 34
4.1.2 SPARRO Start-Up 37
4.1.3 Seed Material 38
4.1.4 Feedwater Quality 41
4.1.5 Hydraulic Performance 43
4.1.6 Membrane Performance 45
4.1.7 Phase 1 Discussion 49
4.2 SPARRO Performance Results - Phase 2 50
4.2.1 Phase 2 Timeline and Operation 50
4.2.2 SPARRO Start-Up 52
4.2.3 Feed Water Quality 54
4.2.4 Hydraulic Performance 55
4.2.5 Membrane Performance 57
4.2.6 Solids Morphology and Production 66
4.2.7 Membrane Autopsy 72
5.0 Summary and Conclusions 76
5.1 Progress with Respect to Project Goals 76
5.2 Additional Conclusions and Observations 77

Appendices

Appendix A Phase 1: Master Field Data Sheet
Appendix B Phase 2: Master Field Data Sheet
Appendix C University of Cape Town – Gypsum Crystallization Particle Analysis
Appendix D Additional Graphs
Appendix E OMYA – Gypsum Purity Analysis
Appendix F American Water Chemical – Membrane Autopsy on pressure vessel (PV) PV-1 TFC Membranes

Tables

Table 1. Summary of SPARRO Water Quality Data (2008 Study at EMWD) 4
Table 2 Phase I Testing Conditions Matrix 11
Table 3. SPARRO Pilot Modifications List 15
Table 4. Phase 1 SPARRO Pilot Design Criteria 23
Table 5. Phase 2 SPARRO Pilot Design Criteria 25
Table 6. Phase 1 – EMWD Laboratory Testing Plan 28
Table 7. Phase 2 – EMWD Laboratory Testing Plan 29
Table 8. TFC vs. CA Permeate Flow Variation 36
Table 9. EDX Analyses for Silica on End of Condition 2 and Start of Condition 3 Recirculating Seed (Analyzed by UCT)[(1)] 41
Table 10. Average SPARRO Feedwater Quality – Phase 1 42
Table 11. Average SPARRO Water Quality Analyzed by EMWD –Phase 1[(1)] 46
Table 12. Average SPARRO Feedwater Quality – Phase 2 54
Table 13. Average SPARRO Water Quality Analyzed by EMWD –Phase 2[(1)] 58
Table 14. Mass Balance Based on Laboratory Data for September 6, 2016 65
Table 15. Mass Balance Based on Laboratory Data for September 21, 2016 65
Table 16. Solids Samples Analyzed by EMWD for Metals 71

Figures

Figure 1. Schematic of seeding and precipitation concept in SPARRO. 3
Figure 2. SPARRO permeate flux and rejection. 5
Figure 3. SPARRO recovery and apparent seed concentration. 5
Figure 4. SEM and EDX analysis of gypsum seed (Reclamation, 2008) 6
Figure 5. SPARRO feed, permeate, and concentrate conductivity 7
Figure 6. EDR Recovery With and Without SPARRO Operation 8
Figure 7. EDR/SPARRO makeup flow concentration changes. 9
Figure 9. Pharmaceutical food grade gypsum sample washed. 13
Figure 8 Commercially available gypsum sample washed. 13
Figure 10. Gypsum seed made in Carollo's laboratory that show the "platelet" morphology. 14
Figure 11 . SPARRO feed line piping from Train C. 17
Figure 12. Feed tank controls and elements. 18
Figure 13. Permeate tank with submersible pump. 19
Figure 14. Configuration of the single-tube testers that shows the TFC backpressure valve and pressure gauge. 20
Figure 15. Elements of the automatic blowdown system. 21
Figure 16. 6-mgd (22,700 m3/d) Arlington Desalter. 22
Figure 17. Side view of Phase 1 Pilot Unit. 23
Figure 19. Phase 2 process flow diagram (single-tube testers not shown). 26
Figure 20. Timeline of Phase 1 pperations. 35
Figure 21. pH vs Time for Phase 1 That Show Uncontrollable pH Readings up Until the End of Condition 2 36
Figure 22. Salt test - salt rejection vs. time for Condition 1 Run 2. 37
Figure 23. Salt test - salt rejection vs. time for Condition 4. 38
Figure 24. Crystal morphology of the gypsum seed crystals by the end of Phase I Condition II. 39
Figure 25. Crystal morphology of the gypsum seed crystals at the Beginning of Phase I Condition III. 39
Figure 26. SEM image of 0.4 M gypsum. 40
Figure 27. SEM image of 0.6 M gypsum. 40
Figure 28. SPARRO feedwater quality for Phase 1 (EMWD). 43
Figure 29. SPARRO concentrate flow vs. time for Phase 1. 43
Figure 30. TFC and CA permeate flow vs. time (Phase 1). 44
Figure 31. SPARRO system pressure vs. time (Phase 1). 44
Figure 32. TFC and CA normalized permeate flow vs. time (Condition 1 and 2). 45
Figure 33. Phase 1 Conductivity vs. time (measured by EMWD). 47

Figure 34. Phase 1 Conductivity vs. Time (Site Measurements).....48
Figure 35. pH vs. time for Phase 1. 48
Figure 36. Phase 1 solids concentration vs. time (site measurements). 49
Figure 37. Timeline of Phase II Operation 51
Figure 38. Kinked membrane during removal for cleaning after blockage on September 23. 52
Figure 39. Salt rejection vs. time for beginning and end of Phase 2 53
Figure 40. SPARRO feedwater quality for Phase 2 (EMWD). 55
Figure 41. TFC permeate flow vs time for Phase 2. 56
Figure 42. TFC normalized permeate flow vs. time (Phase 2). 56
Figure 43. SPARRO system pressure vs. time (Phase 2). 57
Figure 44. pH vs. time (Phase 2). 59
Figure 45. TDS vs. time (Phase 1 and 2). 60
Figure 46. Silica vs. time (Phase 1 and 2). 60
Figure 47. Normalized salt passage vs. time (Phase 2). 61
Figure 48. Total suspended solids vs. time for Phase 2 (measured by EMWD). 61
Figure 49. Solids concentration vs. time for Phase 2 (site measurements).....62
Figure 50. Comparison of on-site measurements and EMWD laboratory solids concentration values 63
Figure 51. Membrane rejection for each parameter measured before blockage. 64
Figure 52. New batch of seed crystals at start of Condition 3. 67
Figure 53. Combined seed sample after three weeks of operation from the start of Phase 1. 67
Figure 54. Sample of feed tank seed at start of Phase 2. 68
Figure 55. Sample of solids from feed tank after 230 hours of operation. 69
Figure 56.Sample of seed material from the feed tank taken at the end of Phase 2 70
Figure 57. Inspection of feed and permeate side of fouled and virgin membrane that . shows brown foulant (top left), sporadic brown spots (top right), and brown, green, and yellow deposit along seam (bottom). 73
Figure 58. Dye test of fouled membrane that shows feed (left) and permeate (right) sides after dye penetration. 74
Figure 59. Dye test of virgin membrane showing feed (left) and permeate (right) sides. 74
Figure 60 . Superimposed elemental imaging (SEI) of barium sulfate, calcium sulfate, and amorphous silica. 75
Figure 61. Electron micrograph of the membrane surface damage at 500 times magnification.....76

1.0 Executive Summary

To increase the supply of usable water from existing and future groundwater desalting systems, technologies to increase recovery and decrease the volume of concentrate from these systems need to be developed. To reduce the volume of concentrate for disposal, the recovery of desalting processes needs to increase.

One approach couples electrodialysis reversal (EDR) with the Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) process to increase recovery.[1] The SPARRO process allows salts to precipitate naturally, as concentration increases, on calcium sulfate seed crystals, does not require chemicals for softening, and produces a calcium sulfate byproduct that has potential uses by local industries. Previous tests of this approach indicated the need to investigate the membrane life using this process. This laboratory study's goal was to determine factors that might increase membrane life in a seeded-slurry treatment process, thereby reducing the operational costs of the process, making it a more viable alternative.

The project was split into two phases. During Phase 1, two tubular membrane types, a polyamide thin-film composite (TFC) and a cellulose acetate (CA) membrane, were tested concurrently over a six-week period under different conditions. The conditions were different feed water seed-slurry concentrations (the goal was to operate at concentrations of 10 and 18 gallons per liter (g/L), but the actual measured values averaged 9.6 g/L) and two different cross-flow velocities (1.0 and 1.5 meters per second [m/s]). The seed material used during Phase 1 had a rod-like (needle) morphology. Throughout the six-week Phase 1 period, both membranes performed well and there was no significant difference in performance under the different conditions of feed water seed-slurry concentration or cross-flow tube velocity. There was also no evidence of impingement or damage to the membrane surface by the recirculating crystals of calcium sulfate.

As the TFC membrane achieved a slightly better salt rejection and higher flux during Phase 1, this membrane was selected for the Phase 2 operation. Phase 2 was set up with two full-scale modules in series to run at a feed water seed-slurry concentration of 15 to 18 g/L and a tube velocity of 1.3 m/s. Unfortunately, due to an error in the on-site method used to estimate the concentration of the seed crystals in the feed water, Phase 2 operation began with a seed-slurry concentration of only 1.9 g/L. During this time the precipitation rate of gypsum in the system was calculated to be 5.0 pounds per hour (lb/h) (2.3 kilograms per hour [kg/h]). The high precipitation rate coupled with the very low seed-slurry concentration is thought to have overwhelmed the crystal formation capacity of the seed material, leading to precipitation (scale) on other parts of the system.

[1] Carollo has received a U.S. patent for this combination referred to as the Brine Loop Treatment Process (Patent No. U.S. 9,561,471 B2).

Within 130 hours of operation, the system became clogged with large chunks of solid precipitate. This event and the effort that followed to unclog the membranes resulted in severe damage to the membranes and early termination of the Phase 2 test period after about 530 hours of operation.

Despite the unfortunate events at the start of Phase 2, several of the goals of the study were achieved and there were several positive outcomes of this study. Firstly, the results demonstrated that recirculating seed-slurry crystals of calcium sulfate at around 10 g/L concentration for one week does not cause wear and tear of the membrane surface. This was demonstrated over four separate runs. There was no significant change in performance of both membrane types between the start and end of any of the conditions tested during Phase 1. Secondly, the crystal morphology present in Phase 1 was rod-like (needles), and as mentioned, there was no evidence of any abrasion or damage to the membrane surface due to the recirculation of this material. Thirdly, operating at a seed-slurry concentration below 2 g/L under the conditions of the test is not recommended. A seed-slurry concentration of 2.5 g/L appears to be the lower limit for operating this system under the conditions encountered. Fourthly, the results indicated that gypsum formed during the Phase 2 operation had a purity of approximately 95 percent. Other salts such as barium and silica did not appear to form on the gypsum crystals.

2.0 Background

As water scarcity continues in many regions throughout the United States, there is a growing interest in desalination of impaired water sources. One of the major limitations of desalination is the concentrated waste stream that is produced by traditional technologies, such as reverse osmosis (RO). Typically, RO can recover between 70 and 85 percent of the influent water in brackish water systems, resulting in a significant amount of concentrate that requires disposal. The disposal of the concentrate stream is often challenging and can be cost prohibitive for locations where ocean disposal is not feasible. Even for inland regions of Southern California where a regional concentrate pipeline to the ocean exists, concentrate disposal costs continue to increase as long-term operational issues arise with pipeline scaling, maintenance, and decreased line capacity.

To reduce the volume of concentrate for disposal, the recovery of desalting processes needs to increase. However, increasing recovery can be challenging because the overall recovery of a desalination process is determined by the concentration of the least soluble sparingly soluble salt (e.g., calcium carbonate, calcium sulfate, silica). To recover water beyond the solubility limit, solid salts must be removed from the process. Several processes, including lime softening followed by a secondary desalting unit, have been tested, and some full-scale installations are now being implemented. While these processes successfully reduce concentrations of sparingly soluble salts, they can use a significant amount of chemicals and produce a large amount of solid waste.

In 2013, Carollo Engineers (Carollo) completed a DWPR-funded project that evaluated a new treatment approach using a combination of two proven membrane processes. This technology approaches concentrate minimization from a different angle by allowing salts to precipitate, in a controlled manner, in the secondary desalting unit instead of removing salts ahead of secondary desalting. The approach couples EDR with the SPARRO process to increase recovery. The SPARRO process allows salts to precipitate naturally, as concentration increases, on calcium sulfate seed crystals, does not require chemicals for softening, and produces a calcium sulfate byproduct that has potential uses by local industries.

2.1 Description of the SPARRO Process

The SPARRO process is a hybrid of conventional RO technology. It incorporates the recirculation of seeded slurry through the RO system, promoting homogeneous nucleation and precipitation of super saturated salts from the solution. This process was first developed to treat cooling tower blowdown from power plants high in calcium and sulfate ions. Seed crystals (gypsum) are introduced to the feed stream, which are then pumped into tubular RO membranes. As the water is concentrated along the membranes, the solubility product of calcium sulfate is exceeded; and it preferentially precipitates on the seed material rather than on the membranes. Figure 1 shows a schematic of the seeding concept in the SPARRO process.

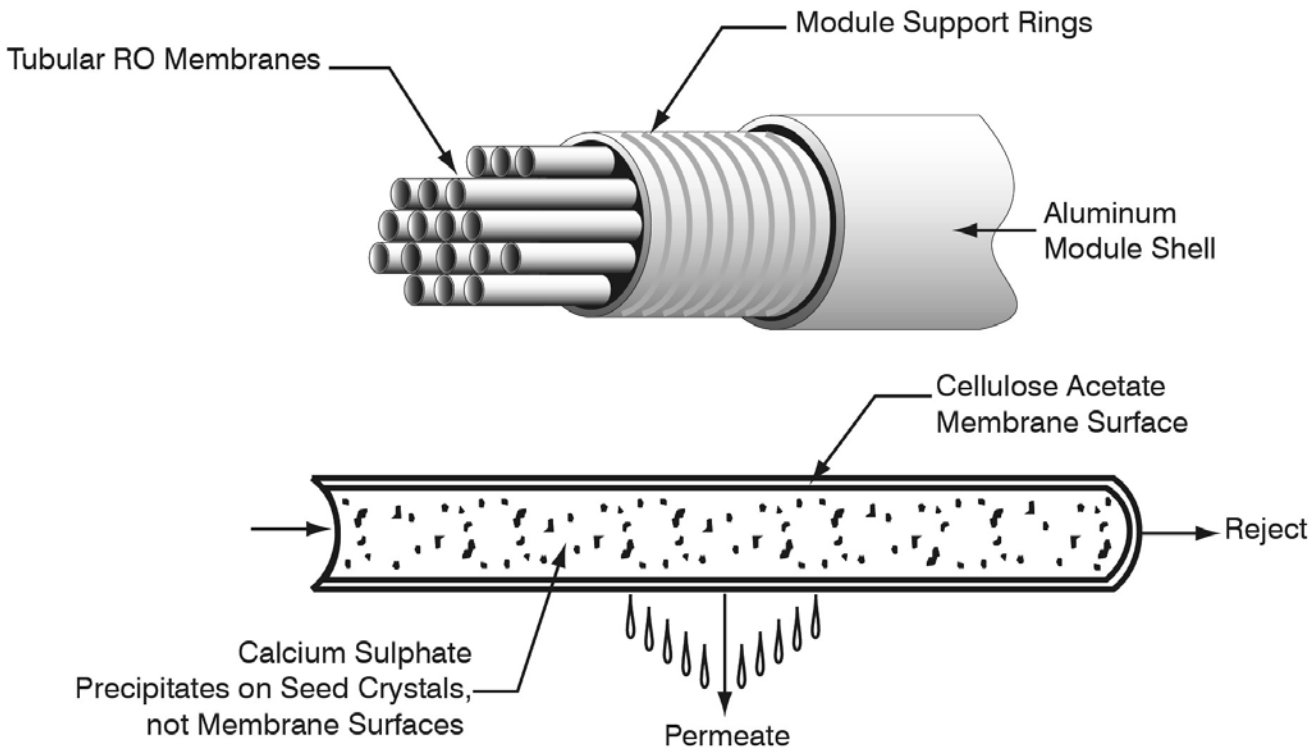

Figure 1. Schematic of seeding and precipitation concept in SPARRO.

2.2 Previous Research

The seeded RO process has been tested at the pilot-scale for treating cooling tower blowdown (O'Neail et al., 1981), and the SPARRO process has been tested at pilot-scale for treating highly scaling mine water (Juby, 1996), and more recently for treating secondary concentrate (Reclamation, 2008; DWR, 2010; USBR, 2013). The following subsections will summarize Carollo's previous SPARRO pilot research findings and the justification for this project.

2.2.1 SPARRO Pilot Testing 2008

The SPARRO process was tested at the Eastern Municipal Water District (EMWD) in Sun City, California, in 2008. The complete results of the study were published in a Reclamation report (2008). For the 2008 study, the pilot unit was operated as a batch process for approximately 3 hours per day over several days and nanofiltration (NF) membranes were used in the SPARRO membrane vessel. The permeate produced from the SPARRO process was removed and periodically sampled for laboratory analysis. The concentrate leaving the membrane vessel was piped through a pressure-reducing system and returned to the feed tank. The solution in the feed tank was allowed to increase in concentration to simulate operation at different water recovery levels. Solid gypsum was not removed from the system in this case and, therefore, the gypsum concentration in the feed solution increased with time.

The SPARRO process was tested on a concentrate solution from an RO process that was supersaturated with calcium sulfate and had a total dissolved solids (TDS) concentration of 18,600 milligrams per liter (mg/L). Water quality data from the testing is summarized in Table 1.

Table 1. Summary of SPARRO Water Quality Data (2008 Study at EMWD)

Parameter	Units	Feed	Product	Concentrate
TDS	mg/L	18,600	10,400	22,300
Sodium	mg/L	4,100	1,700	5,500
Calcium	mg/L	2,200	950	1,600
Magnesium	mg/L	600	300	700
Chloride	mg/L	9,900	5,700	10,600
Sulfate	mg/L	2,200	600	3,300
Bicarbonate	mg/L	200	100	300

The SPARRO process, with NF membranes, was able to achieve an overall salt rejection of 50 to 60 percent and a permeate flux rate as shown on Figure 2. The highest recovery that was achieved during operation was about 60 percent, as shown on Figure 3. In this case, the SPARRO system was operated in batch mode

with recycle and, hence, a linear trend in recovery from 0 to 60 percent was observed. The recovery was limited by the size of equipment and not by membrane performance. After 180 minutes of operation, the feed volume in the tank had decreased to below the level of the mixer and the system had to be shut down to prevent settling of the gypsum seed crystals.

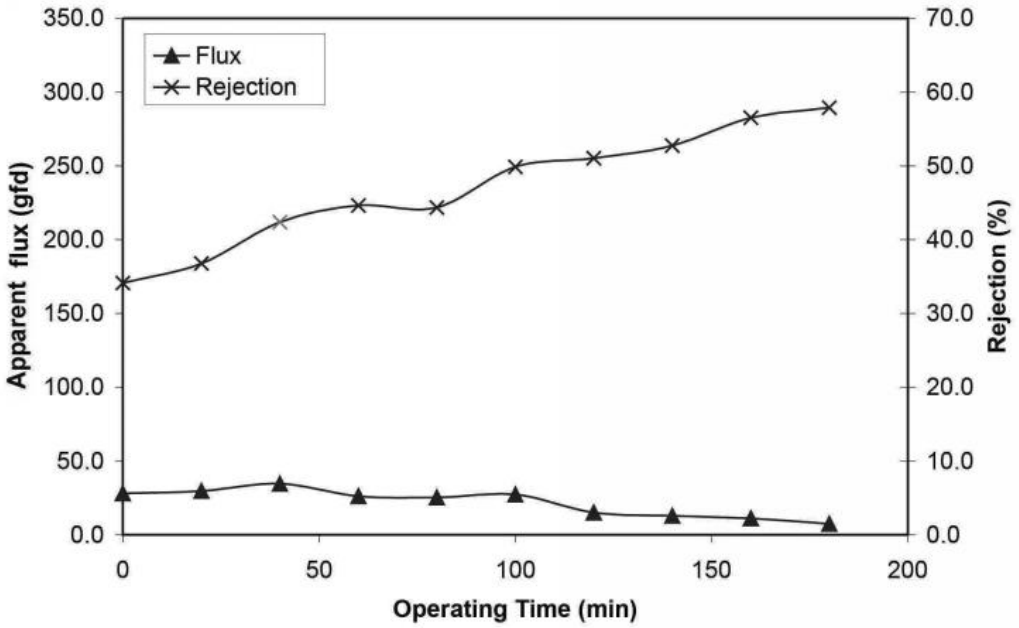

Figure 2. SPARRO permeate flux and rejection.

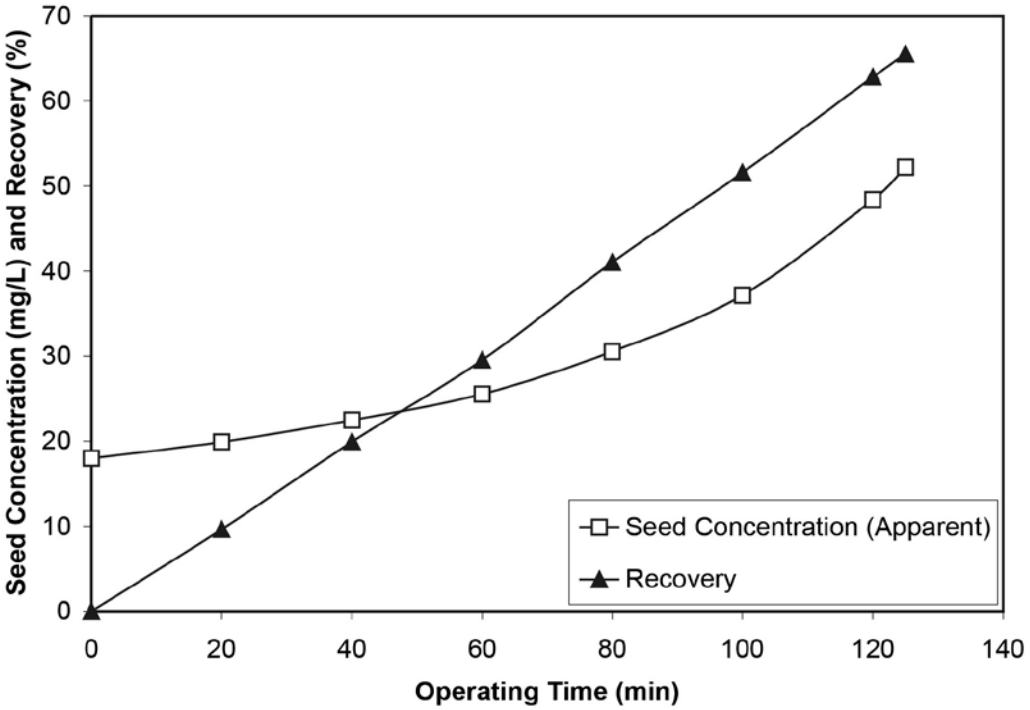

Figure 3. SPARRO recovery and apparent seed concentration.

The success of the seeded technique could be inferred not only from the apparent concentration increase of gypsum seeds in the system as shown on Figure 3, but also from scanning electron microscopy (SEM) imaging and energy dispersive x-ray spectrometer (EDX) analysis of the resulting gypsum seed. The presence of crystallites in the 1- to 5-micrometer (µm) size range on larger gypsum seeds (10 to 50 µm) (Figure 4 top) indicates that mineral salts precipitated on the seed crystals. EDX analysis (Figure 4 bottom) confirmed that predominantly only calcium and sulfate precipitation occurred, shown by the large "Ca," "O," and "S" identification peaks; indicating a predominantly calcium sulfate by-product.

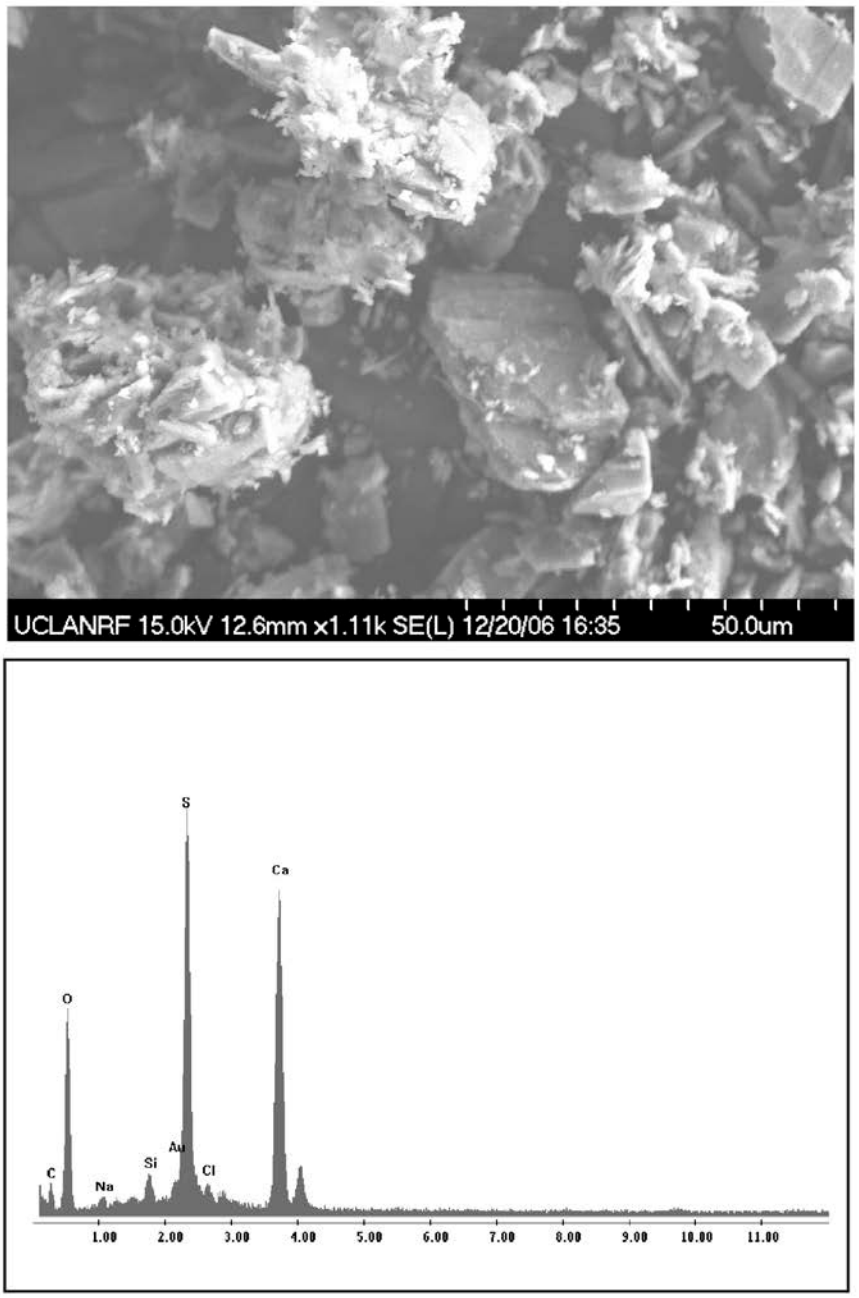

Figure 4. SEM and EDX analysis of gypsum seed (Reclamation, 2008)

The integrity of the tubular NF membrane was intact for the duration of the SPARRO testing, as demonstrated by the data shown on Figure 5. The permeate conductivity was monitored throughout the pilot-testing duration and remained constant at around 21 millisiemens per centimeter (mS/cm). In addition, the clarity of the permeate stream was monitored throughout plant operation. If the seeded slurry had punctured the membrane surface, the damage would translate to an increase in the permeate conductivity and/or visible turbidity in the water. No such observations were made during the course of testing.

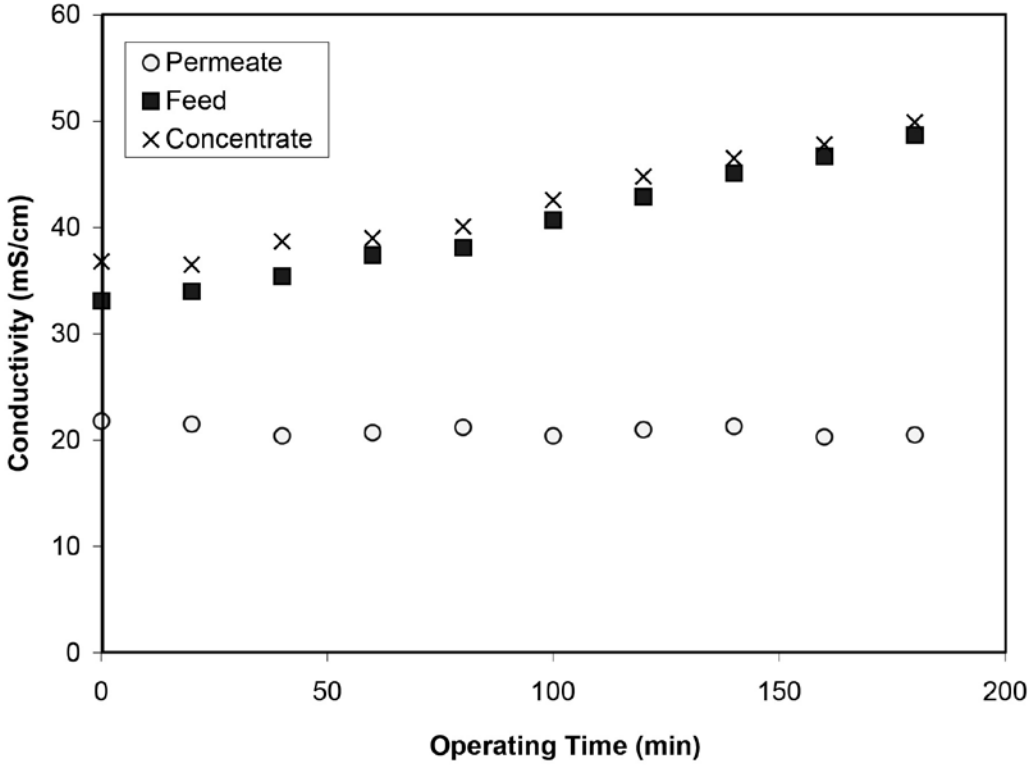

Figure 5. SPARRO feed, permeate, and concentrate conductivity

2.2.2 EDR/SPARRO Testing 2010

The EDR/SPARRO process combination was tested at the Indian Wells Valley Water District (IWVWD) in Ridgecrest, California, during 2009 and 2010. The results are published in a California Department of Water Resources (DWR) report (DWR, 2010). During this pilot testing, the SPARRO system was tested in conjunction with an EDR unit using tubular RO membranes, for two weeks to determine whether the overall recovery of the EDR unit could be increased. Similar to the previous study, the SPARRO process was operated with the EDR batch-wise, but in this case for approximately 8 hours per day. During the other 16 hours of the day, the EDR was operated without the SPARRO unit to compare EDR performance, both with and without the SPARRO system.

Comparing the recovery of the EDR only and the EDR/SPARRO process combination (Figure 6), it can be seen that the EDR/SPARRO combination

resulted in a greater recovery. The average recovery with the EDR alone was 77 percent, whereas recovery of the EDR/SPARRO combination unit was 84 percent. This 7-percent increase equates to a 37-percent reduction (1.6 gallons per minute [gpm] to 1.0 gpm) in concentrate flow from the EDR unit. Such a reduction would have a significant cost benefit for any downstream concentrate disposal process, be it a highly capital-intensive brine concentrator or double-lined evaporation pond.

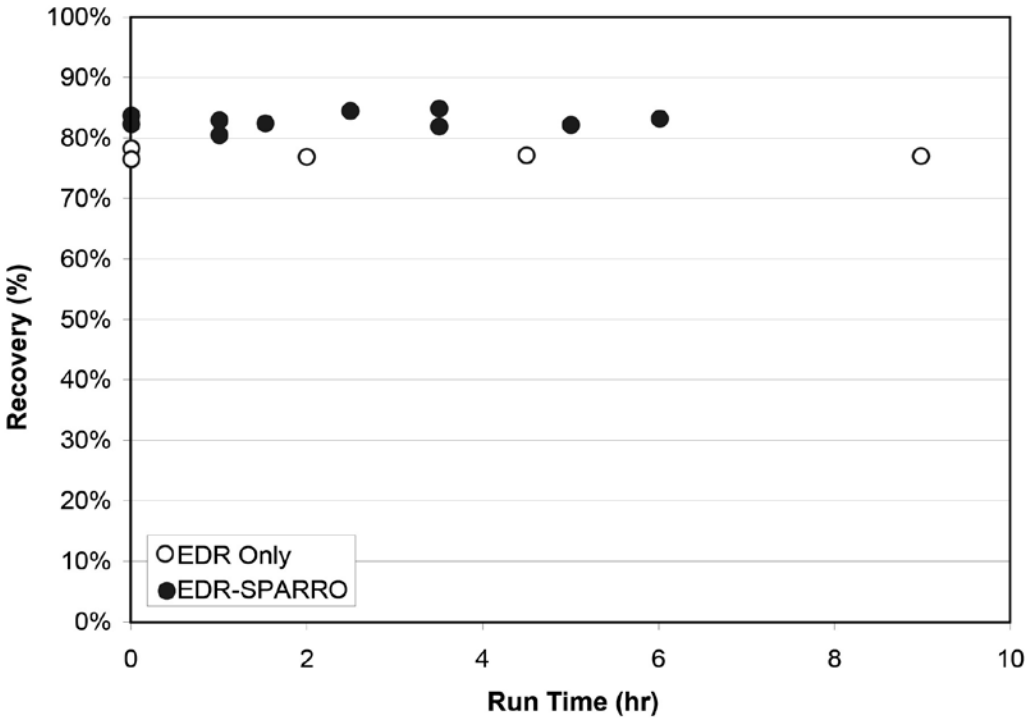

Figure 6. EDR Recovery With and Without SPARRO Operation

In addition to increased recovery, the SPARRO process improved the performance of the EDR. The EDR product conductivity was consistently 10 microsiemens per centimeter (µS/cm) lower when operating with the SPARRO than without. The SPARRO unit also improved the quality of the EDR makeup water. The makeup water in the EDR process is used to replace the volume of water that is lost to the concentrate blowdown and is typically comprised of EDR feedwater. In the EDR/SPARRO process, a portion of the EDR makeup is replaced with permeate from the SPARRO process. By replacing the EDR makeup with SPARRO permeate, the concentrations of sparingly soluble salts are reduced in the EDR concentrate loop. The SPARRO process reduced the calcium, sulfate, and silica concentrations in the EDR makeup flow by 72, 43, and 77 percent, respectively (Figure 7).

The 2010 report concluded that the EDR/SPARRO process combination was able to improve EDR performance and increase EDR recovery, but further testing to determine the reliability of the process was necessary.

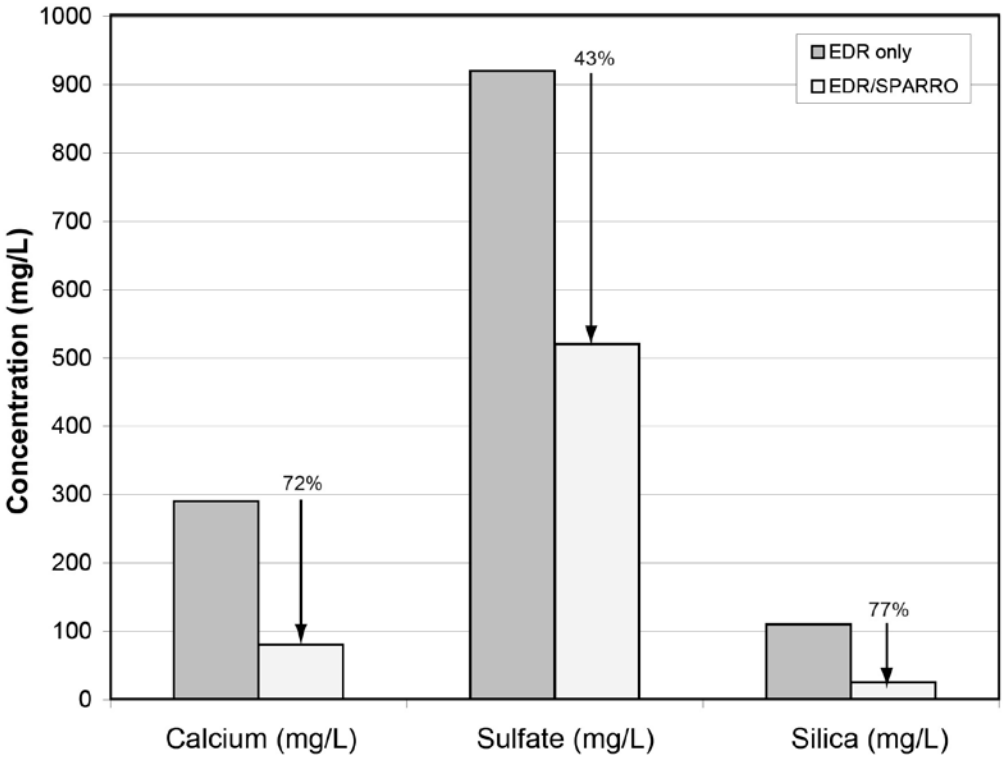

Figure 7. EDR/SPARRO makeup flow concentration changes.

2.2.3 EDR/SPARRO Testing 2013

The combination of the EDR and SPARRO processes was further tested at pilot scale on RO concentrate from the Temescal Desalter for the City of Corona, California, in 2013. The complete results of the study have been published in Reclamation (2013). During this testing, the EDR process operated for a total of 1,950 hours, while the EDR/SPARRO combination operated on and off for two months, which included 200 hours of combined operating time on RO concentrate. Carollo carried out this test through funding received from the DWPR Program in 2011 (Reclamation, 2013).

The 2013 study proposed to demonstrate that the EDR and SPARRO process can continuously operate well in combination, to establish optimum operating parameters of the EDR/SPARRO process, to estimate capital and operation and maintenance (O&M) costs of the EDR/SPARRO process, and to investigate marketability of high-purity gypsum solids produced in the EDR/SPARRO process. Most of the project goals were achieved:

- It was clearly demonstrated that the two processes can operate well in combination, and that the EDR process automatically adjusts its hydraulic balance to accommodate return flows to the EDR brine loop from the SPARRO process.

- Combining the two processes increases the EDR recovery. Using the values obtained from the pilot study and extrapolating them to account for a system in which all EDR concentrate would be fed to the SPARRO unit, the overall recovery of the combined system would be 85 percent. This compares with a recovery of 60 to 65 percent for the EDR operating on its own. The increase in recovery for the EDR/SPARRO combination would reduce the volume of brine for final disposal by 57 percent, and increase the overall recovery at the desalter to around 96.6 percent.

- The EDR/SPARRO combination improves the EDR quality. The EDR product water TDS concentration dropped by 15 percent when the SPARRO unit was in operation.

- Preliminary cost estimates showed that using the EDR/SPARRO combination would make economic sense where current brine disposal costs are high, and where the cost of alternative water sources is also high.

A market survey indicated that the solid byproduct could be used in local industries and/or as a soil amendment.

One key goal of the 2013 work was to establish the life expectancy of tubular RO membranes operating in the SPARRO configuration. However, due to the limited operating time in combination with the EDR unit (about 200 hours) and some limitations with the equipment, this goal could not be achieved. Consequently, the life expectancy of tubular RO membranes operating in the seeded slurry environment remained unclear. Additional studies are needed to investigate the membrane life.

2.2.4 Project Goals and Objectives

Based on the above, the major goal of the current study work in 2016 was to identify the impact of membrane material, seed concentration, and tube velocity on the membrane life in the seeded environment. The specific goals of the project were to:

Goal 1. Establish whether there is a difference in performance between polyamide, TFC chemistry and CA chemistry for tubular RO membranes in the seeded environment

Goal 2. Establish whether operating at different gypsum seed concentrations impacts membrane performance/life

Goal 3. Establish whether operating at different feed water velocities impacts membrane performance/life

Goal 4. Operate a pilot plant with the selected membrane type, seed concentration, and feed velocity conditions—obtained from the screening tests—and achieve 700 hours of operation

To achieve the above goals, the project was split into two phases:

Phase I Screening Phase. The SPARRO pilot plant was modified to operate two different membrane materials in series to determine which operating condition resulted in the best membrane performance. The operating conditions – seed concentration, tubular velocity, and membrane material – varied in accordance with Table 2, and the impact on the short-term membrane performance was monitored.

Phase 2 Pilot Operation Phase. The pilot unit was fitted with the best performing membrane material determined in Phase I and the system was set up to operate under the best performing conditions (also determined in Phase I) to achieve a continuous run time of 700 hours, or approximately four weeks of runtime.

Table 2 Phase I Testing Conditions Matrix

Condition	Duration (days)	Membrane Type	Seed Concentration (g/L)	Tube Velocity (m/s)
1	7	CA/TFC	10	1.0
2	7	CA/TFC	10	1.5
3	7	CA/TFC	18	1.5
4	7	CA/TFC	18	1.0

3.0 Technical Approach

The overall approach for this project was, first, to find a source of calcium sulfate dihydrate, or gypsum, that has a platelet morphology; and modify the SPARRO pilot unit to overcome previous limitations identified during the EDR/SPARRO pilot testing at Corona, California, in 2013. The following sections describe the pilot plant setup, commissioning, and operating protocol; sampling and data collection process; and data interpretations and methodologies.

3.1 Methodology

3.1.1 Equipment and Site

The SPARRO pilot unit was delivered to the Arlington Desalter in Riverside, California, on March 23, 2016, and placed in the identified area for the test work.

Shortly after, Western Municipal Water District (WMWD) provided the electrical power connection for the pilot unit.

3.1.1.1 Sulfuric Acid

Sulfuric acid was used to minimize calcium carbonate scaling by lowering the feed tank pH to 4.5 - 5 whenever the feed tank received RO brine from the Arlington Desalter, which had a typical pH of around 7.6.

3.1.1.2 Membranes

For Phase I, two 4-foot (1.2 meter) long, 0.5-inch diameter stainless steel (SS) single-tube-testers (S.T.T.) and six 4-foot long, 0.5-inch diameter CA and TFC membranes were purchased from Membrane Specialist. In addition, a new end cap connector for the membrane vessel system was ordered to replace the one on the pilot that was damaged. After determining which membrane-type performed optimally during Phase 1, thirty-six 12-foot (3.7 meter) long, 0.5-inch diameter TFC membranes were purchased for the two B1 series flow membrane vessels. These membranes were delivered to the Arlington Desalter on August 16, 2016, and were immediately placed in the Arlington Desalter's electrical room to provide a temperature controlled environment.

3.1.1.3 Gypsum (Calcium Sulfate Dihydrate)

Prior to the start of Phase 1, three different samples of gypsum were sent to the University of Cape Town, South Africa (UCT) for SEM analysis: two commercially available purchased gypsum; and one gypsum made by Carollo using a recipe developed by UCT. Since the initial seed crystals play a role in determining the final seed morphology (WRC, 2006), the purpose of the analysis was to confirm whether the crystal structure was dominated by "platelet" or "needle" forms. The platelet-type morphology is also thought to present a lower probability of membrane surface damage as compared with the "needle-type" morphology. To create the platelet-like gypsum seed crystals, first, we sought a source of high purity sodium sulfate and calcium chloride.

3.1.1.3.1 Commercially Purchased Gypsum

The first purchased gypsum sample that was sent to the UCT was a commercially available pharmaceutical food grade gypsum (Alpha Chemicals). This gypsum was used as the seed material for the 2013 SPARRO Pilot Testing at the Temescal Desalter for the City of Corona, California. The second purchased gypsum was also a commercially available gypsum (Mycopath.com). Both of the gypsum samples had mixed morphology in washed samples as shown in Figure 8 and Figure 9. Neither sample displayed the desired platelet type morphology. Therefore, rather than use the commercially available gypsum, we decided to try making gypsum with the desired morphology.

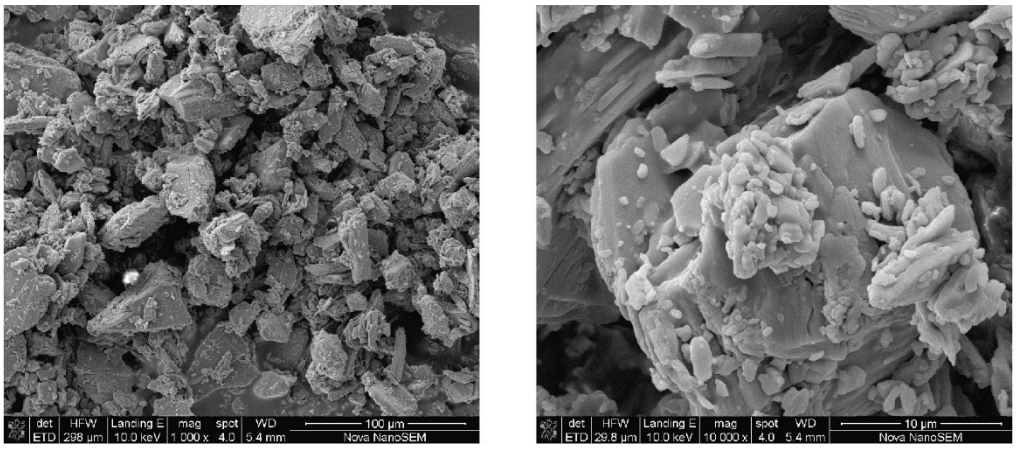

Figure 8. Pharmaceutical food grade gypsum sample washed.

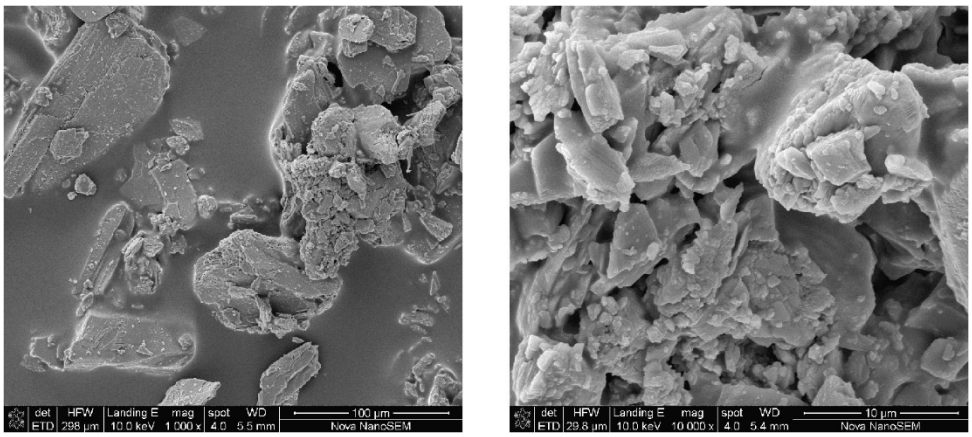

Figure 9 Commercially available gypsum sample washed.

3.1.1.3.2 Precipitated Gypsum

The third gypsum sample that was sent to UCT was prepared in Carollo's laboratory using a recipe provided by UCT (Seewoo et al., 2004). This recipe specifically explains the preparation process of creating platelet-like gypsum seed crystals as well as needle-like gypsum seed crystals. Carollo purchased 50 pounds (22.7 kilograms) of 99+ percent pure, crystalline/granular, anhydrous, food grade natural sodium sulfate and 50 pounds of 94-97 percent pure anhydrous calcium chloride. Then, 0.4 molarity solutions of sodium sulfate and calcium chloride solution were prepared using RO permeate produced in Carollo's laboratory. The two solutions were then mixed together and stirred at 500 revolutions per minute (rpm) (8.3 hertz) for about one minute. The solids that formed were allowed to settle to the bottom of the beaker, and then recovered. This sample had the desired platelet-type morphology, as shown in Figure 9.

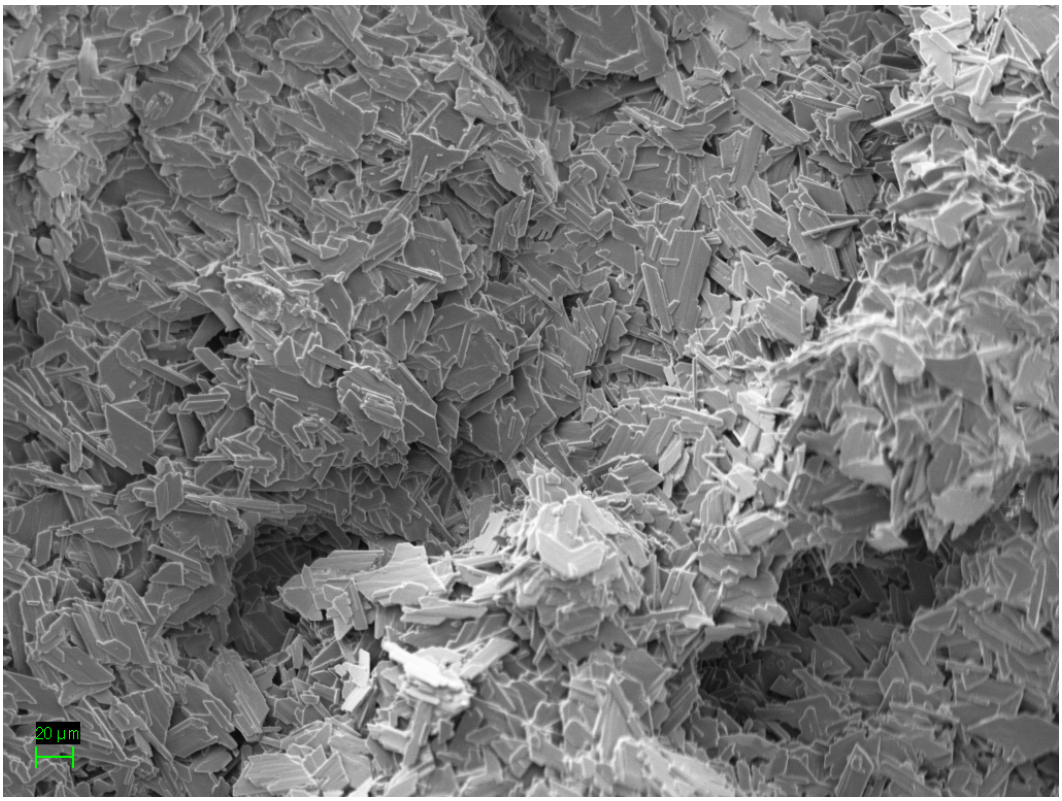

Figure 10. Gypsum seed made in Carollo's laboratory that show the "platelet" morphology.

3.1.2 Repairs and Modifications to SPARRO Pilot Plant

As reported previously, Carollo identified operational limitations during the EDR/SPARRO pilot testing in 2013, and the planned repairs were aimed to improve the reliability of the unit. However, due to the high cost of the quotes obtained for the repair work and the limited budget, Carollo decided to undertake only the major items of the repair work with the assistance of WMWD. Table 3 summarizes which identified modifications were or were not implemented and why.

Table 3. SPARRO Pilot Modifications List

	Scope of Work	Description	Completed (Y/N)	Reason
1.	100-Gal Tank	Replace existing 100-gallon HDPE feed tank with fiberglass reinforced plastic (FRP) tank. Also, increase drain size to 2 inches.	N	Too costly
2.	200-Gal Tank	Replace existing 200-gallon high-density polyethylene (HDPE) concentrate tank with FRP tank. Also, increase drain size to 2 inches.	N	Too costly
3.	Hydro-cyclone	Raise location of hydro-cyclone separator. Remove existing large aluminum cone and replace with smaller version. Direct underflow solids from cone into hose that includes inverted Y connection and pinch valve linked to timer; to allow for solids diversion from concentrate tank periodically. Weld equipment to frame.	Y	
4.	SS needle Valve	Replace stainless steel (SS) needle valve on concentrate line (x2). Tags ND 601 and ND 602.	Y	
5.	Control Panel	Install loose terminal blocks in control and wire up. Also, wire new timer for solids blowdown. Reprogram PLC logic and provide copy of program and access to programmable logic controller (PLC) logic.	Y/N	Re-programming too costly
6.	Flushing Line	Replace polyvinyl chloride (PVC) flushing water line with 1-inch diameter PVC pipe.	Y	
7.	RO Vessels	Pipe RO vessel to allow for separate sampling of permeate.	Y	
8.	Pressure Relief Valve	Check pressure relief valve (PRV) on discharge of feed pump and replace if needed. It was not opening at set pressure.	Y	
9.	Flowmeter	Replace concentrate flowmeter with 0.5-inch magnetic flowmeter.	N	Too costly
10.	Add "Full Recycle Mode" Piping	Provide permeate return to feed tank by connecting a three-way valve to the permeate line and providing 0.5-inch PVC pipe into the 100-gallon tank.	Y	
11.	Conductivity Meter	Replace permeate conductivity meter with higher range constant (1,000 to 1,500 TDS).	Y	

Table 3. SPARRO Pilot Modifications List

Scope of Work	Description	Completed (Y/N)	Reason
12. Pressure Gauges	Replace three pressure gauges. Investigate whether diaphragm can be reused and gauges replaced in factory. 0 to 1,000 psi (one gauge); 0 to 600 psi (two gauges).	Y	
13. Y-Strainer in Suction Line	Add new Y-strainer in feed pump suction line with 1-mm opening size.	Y	
14. Reconnect RO Vessels in Series	RO vessels were modified for parallel operation. Reconnect for series operation.	Y	
15. Single-Tube Tester	Install an SS connection from the high-pressure feed line to the RO vessels, to a location above the RO vessels where the single-tube tester apparatus will be connected. The return line from the single-tube tester will bypass the RO vessels and connect to the existing SS tubing.	Y	
16. 100- and 200-Gal Support	Improve the support for both tanks to prevent deformation or rupturing of the tank bottom cone area.	N	Too costly
17. RO Vessel End Cap	Replace bent end cap of RO vessel from Membrane Specialists.	Y	

psi = pounds per square inch

3.1.3 Installation, Testing, and Commissioning

This section will first discuss the general tasks related to installation, testing, and commissioning similar to both phases. Then it will discuss phase specific tasks related to installation, testing, and commissioning.

3.1.3.1 General Installation, Testing, and Commissioning

For the SPARRO pilot unit to operate continuously overnight without supervision, the unit had to be set up to operate automatically.

The SPARRO pilot feed tank was piped to receive brine from Train C of the Arlington Desalter. The piping consisted of $^{1}/_{2}$-inch (12.7 millimeter [mm]) SS tubing, the necessary bends, an SS needle valve, a solenoid isolation valve near the feed tank, and a rotameter closest to the feed tank. The actuator was set up to "open" and refill the feed tank to the first level switch whenever the water level in the tank dropped below the second level switch. The SPARRO feed needle valve allowed control of the influent flow to the feed tank. The SPARRO feed piping from Train C is shown on Figure 11 and the level switches to actuate the feed are shown on Figure 12.

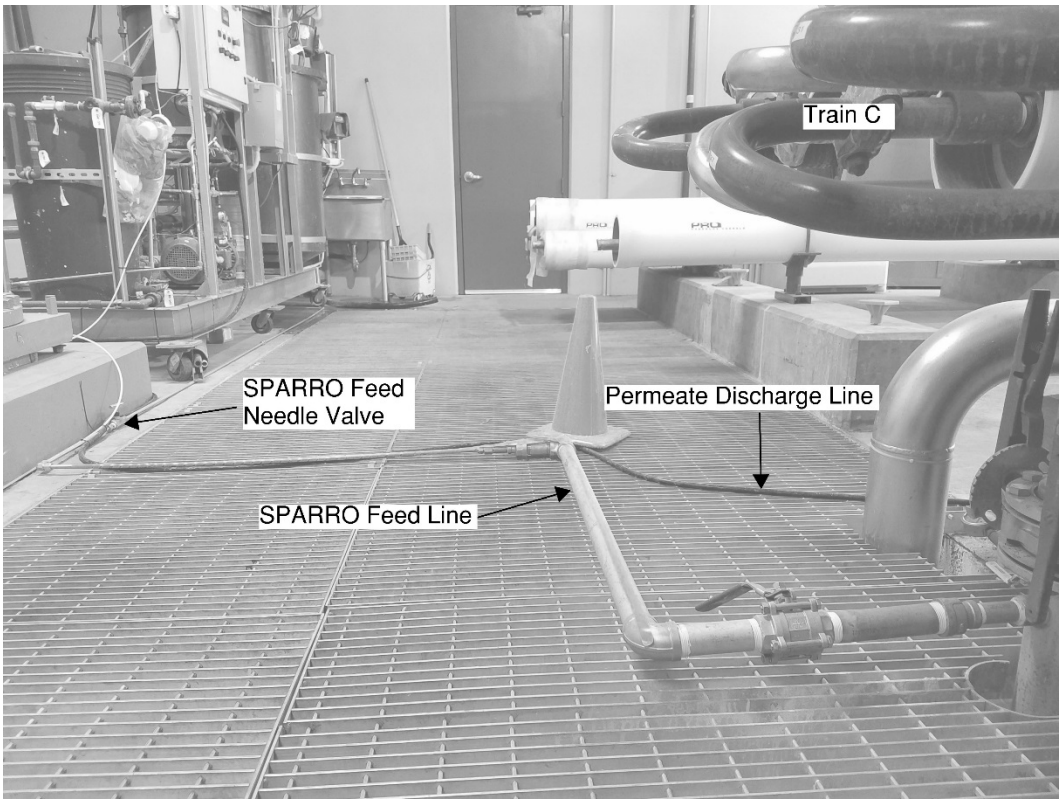

Figure 11 . SPARRO feed line piping from Train C.

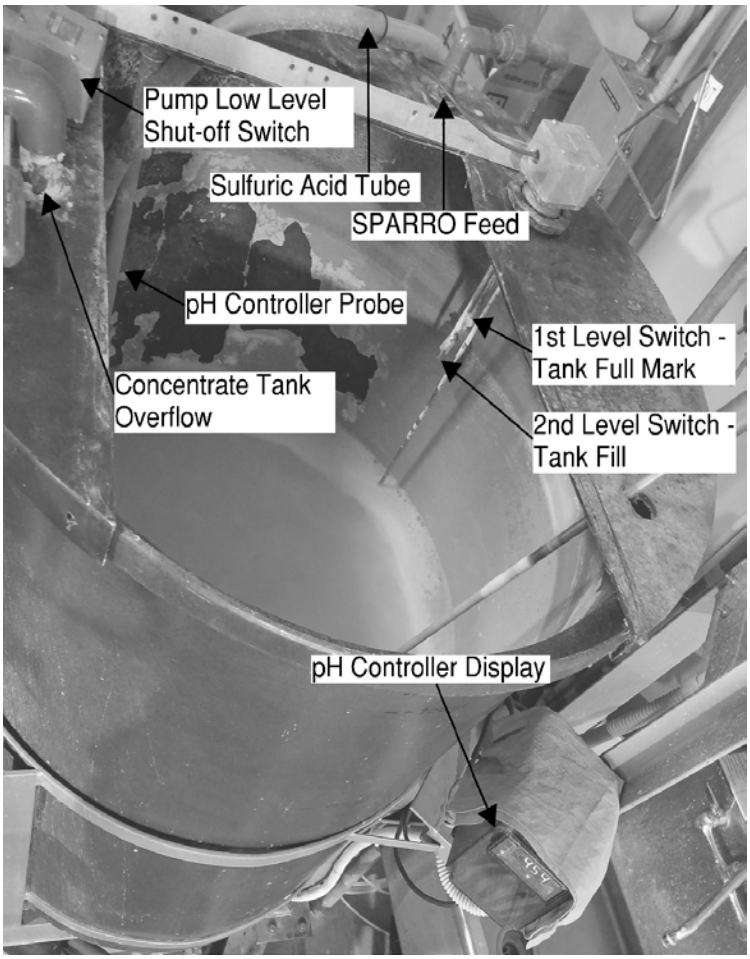

Figure 12. Feed tank controls and elements.

The product water, or permeate, from the membranes was collected in a permeate tank and discharged to the desalter's brine line using a submersible pump. The submersible pump was placed in the permeate tank and a long hose (permeate discharge line) was used to connect the submersible pump to the brine disposal point. An integrated float-switch activator was attached to the submersible pump (Figure 13).

A feed tank pH controller was installed towards the end of Condition 2 (Phase 1) to control the sulfuric acid dosing pump. The pH controller consisted of a pH probe, electrical wiring, and a pH display screen. Whenever the pH in the feed tank rose above 4.7, the pH controller would actuate the sulfuric acid dosing pump and start dosing into the feed tank to bring the pH back down to about 4.5. The feed tank, pH controller display screen, PVC pipe connecting to the pH probe, and sulfuric acid tubing is shown on Figure 12.

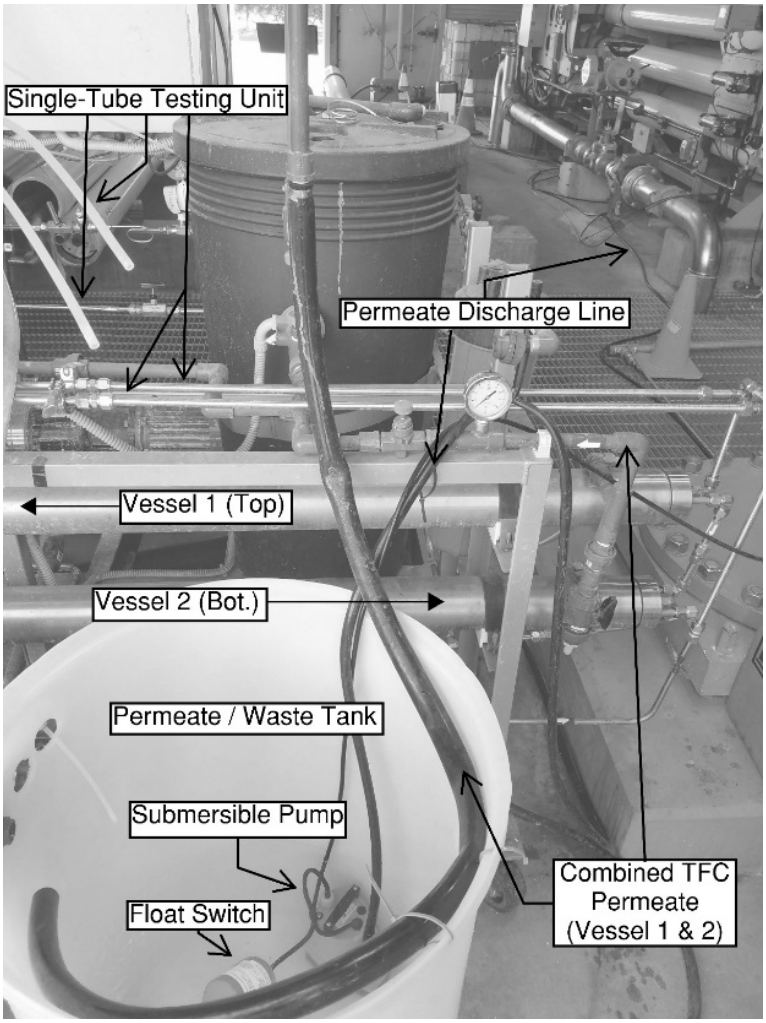

Figure 13. Permeate tank with submersible pump.

3.1.3.2 Phase 1

At the start and end of each test condition, a standard salt test was carried out to establish the initial and final salt rejection and flux of both the CA and TFC membranes. The salt test was carried out using commercial grade NaCl dissolved in RO permeate. Approximately 500 grams of NaCl was dissolved in about 280 liters (74 gallons) of RO permeate to give a conductivity of 3,810 µS/cm. Performing the initial salt test also served as a check for verifying the health of the unused membranes. The initial salt test was compared to the ending salt test to determine the effects of each condition on the membranes. Prior to the first salt test, citric acid and permeate was left recycling in the system overnight to remove any scale present on the pipes that may have been left behind from the previous pilot study.

For Phase 1—Screening Phase, the SPARRO pilot plant was set up together with two single-tube testing apparatuses connected by a 180 degree bend to operate the two different membrane tubes. The CA membrane was the first upstream tube,

and the TFC membrane was the second in series as shown on Figure 14. The single-tube testers were designed to house 4-foot (1.21 meter) long tubular RO membranes. The tools and equipment required for this assembly was provided by Membrane Specialists. In addition, a pressure gauge and manual needle valve were installed on the TFC permeate line. Throttling this valve created backpressure on the membrane, allowing for conditions in which the flux of both membranes would be about the same.

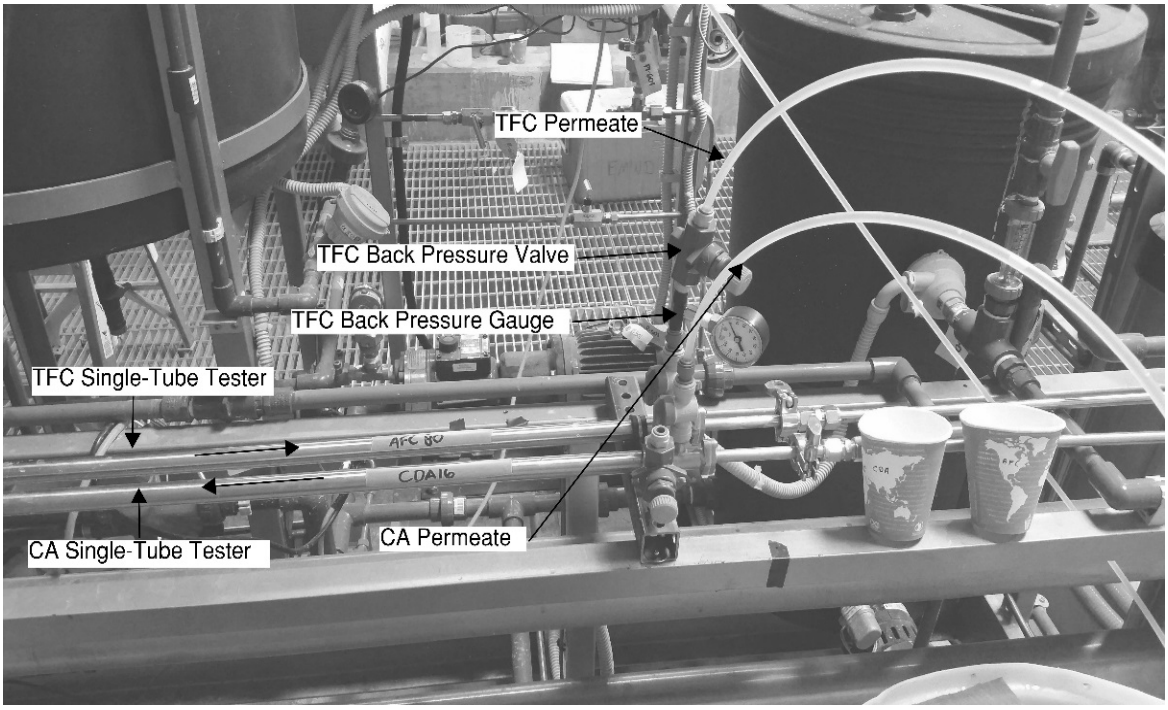

Figure 14. Configuration of the single-tube testers that shows the TFC backpressure valve and pressure gauge.

3.1.3.3 Phase 2

For Phase 2—Bench Scale Operation Phase, the SPARRO pilot plant was set up with two tubular RO membrane vessels in series that housed eighteen 12-foot (3.7-meter) long tubular RO membranes per vessel. During the transition between Phase 1 and Phase 2, it was decided that the single-tube testers would remain in operation upstream of the large membrane vessels.

During Phase 1 operation, the seed concentration was maintained by manually removing 10.8 liters (2.85 gallons) of concentrate per day from the system. However, with the increase in membrane operating area for Phase 2, the amount and frequency of concentrate needing to be removed increased significantly. During the transition phase between Phase 1 and Phase 2, an automatic concentration blowdown system was designed and installed to keep the feed tank seed concentration fixed at 15 to 18 g/L. This consisted of adding a small mixed reactor between the hydrocyclone (cyclone) and the concentrate tank, including a

solenoid ball valve and a timer to allow for blow down of excess solids on a regular basis. The volume of underflow solids that was discharged depended on the length of a stand pipe and the timer setting. When the timer setting was set to "off," the solenoid ball valve would close and the underflow solids level would rise and overflow into the concentrate tank. When the timer setting was set to "on," the solenoid ball valve would open and the amount of liquid above the stand pipe would be discharged to the solids blowdown tank and continue discharging until the timer setting switched back to the "off" setting. The solids blowdown tank was designed to overflow into the permeate tank as shown in Figure 15. The first week of Phase 2 was dedicated to finding what timer setting kept the seed concentration fixed at 15 to18 g/L.

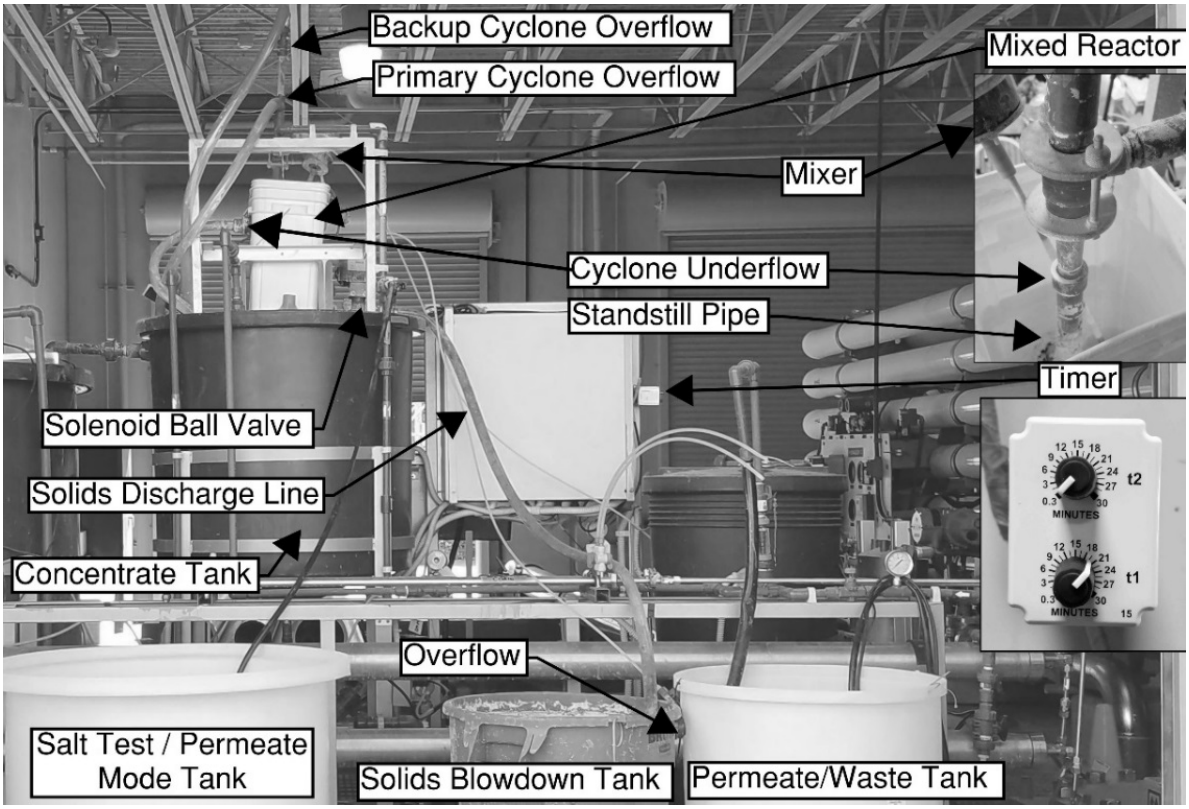

Figure 15. Elements of the automatic blowdown system.

A salt test was performed at the start and the end of Phase 2. The results are discussed in Section 4.0. Prior to the salt test at the beginning of Phase 2, the RO membrane vessels were cleaned by increasing the tube velocity and recirculating citric acid and permeate through the system overnight.

3.1.4 Source Water for Pilot Testing

The Arlington Desalter is an existing groundwater RO facility owned and operated by the WMWD. This 6-million gallons per day (mgd) (22,700 cubic meters per day [m^3/d]) facility includes preliminary filtration of RO feed through 5-micron cartridge filters before entering a 5-mgd (18,900 m^3/d) RO

treatment process. This facility has been operating for approximately 25 years. The plant is comprised of three parallel RO treatment trains, each containing 44 pressure vessels, 8-inch diameter, in a two pass 33:11 array and operating at 77-percent recovery (Wilf, no date). The RO Train C supplied the RO concentrate, or brine, to the SPARRO pilot plant. The three RO trains inside of the Arlington Desalter facility are shown on Figure 16, where train C is in the foreground.

Figure 16. 6-mgd (22,700 m^3/d) Arlington Desalter.

3.1.5 SPARRO Pilot Unit Description

The SPARRO skid is approximately 5 feet wide, 13 feet long, and 8 feet tall (1.5 by 3.9 by 2.4 meters), and consists of the following components:

- Feed Tank
- High-Pressure Feed Pump
- Two Single-Tube-Testers
- Two Membrane Vessels (Phase 2)
- Hydrocyclone Separator
- pH Controller
- Automatic Solids Blowdown System (Phase 2)
- Concentrate Tank
- Permeate Tank
- Solids Blowdown Tank (Phase 2)
- Sulfuric Acid Dosing Pump and Tank

The design criteria and pilot process description for the Phase 1 and Phase 2 SPARRO pilot unit are summarized in the following sections.

3.1.5.1 Phase 1 SPARRO Pilot Unit Description

Design criteria for the Phase 1 SPARRO pilot unit are summarized in Table 4. Figure 17 shows a photograph of the unit in position at the facility, and Figure 18 provides a process flow diagram showing the Phase 1 arrangement.

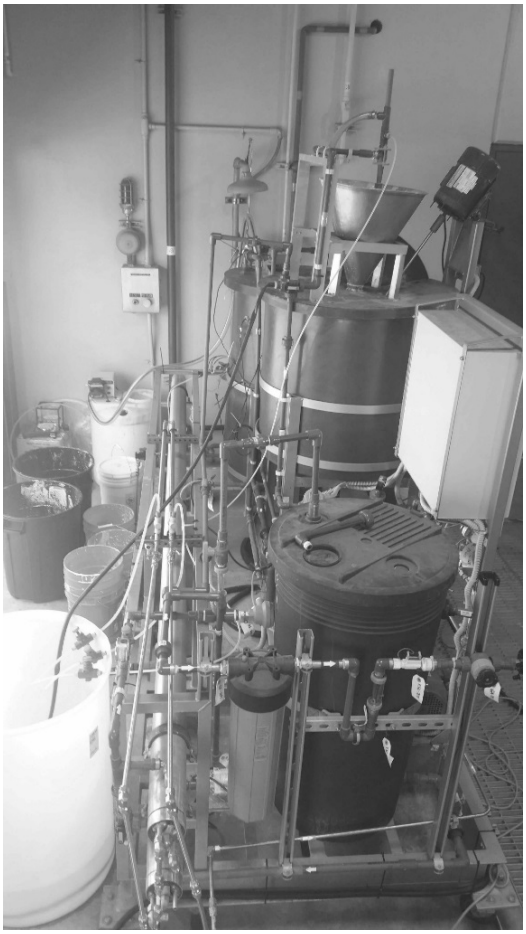

Figure 17. Side view of Phase 1 Pilot Unit.

Table 4. Phase 1 SPARRO Pilot Design Criteria

Parameter	Value
Raw Feed Flow (gpm)	0.0076 (41.4 L/day)
Membrane Feed Flow (gpm)	2 – 3 (7.6 – 11.4 L/min)
Product Flow (gpm)	0.005 (28 L/day)
Recovery (%)	50 – 85
Feed Pressure (psi)	180 – 200 (1.2 – 1.4 MPa)
Concentrate Flow Velocity (ft/s)	3.3 – 4.9 (1.0 – 1.5 m/s)
Cyclone Feed Pressure (psi)	10 – 20 (68 – 137 kPa)
Single-Tube-Testers (No.)	2
Membrane Area per Single-Tube-Tester (ft^2)	0.52 (0.05 m^2)

L/day = liter per day
L/min = liter per minute
MPA= megapascal
ft/s = foot per second
kPA= kilopascal
ft^2 = square foot
m^2 = square meter

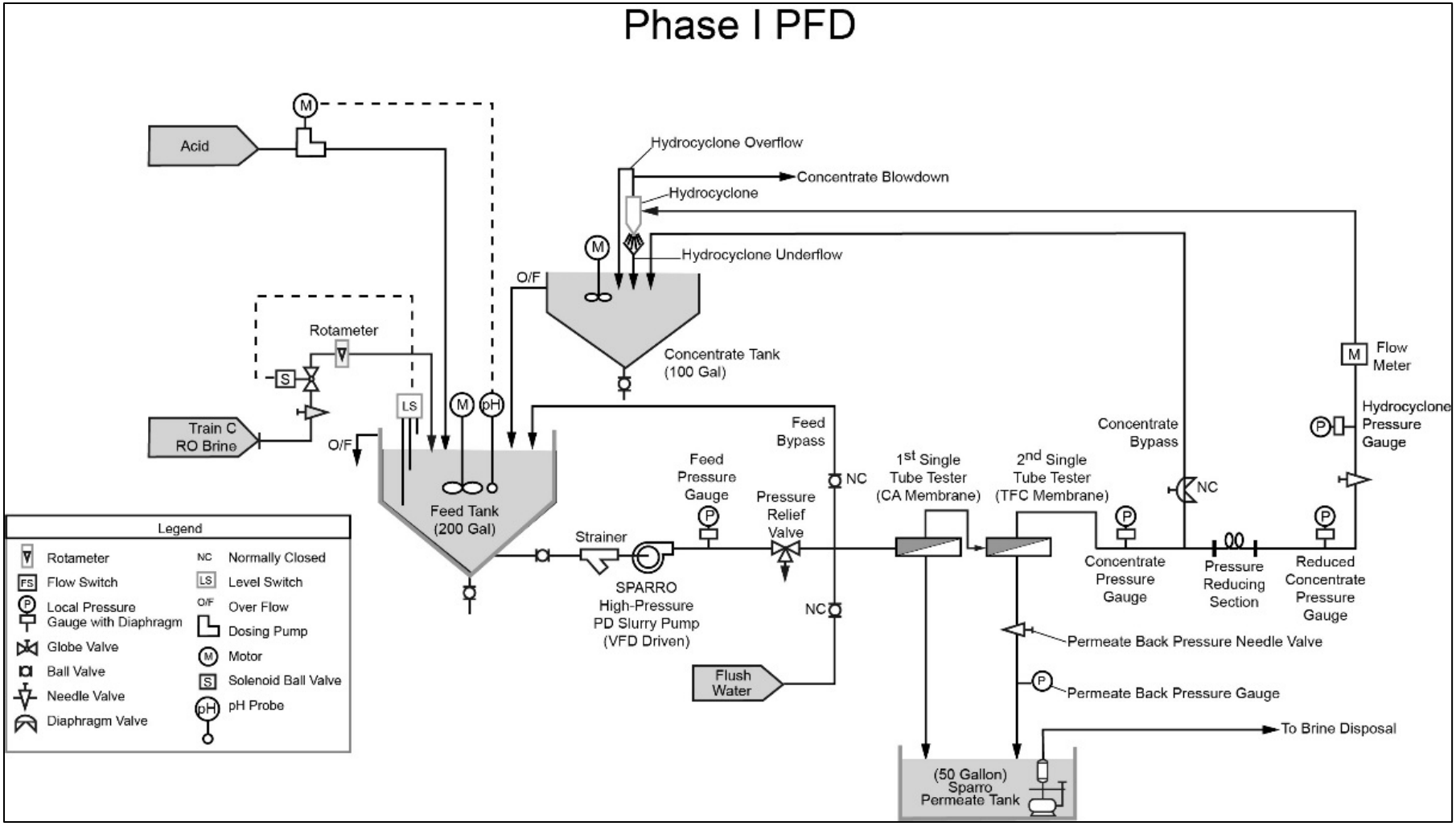

Figure 18. Phase 1 process flow diagram.

The Phase 1 SPARRO pilot unit was designed to treat 40 L/day of RO concentrate and consists of two "single-tube-testing" units to operate two different membranes in series as described previously. Concentrate slurry flows to a hydrocyclone separator where smaller particles and most of the liquid are separated (overflow) from the larger particles (underflow). This separation allows for individual control of the gypsum solids mass balance and liquid TDS by wasting calculated volumes of the high suspended solids cyclone underflow and the high TDS cyclone overflow, respectively. It was planned to continually waste 10.8 L/day (0.002 gpm) of the overflow to maintain TDS levels in the system. The remaining liquid in the overflow (2.0 gpm to 7.6 L/min) was returned to the concentrate tank. The larger, heavier gypsum solids in the underflow were typically discharged into the concentrate tank, which continually overflowed into the slurry feed tank. Gypsum solids were regularly removed to maintain the solids balance in the system. These solids, collected in waste buckets until decommissioning, were retained in case re-seeding was required and for sampling purposes.

3.1.5.2 Phase 2 SPARRO Pilot Unit Description

Design criteria for the Phase 2 SPARRO pilot unit are summarized in Table 5 and the Phase 2 SPARRO pilot unit process flow diagram is shown on Figure 19.

Table 5. Phase 2 SPARRO Pilot Design Criteria

Parameter	Value
Raw Feed Flow (gpm)	1 – 1.5 (3.8 – 5.7 L/min)
Membrane Feed Flow (gpm)	3.5 (13.2 L/min)
Product Flow (gpm)	0.5 (1.9 L/min)
Feed Tank Seed Concentration (g/L)	15 – 18
Recovery (%)	50 – 85
Feed Pressure (psi)	150 – 300 (1.0 to 2.1 MPa)
Concentrate Flow Velocity (ft/s)	~ 4.2 (1.3 m/s)
Cyclone Feed Pressure (psi)	> 20 (138 kPa)
RO Membrane Vessels (No.)	2
Membrane Area per Vessel (ft2)	28 (2.6 m2)

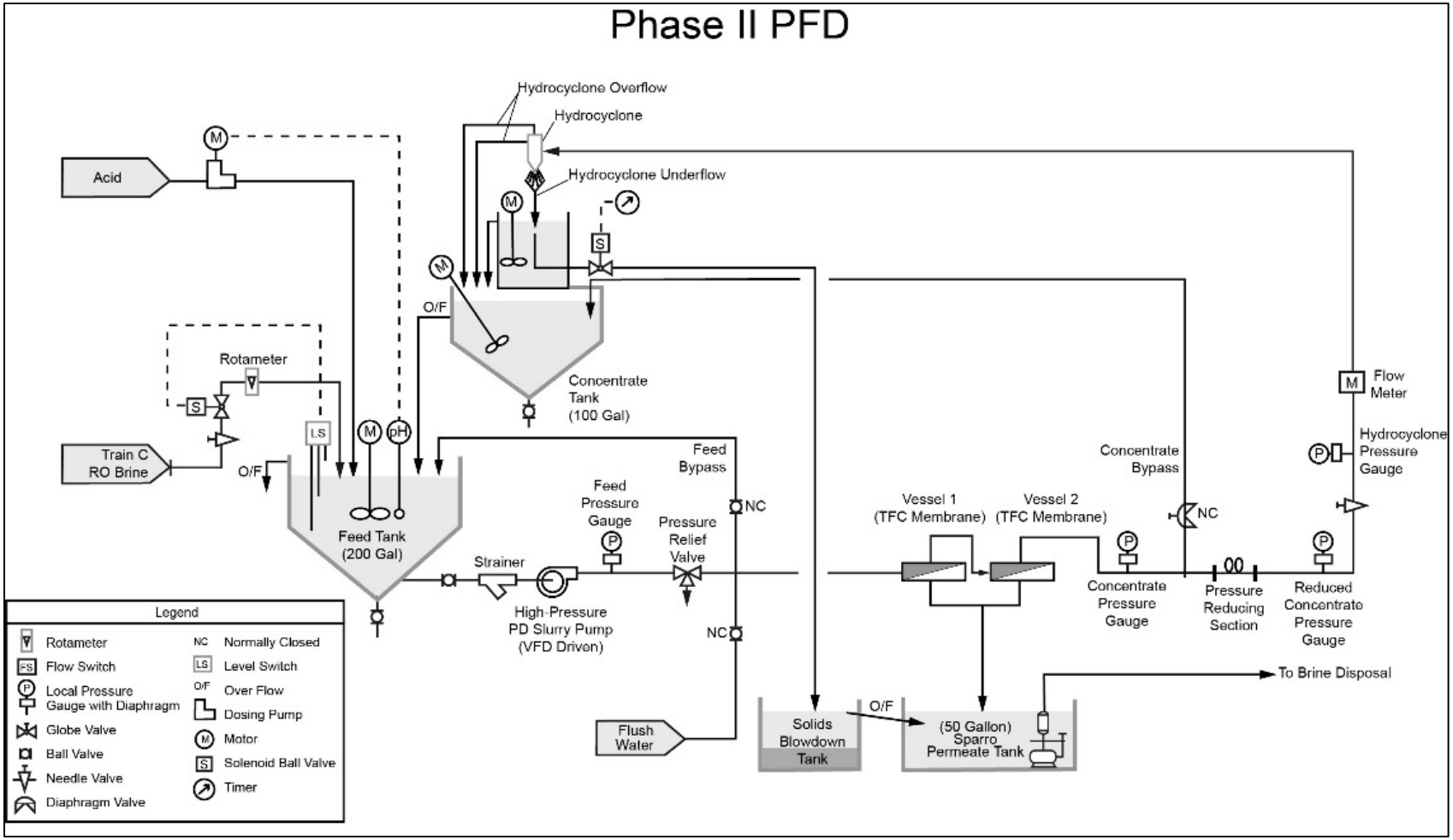

Figure 19. Phase 2 process flow diagram (single-tube testers not shown).

Each of the two membrane vessels housed eighteen 12-foot (3.7 meter) long, 0.5 inch diameter, tubular RO membranes for a total membrane area of 28 ft^2 (2.6 m^2) per vessel. The permeate from both vessels was collected in a permeate break tank and discharged to the Arlington Desalter's brine line using an automatic discharging submersible pump. The concentrate from the pressure vessels flowed to a pressure reducing station (PRS) that consisted of a short section of $^3/_8$-inch (9.5 mm) stainless steel tubing. The PRS was incorporated into the design of the pilot skid because the high pressure and abrasive nature of the slurry would cause significant wear to a control valve. Following the PRS, concentrate slurry flows to a hydrocyclone separator where smaller particles and most of the liquid are separated (hydrocyclone overflow) from the larger particles and most of the solids (hydrocyclone underflow). The hydrocyclone overflow flowed directly into the concentrate tank. The underflow flowed into a small mixed reactor that was designed to allow for overflow into the concentrate tank and an automatic discharge to the solids blowdown tank depending on the timer setting that controlled a pneumatic ball valve. This system was used to waste calculated volumes of the high suspended solids (total suspended solids [TSS]) from the cyclone underflow. About 0.16 gpm (0.73 L/min) of the underflow was periodically wasted to maintain TSS levels in the system. This resulted in a system recovery of 65 to 76 percent. The remaining liquid in the overflow (1.8 gpm to 6.8 L/min) was returned to the concentrate tank, which continually overflowed into the slurry feed tank as it did during Phase 1. The solids in the solids blowdown tank were retained until decommissioning in case re-seeding was required and for sampling purposes.

3.2 Laboratory Sampling and Data Collection

3.2.1 Water Samples

For Phase 1, EMWD provided a total of 48 half-gallon (1.89 liters) sample bottles, six bottles for each sample collection event: one sample bottle filled with 1.5 liters for each of these streams:

- Train C RO brine
- SPARRO feed
- Hydrocyclone underflow
- Hydrocyclone overflow
- TFC permeate
- CA permeate

As mentioned in Section 3.0, the pilot operated at four different conditions and each condition ran for about a week. Water samples were collected at the start and end of each testing condition, stored in WMWD's sample refrigerator, and the chilled samples were taken to EMWD's analytical laboratory in Perris, California. The water removed from the system was taken into account when normalizing the

data. The list of chemical analyses performed by EMWD on each sample for Phase 1 is presented in Table 6 below. The results are discussed in Section 4.0.

Table 6. Phase 1 – EMWD Laboratory Testing Plan

Stream No.		1	2	3	4	5	6	
Stream Name		Train C Brine (SPARRO Feed)	Feed Tank	TFC Permeate	CA Permeate	Cyclone Overflow / SPARRO Concentrate	Cyclone Underflow	Total Analyses per week
Parameter	Type	Sampling Frequency (per week)						
pH	G(1)	2	2	2	2	2		10
ORP(2)	G		2					2
Conductivity	G	2	2	2	2	2		10
Hardness	G	2	2	2	2	2		10
Alkalinity	G	2	2	2	2	2		10
TDS	G	2	2	2	2	2		10
TSS	G	2	2			2	2	8
Sulfate	G	2	2	2	2	2		10
Sodium	G	2	2	2	2	2		10
Calcium	G	2	2	2	2	2		10
Magnesium	G	2	2	2	2	2		10
Chloride	G	2	2	2	2	2		10
Total Silica	G	2	2	2	2	2		10

(1) G = Grab Samples
(2) ORP = oxidation reduction potential

As mentioned, the first week of operating the SPARRO system was used to gain experience operating the pilot and to identify operational procedures needed to maintain the desired test conditions. This run was carried out between June 17 and June 27 and Condition 1 officially started on June 27.

For Phase 2, the frequency of sampling increased to three times per week. As in Phase 1, EMWD provided all sample bottles. It was planned to collect samples every Monday, Wednesday, and Friday for four weeks. The configuration of the pilot was modified to include the large membrane vessels in series. After analyzing the results from Phase 1, it was decided that the single tube testers would remain in the system upstream of the large membrane vessels. The single tube testers contained one TFC and one CA membrane, while the large membrane vessels contained the TFC membranes. Similar to Phase 1, the six sample bottles were filled with 1.5 liter of Train C brine, SPARRO feed, SPARRO hydrocyclone

underflow and overflow, TFC permeate from the full-scale pressure vessels, and the CA and TFC permeate from the single-tube testers. The list of chemical analyses performed by EMWD on each sample for Phase 2 is presented in Table 7. The results are discussed in Section 4.0.

Table 7. Phase 2 – EMWD Laboratory Testing Plan

Stream No.		1	2	3	4	5	6	
Stream Name		Train C Brine (SPARRO Feed)	Feed Tank	CA & TFC Permeate (Single Tube Testers)(1)	TFC Permeate (Vessel 1 and 2) (2)	Cyclone Overflow / SPARRO Concentrate	Cyclone Underflow	Total Analyses per week
Parameter	Type	Sampling Frequency (per week)						
pH	G(3)	3	3	3	3	3	-	15
Conductivity	G	3	3	3	3	3	-	15
Hardness	G	3	3	3	3	3		15
Alkalinity	G	3	3	3	3	3	-	15
TDS	G	3	3	3	3	3	-	15
Turbidity (NTU)(4)	G	-	-	3	3	-	-	6
Total Suspended Solids (TSS)	G	3	3	-	-	3	3	12
Sulfate	G	3	3	3	3	3	-	15
Sodium	G	3	3	3	3	3	-	15
Calcium	G	3	3	3	3	3	-	15
Magnesium	G	3	3	3	3	3	-	15
Chloride	G	3	3	3	3	3	-	15
Total Silica	G	3	3	3	3	3	-	15

(1) The CA and TFC permeate from the Single-Tube Testers was collected in the same sample bottle
(2) The combined permeate stream of both membrane vessels was collected in the same sample bottle
(3) G = Grab Samples
(4) NTU = Nephelometric Turbidity Unit

3.2.2 Seed Samples

During Phase 1 operation, samples of seed from the solids-waste bucket and SPARRO feed stream were removed, drained, and sent to UCT at the end of Condition 2 and at the beginning of Condition 3, respectively, for analysis and evaluation. For Phase 2, samples were sent at the beginning, middle, and end of the testing. Approximately 200 grams of seed was required for each analyses.

At the end of Phase 2, samples of seed were also removed, dewatered, and sent to Omya Inc. to determine the percent purity of gypsum in the sample.

3.2.3 Data Collection

The data collection consisted of manually recording the following parameters during the pilot operation:

- Date
- Time
- Timer Setting (Phase 2)
- Pump Speed
- Feed Tank Water Level
- Feed Pressure Gauge
- Concentrate Pressure Gauge
- Reduced Concentrate Pressure Gauge
- Cyclone Pressure Gauge
- TFC Permeate Pressure Gauge (Phase 1)
- Seed Concentrations of Feed Tank, Concentrate Tank, and Cyclone Underflow and Overflow
- SPARRO Feed Flow
- SPARRO Concentrate Flow
- Cyclone Underflow (Phase 1) and Overflow (Phase 2)
- CA Permeate Flow
- TFC Permeate Flow
- Feed Tank pH Controller (Phase 2)
- pH, Conductivity, ORP, and Temperature of Train C Brine
- Feed Tank
- Concentrate Tank
- CA Permeate (Phase 1)
- CA & TFC Permeate from Single Tube Testers (Phase 2)
- TFC Permeate
- TFC Vessel 1 and 2 (Phase 2)
- SPARRO Concentrate

This list indicates parameters that were specific to each phase. The parameters that do not have this indication were common for both phases.

A pycnometer (Cole-Parmer Gay-Lussac 25.03 mL Bottle with Stopper) and an analytical scale were used to estimate the seed concentrations. After filling the pycnometer with the sample to be measured and putting on the stopper, the pycnometer was thoroughly wiped off with a dry cloth and then weighed on the analytical scale. An equation was developed to convert the weight of the bottle plus the sample (grams) to seed concentration (g/L). This equation incorporated the density of gypsum, weight of bottle, weight of bottle plus RO concentrate, an

estimated specific gravity (SG) of the concentrate stream, and volume of the pycnometer.

The SPARRO feed flow was calculated from the sum of the concentrate flow and the product flow. The flow measurements for the SPARRO concentrate flow were obtained using the bucket and stopwatch method. The flow measurements for the cyclone underflow and overflow and TFC permeate flow (Phase 2) were obtained in milliliters per fifteen seconds (mL/15 seconds) using a one liter (L) graduated cylinder and a stopwatch. The flow measurements for the CA and TFC permeate flow (Phase 1) and CA permeate flow (Phase 2) were obtained in milliliters per minute (mL/min) using a 25 mL graduated cylinder and a stopwatch. All these values were converted to GPM when inputting into the normalization calculations.

A handheld pH probe (Myron L Company 6P Ultrameter II™) was used to measure the pH, conductivity, ORP, and temperature. A new pH sensor had been installed prior to Phase 1. Before taking sample readings with the pH probe, the sensor was rinsed 3 times with the sample to be measured. The pH probe was calibrated regularly. The feed tank was fitted with a pH monitor/controller and the reading was frequently compared to the handheld pH probe reading to check the calibration.

All data collected was entered directly into a master data spreadsheet on site and uploaded to Carollo's file management system at the end of the day. See Appendix A and B for Phase 1 and 2 final master data sheet results, respectively.

3.3 Interpretation of Performance Data

The SPARRO pilot performance is influenced by feedwater composition, temperature, and operating factors such as pressure and system recovery. To distinguish between variations over time in these feed and operating characteristics and to identify any performance changes due to fouling and scaling problems, the data must be normalized. Normalization allows a comparison of the actual performance to be given while the influences of operating parameters are taken into account. Reference performance was based on measured initial performance.

Two parameters used to evaluate the performance of the membranes in the SPARRO system were normalized permeate flow (NPF) and normalized salt passage (NSP). NPF is the permeate flow normalized for feed concentration, temperature, and applied transmembrane pressure. NSP is the salt passage normalized for feed concentration, transmembrane pressure, and the feed-concentrate salt concentration. The salt passage in this study was expressed as the percent rejection, thus the normalized salt rejection (NSR) would be equal to 100 percent minus the NSP. The NPF and NSP equations are as follows:

Normalized Permeate Flow

$$Q_{npa} = \frac{(NDP_s)(TCF_s)}{(NDP_a)(TCF_a)}(Q_{pa})$$

where:

Q_{npa}	=	NPF under actual conditions, gpm
NDP_s	=	Net driving pressure at standard conditions, psig
NDP_a	=	Net driving pressure under actual conditions, psig
TCF_s	=	Temperature Correction Factor (TCF) based on standard temperature
TCF_a	=	TCF based on actual temperature
Q_{pa}	=	Actual permeate flow, gpm
TCF	=	$1.03^{(T-25)}$ where TCF_s uses T_s and TCF_a uses T_a
NDP	=	$P_f - \frac{\Delta P_{fb}}{2} - P_p - \pi_{fb} + \pi_p$
P_f	=	High-pressure feed pump discharge pressure, pounds per square inch gauge (psig)
P_b	=	Concentrate pressure, psig
P_p	=	Permeate pressure, psig
ΔP_{fb}	=	Differential pressure at standard conditions, psig
	=	$P_f - P_b$
π_{fb}	=	Feed-brine osmotic pressure, psig
	=	$\frac{(0.03851)(C_{fb})(T+273.15)}{\left(1000 - \frac{C_{fb}}{1000}\right)}$
π_p	=	Permeate osmotic pressure, psig
	=	$\frac{(0.03851)(C_p)(T+273.15)}{\left(1000 - \frac{C_p}{1000}\right)}$
C	=	TDS, mg/L
	=	$EF_{sn} \times U$

EF_{sn}	=	TDS to conductivity ratio
U	=	Conductivity, µS/cm

Note: Generic equations are presented.

Normalized Salt Passage

$$\%SP_{nspa} = \frac{NDP_a \times (C_{fbs})(C_{fa})}{NDP_s \times (C_{fba})(C_{fs})} \times [\%SP_a]$$

where:	$\%SP_{nspa}$	=	NSP under actual conditions, %
	NDP_s	=	Net driving pressure at standard conditions, psig
	NDP_a	=	Net driving pressure under actual conditions, psig
	C_{fbs}	=	Feed-brine salt concentration at standard conditions, mg/L
	C_{fba}	=	Feed-brine salt concentration under actual conditions, mg/L
	C_{fs}	=	Feed salt concentration at standard conditions, mg/L
	C_{fa}	=	Feed salt concentration under actual conditions, mg/L
	C_{pa}	=	Permeate salt concentration under actual conditions, mg/L
	$\%SP_a$	=	Actual salt passage, the amount of salt that passes through the membrane into the permeate stream, %
		=	$\frac{C_{pa}}{C_{fa}}$

$$NSR = 100\% - NSP$$

where:	NSR	=	NSR, %
	NSP	=	NSP, %

4.0 Results and Discussion

4.1 SPARRO Performance Results - Phase 1

4.1.1 Phase 1 Timeline and Operation

The timeline for Phase 1 (Figure 20) is to help the reader understand the order in which events occurred and to help explain anomalies that appear in the data due to certain operational issues. Each tic interval represents a day starting at 8:00 a.m. and is shaded according to how long the pilot ran. In essence, the timeline illustrates the runtime for each condition for Phase 1 and is drawn to scale. As shown, during phase 1 the equipment was operational for most of the 6-week period and was generally only off-line when changing out the membranes and adjusting parameters for the next operating condition.

During Phase 1 Condition 1 (Run 1), several start-up issues were identified. As shown in the timeline, the SPARRO pilot was turned off overnight for the first two days of operating in seed mode. This was mainly due to the loss of the impeller on the concentrate tank mixer. A new mixer was immediately ordered and installed on June 22, allowing the pilot to run overnight without incident.

Difficulty in controlling the pH of the system was another issue identified during this period. Initially, the sulfuric acid dosing pump was set up to start dosing at a constant dosing speed once the feed tank began refilling with feedwater. The acid pump was set to stop dosing once the feed tank water level reached the high level switch. Finding the precise dosing speed that would balance the high pH feedwater to maintain a pH of 4.5-5 was very difficult without an operator on site. Occasionally, sodium bicarbonate had to be added to the system to raise the system pH to the desired range. The pilot experienced an overdose of sulfuric acid on the Independence Day (July 4th) weekend after an unexpected shutdown at the desalter. Finally, a pH controller was installed (as described in Section 3.1.3.1) towards the end of Phase 1 Condition 2, and this installation completely eliminated problems encountered with maintaining a system pH of 4.5 – 5 as shown on Figure 21.

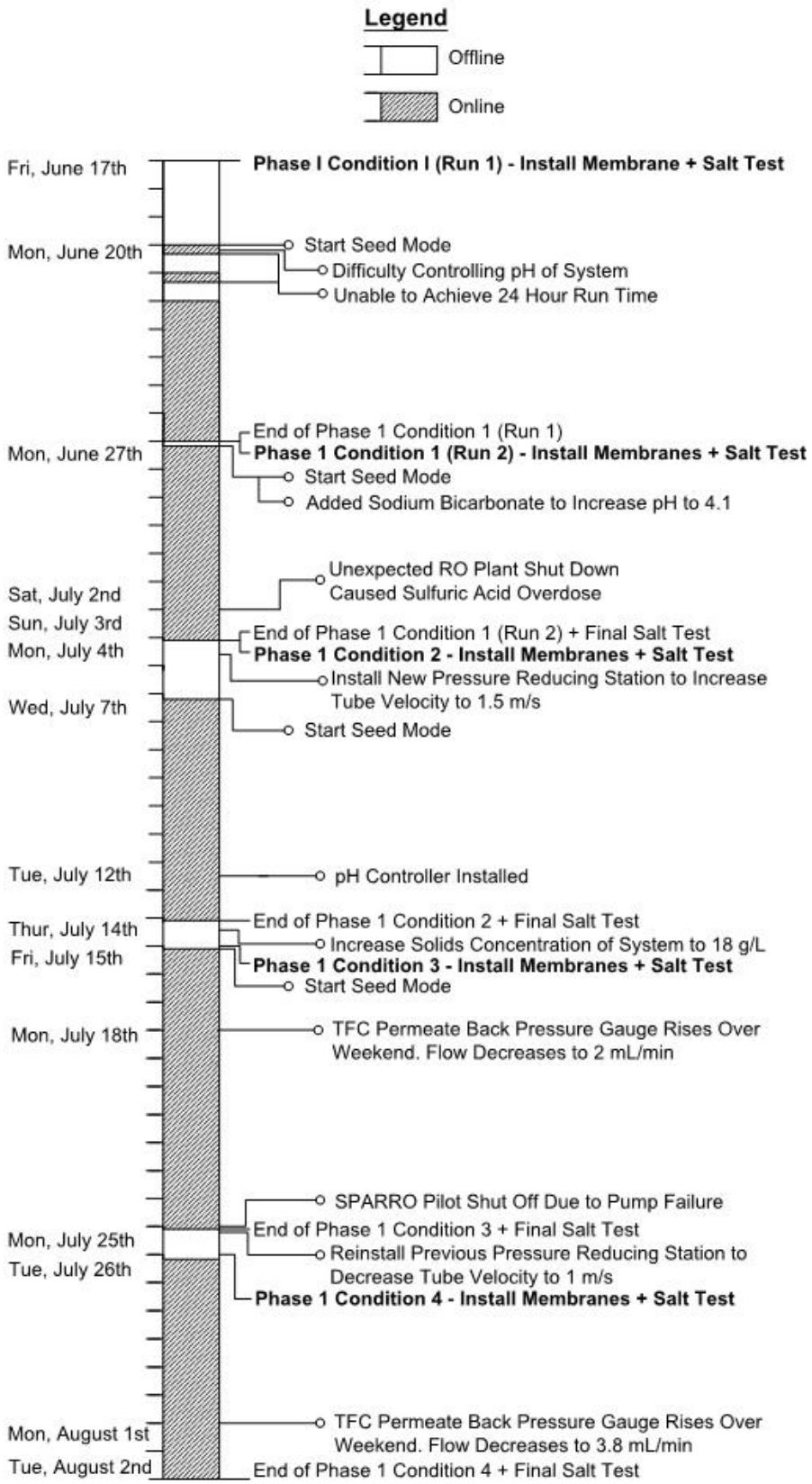

Figure 20. Timeline of Phase 1 operations.

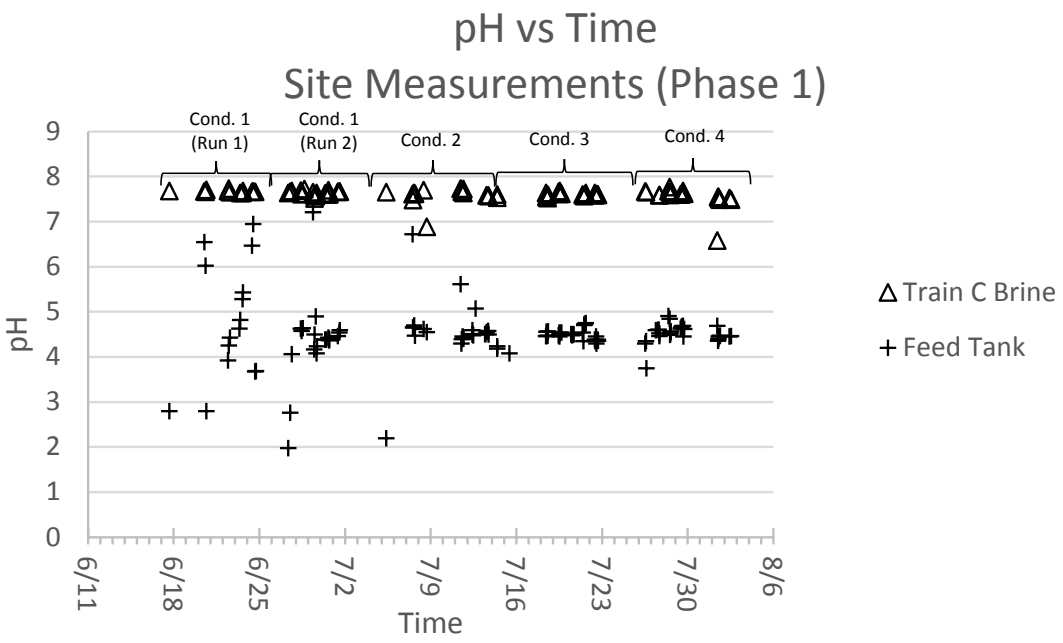

Figure 21. pH vs Time for Phase 1 That Show Uncontrollable pH Readings up Until the End of Condition 2

Balancing the flux values of the TFC and CA membranes was a further operational challenge encountered during Phase 1. The TFC membrane produced significantly more permeate (i.e., had a much higher flux) than the CA membrane at the same feed pressure. To provide similar operating conditions, a manual needle valve and pressure gauge were installed in the TFC permeate line as mentioned in Section 3.1.3.2. This allowed us to provide back pressure on the TFC membrane to reduce the net driving pressure and therefore reduce the flux to about the same value as that of the CA membrane. Because the back pressure valve was manual, the system still experienced some variations in the permeate production and it was not possible to balance the fluxes continuously. Table 8 presents some results to illustrate the variations experienced.

Table 8. TFC vs. CA Permeate Flow Variation

Date	Time	TFC Flow mL/min	TFC Back-pressure psig	CA Flow mL/min	TFC Conductivity µS/cm	CA Conductivity µS/cm
Friday, July 29, 2016	4:30 p.m.	9.6	72	10	2,654	3,860
Monday, August 1	9:40 a.m.	3.8	126	9.4	4,783	3,877
Monday, August 1	11:15 a.m.	9.6	68.5	9.5	2,425	3,742

4.1.2 SPARRO Start-Up

As shown in the Phase 1 Timeline, pilot operation for Phase 1 began in June 2016. Prior to operating Phase 1 Condition I (Run 1), the SPARRO pilot unit was commissioned using permeate water from the desalter. During this period, leaks were repaired and faulty equipment was replaced. Citric acid was then added to the system and was left recycling in the system overnight to remove any calcium carbonate scale remaining from the previous pilot study.

The Phase 1 Timeline also indicates that membranes were installed and a salt test was performed on June 17. The salt rejection versus time results for the Condition 1 and Condition 4 salt test is presented in Figure 22 and Figure 23 respectively. The other salt test results yielded similar outcomes to Condition 1 and Condition 4 and are included in Appendix D.

The results show that both the TFC and CA membranes had a salt rejection of about 70 percent on the NaCl solution used, and this value did not change significantly between the start and end of the Phase 1 operating conditions. This suggests no damage to the membranes during the week-long operating periods for each of the four conditions tested.

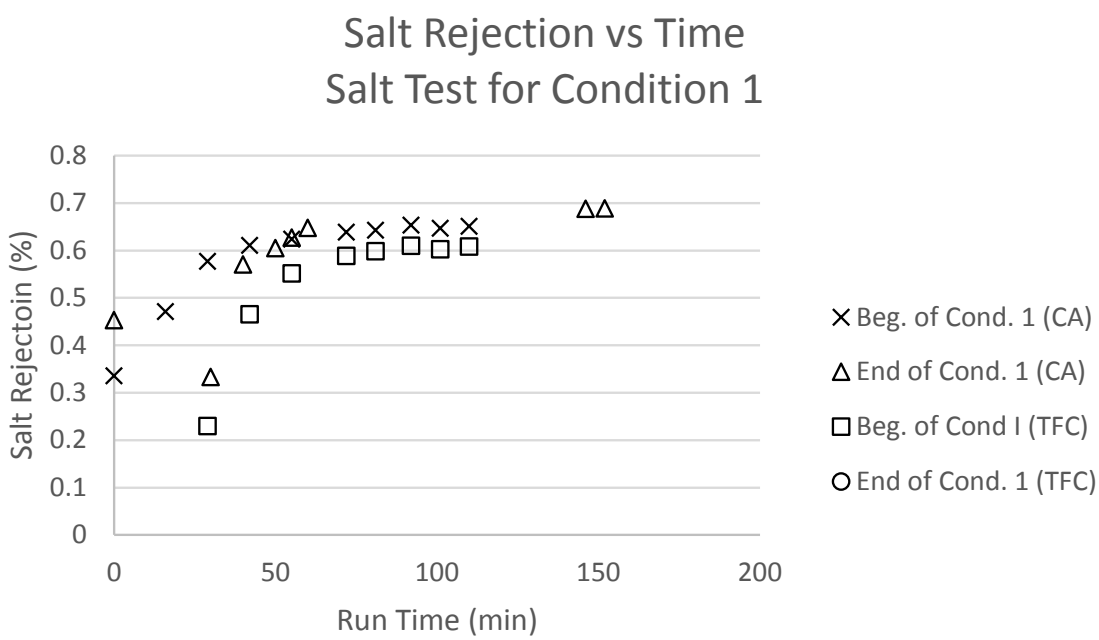

Figure 22. Salt test - salt rejection vs. time for Condition 1 Run 2.

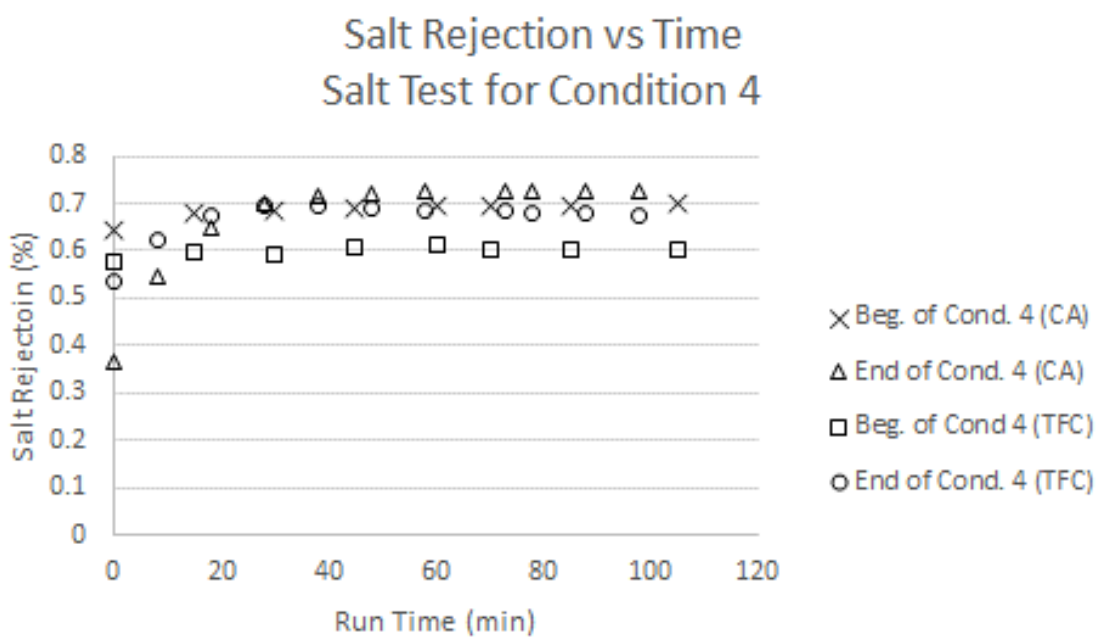

Figure 23. Salt test - salt rejection vs. time for Condition 4.

4.1.3 Seed Material

4.1.3.1 Initial Seed Material

Based on the good results obtained by making gypsum in the Laboratory, larger batches of gypsum were similarly prepared at the Arlington Desalter. However, instead of using RO water from Carollo's laboratory, RO permeate from the Arlington Desalter was used. To make 25 pounds of crystals, 0.6 moles per liter (M) solutions of sodium sulfate and calcium chloride were used . A power drill with a stirrer attached to it was used to mix the solutions for about 2 minutes while the solids formed. These crystals were added to the seed tank to produce 10 grams per liter (g/L) of seed for the Phase I testing.

The change in recipe (moving from 0.4 M to 0.6 M solutions) was selected so that a higher mass of crystals would result from each batch prepared in order to prepare the 25 pounds more efficiently. Results from work at UCT had shown that platelet-type morphology was more likely with high molarity solutions. Thus it was assumed that platelet morphology would result from using 0.6 M solutions.

4.1.3.2 Crystal Morphology of Recirculating Seed

During Phase 1 operation, samples of recirculating seed were sent to UCT to determine if the crystals had changed over time. The first sample of seed was acquired from the solids-waste bucket, which had an accumulation of daily-removed-seed from the beginning of Condition 1 (Run 1) to the end of Condition 2. The second sample was removed from the feed at the beginning of Condition 3 after increasing the feed tank concentration to 18 g/L with new seed

created on site. The SEM images for the end of Condition 2 seed and start of Condition 3 seed are shown on Figure 24 and Figure 25, respectively.

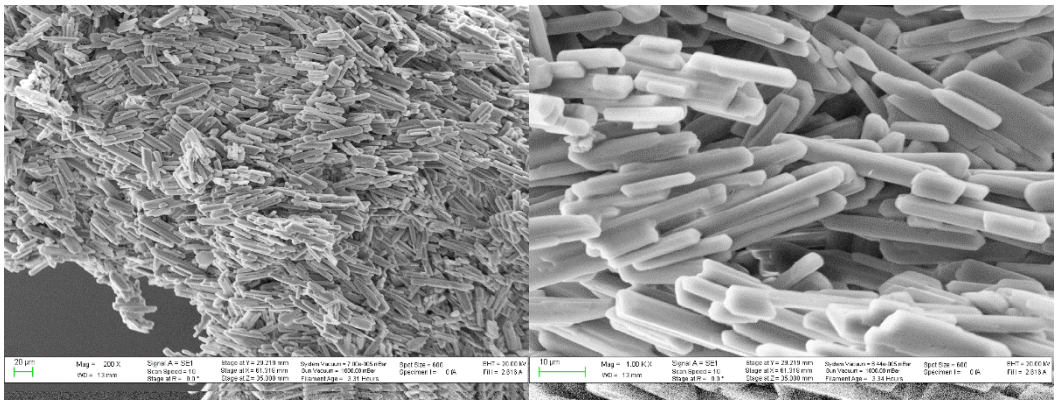

Figure 24. Crystal morphology of the gypsum seed crystals by the end of Phase I Condition II.

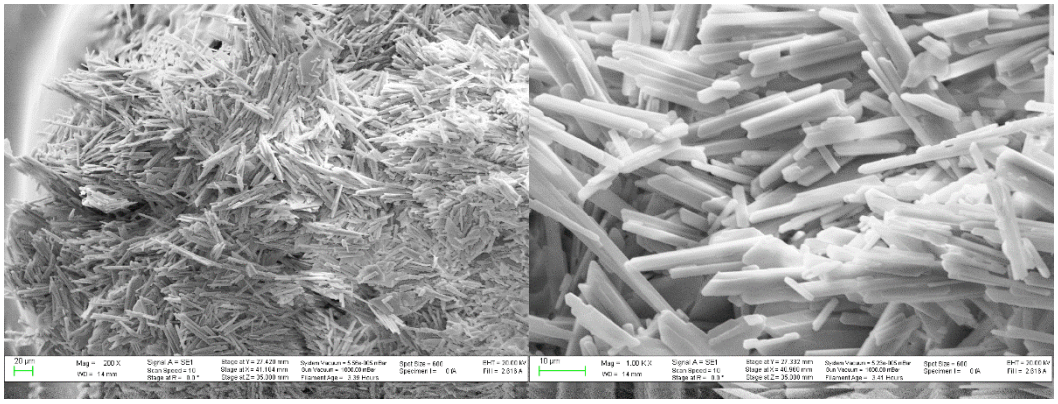

Figure 25. Crystal morphology of the gypsum seed crystals at the Beginning of Phase I Condition III.

As shown in Figure 24 and Figure 25, the crystal morphology of the recirculating seed at the end of Condition 2 and at the start of Condition 3 both resemble more of a rod-shaped morphology rather than a platelet-type morphology. This was unexpected given the earlier success of preparing seed with platelet-type morphology and there may be several possible reasons for the results. As explained above, when compared with the seed batch made in the laboratory larger batches of seed were created at the Arlington Desalter using higher molarity solutions; a different stirrer was used and the mixing time was longer; and different dilution water was used to prepare the calcium chloride and sodium sulfate solutions. These differences could have resulted in the formation of rod-like crystals. Since a sample of the original 25 pounds of seed made from the 0.6 M calcium chloride and sodium sulfate solutions created at the Arlington Desalter did not undergo an SEM analysis, it is not possible to conclude whether the crystals changed from plate-like to needle-like while recirculating in the system. However, we do know that not much crystal growth occurred during Phase 1, because production rates were low. This would tend to suggest that the crystal morphology was non-platelet type at the start of Phase 1.

During the transition period between Phase 1 and Phase 2, gypsum created from the 0.4 M and 0.6 M sodium sulfate and calcium chloride solutions using RO water from Carollo's laboratory were sent to UCT to determine if there were differences in the morphology. The SEM images of the solids formed from the 0.4 M and 0.6 M calcium sulfate solution are shown on Figure 26 and Figure 27, respectively

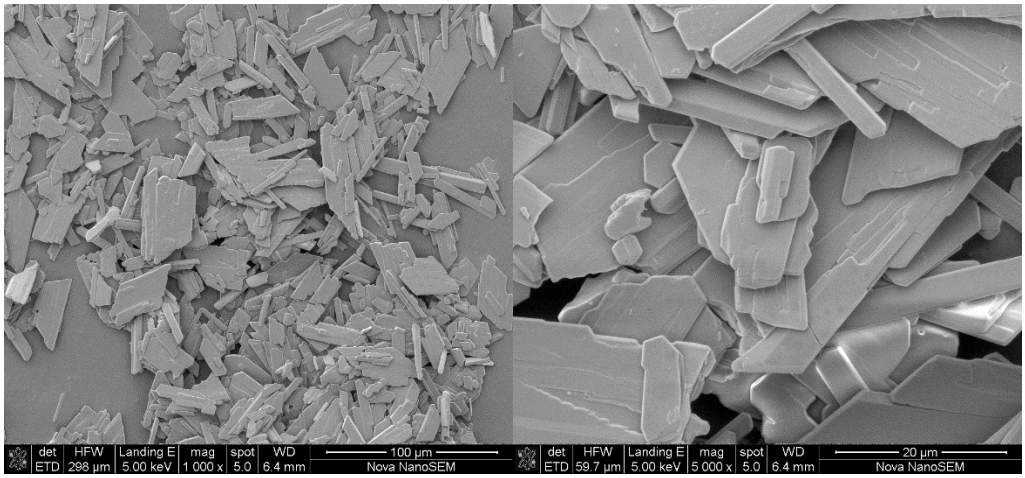

Figure 26. SEM image of 0.4 M gypsum.

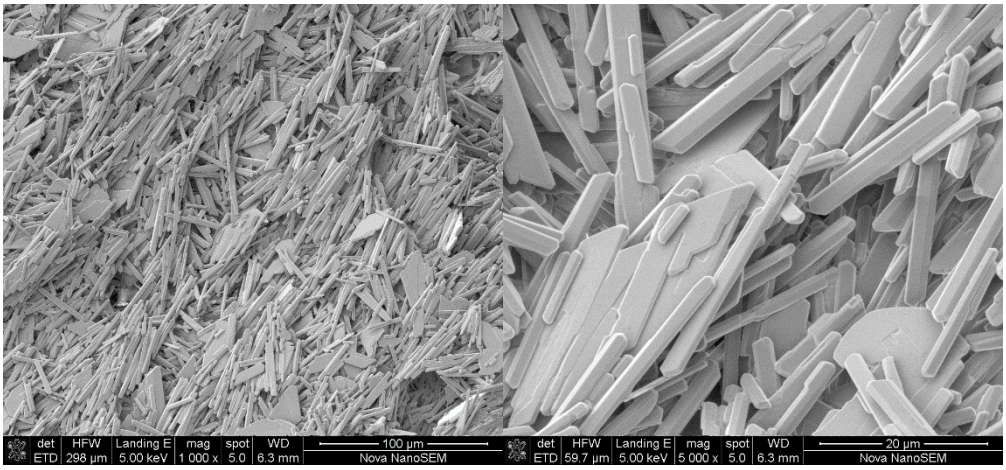

Figure 27. SEM image of 0.6 M gypsum.

A comparison of the images shows that the crystals formed from the 0.4 M solution have a much flatter platelet-type morphology (Figure 26) than those generated from the 0.6 M solution (Figure 27). This test confirmed that the cause of the rod-like crystals observed during Phase 1 was due to the use of the higher strength 0.6 M solutions.

A comprehensive report by the UCT on the crystal morphology of all of the samples of gypsum seed analyzed during the testing is presented in Appendix C.

4.1.3.3 Solids Quality

Since the slurry solution in the SPARRO pilot was supersaturated with silica, an EDX analysis was requested to find out if the silica was precipitating on the gypsum. The EDX analyses results are presented in Table 9. As shown in the table, the solid samples were shown to contain 99 percent calcium sulfate.

Table 9. EDX Analyses for Silica on End of Condition 2 and Start of Condition 3 Recirculating Seed (Analyzed by UCT)(1)

Element	Series	Weight % E.C.2(2) vs B.C.3(3)		Norm. Weight % E.C.2 vs B.C.3		Norm. At. % E.C.2 vs B.C.3		Error in % E.C.2 vs B.C.3	
Oxygen	K-Series	53.01	53.51	64.05	62.84	80.13	79.00	6.67	6.72
Calcium		17.33	17.29	20.94	20.30	10.46	10.19	0.54	0.54
Sulfur		12.26	13.49	14.81	15.84	9.25	9.94	0.47	0.51
Sodium		0.16	0.81	0.19	0.95	0.16	0.83	0.04	0.09
Silicon		0.01	0.05	0.01	0.06	0.01	0.04	0.00	0.00
Sum:		82.76	85.15	100.00	100.00	100.00	100.00		

(1) New membrane tubes were installed on June 27 at the start of the second run under Condition 1.
(2) E.C.2 means Ending of Condition 2
(3) B.C.3 means Beginning of Condition 3

4.1.4 Feedwater Quality

Concentrate from the Desalter RO Train C was the raw water source for the SPARRO pilot plant. Grab samples were collected and analyzed by EMWD twice a week for Phase 1. The sample analyses were used to characterize the SPARRO influent water quality. Table 10 includes the average values for the individual feedwater quality parameters measured throughout Phase 1 and also includes the number of samples that were factored into the average. As shown, the desalter's RO concentrate had a moderate salinity (5,333 mg/L TDS) as well as high levels of alkalinity, calcium and silica. The desalter uses an anti-scalant (Y2K) at a dosage of 4 mg/L to prevent silica and calcium salt precipitation.

Table 10. Average SPARRO Feedwater Quality – Phase 1

Parameter	Units	# of Samples	Average	Max	Min
Alkalinity	mg/L	9	1,663	1,770	1,590
Calcium	mg/L	9	756	800	710
Chloride	mg/L	9	896	970	850
Conductivity	µS/cm	9	6,512	6,690	5,820
Hardness	mg/L	9	3,079	3,240	2,910
Magnesium	mg/L	9	288	300	270
pH	-	9	7.7	7.8	7.7
Sulfate	mg/L	9	1,166	1,240	1,110
Sodium	mg/L	9	706	770	650
Total Dissolved Solids (TDS)	mg/L	9	5,333	5,800	5,000
Total Silica	mg/L	9	223	210	210
Total Suspended Solids (TSS)	mg/L	9	<5.4	12	3

The EMWD TSS values were multiplied by 1.199 to account for the waters of hydration that were lost when drying the samples at 105 degrees Celsius (°C). The 1.199 multiplier was based on the assumption that the solids were 95 percent gypsum ($CaSO_4.2H_2O$)—the purity of the solids sample measured during testing, as discussed below.

Figure 28 includes all 9 feedwater samples analyzed by EMWD for Phase 1. The analyses indicate a very consistent feedwater quality throughout the duration of Phase 1. This is highlighted by the flat, consistent pattern of the TDS, pH, and conductivity data displayed on Figure 28.

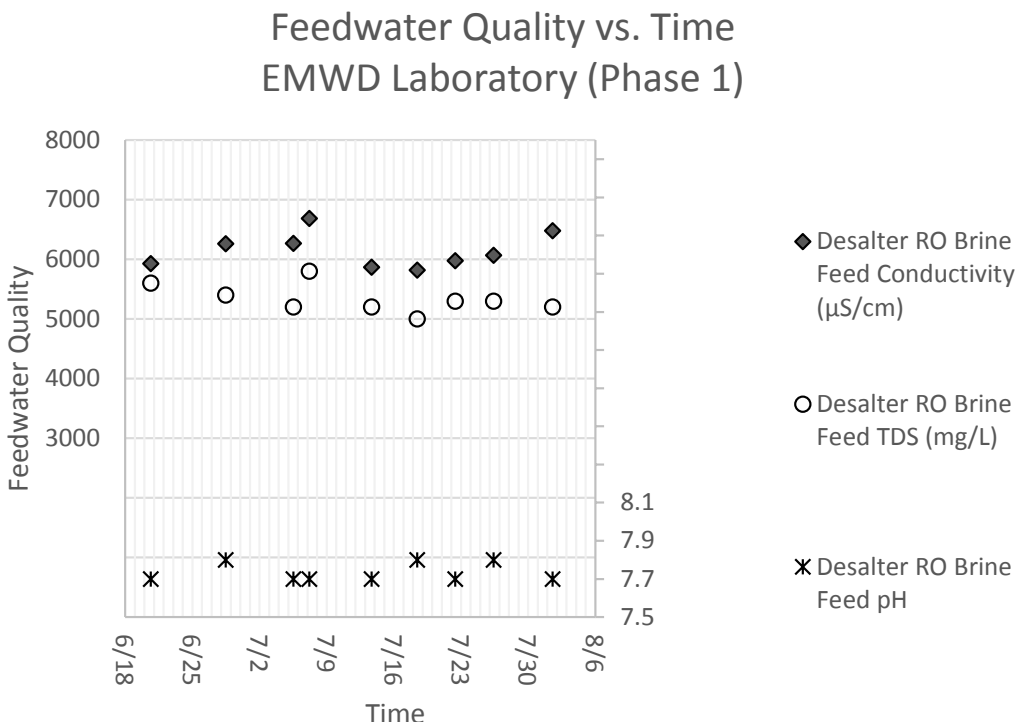

Figure 28. SPARRO feedwater quality for Phase 1 (EMWD).

4.1.5 Hydraulic Performance

Figure 29 shows the variation of concentrate flow during Phase 1, illustrating how the flow was adjusted to provide the desired tube velocity. The flow rate of 2.0 gpm produced a tube velocity of 1 .0 m/s, and the flow rate of 3 gpm increased the velocity to 1.5 m/s.

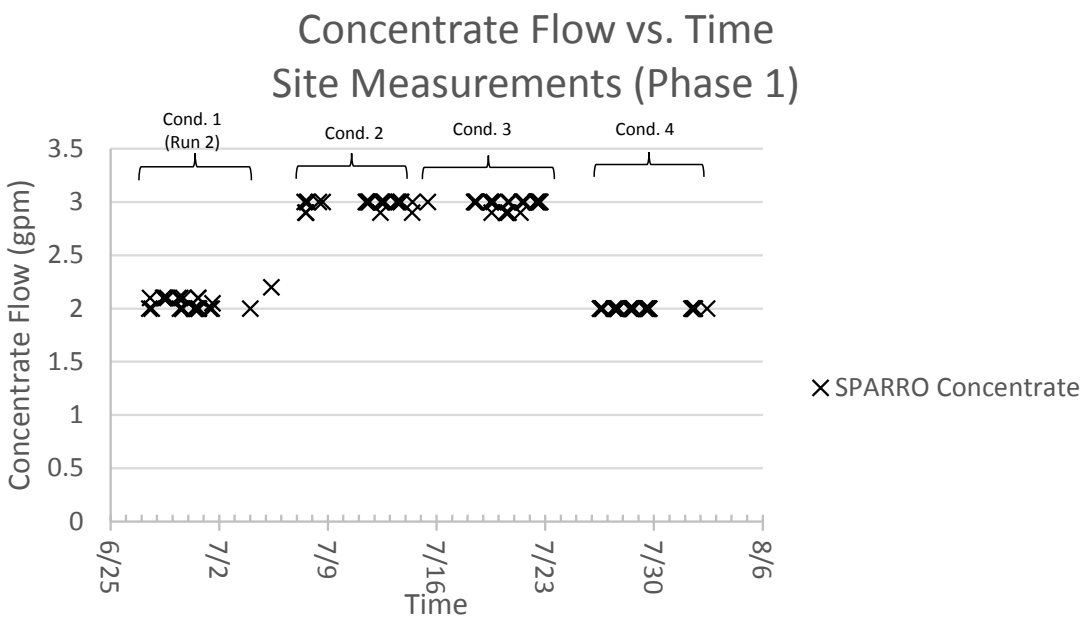

Figure 29. SPARRO concentrate flow vs. time for Phase 1.

Figure 30 shows the measured permeate flow variation during the four operating conditions in Phase 1 for both the TFC and CA membranes.

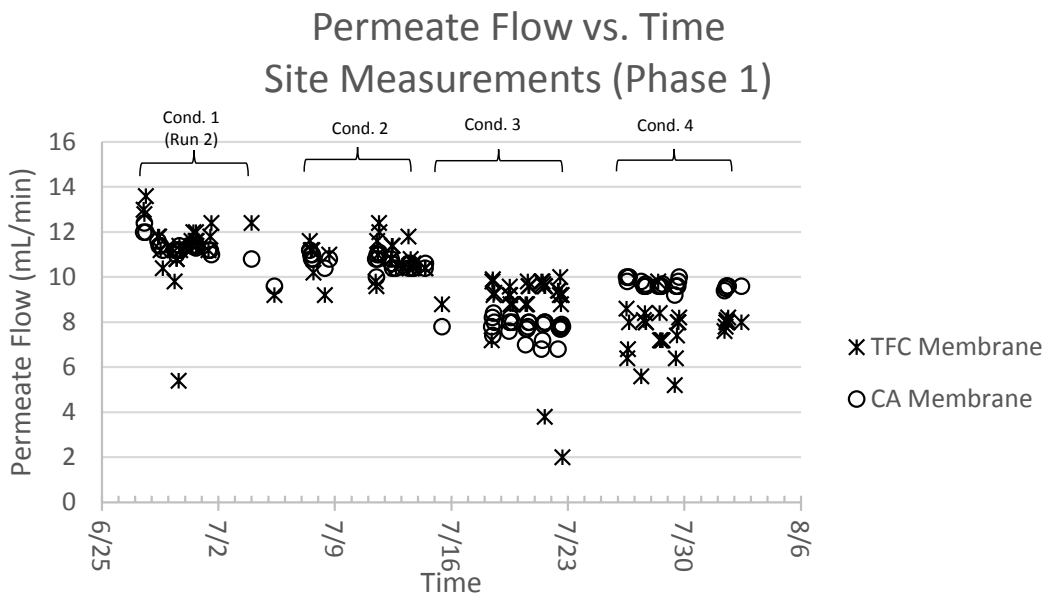

Figure 30. TFC and CA permeate flow vs. time (Phase 1).

As indicated, for about half the operating period the permeate production was similar for both membranes in order to have them both operating at similar flux rates. During Condition 3 and 4, it became more challenging to adjust the back pressure on the TFC membrane, hence the variation in production observed. Figure 31 shows the variation in system pressure during Phase 1. Generally, the pressures were fairly stable. Most variations occurred in the TFC permeate back pressure which explains the variations in TFC permeate flow stream on Figure 30.

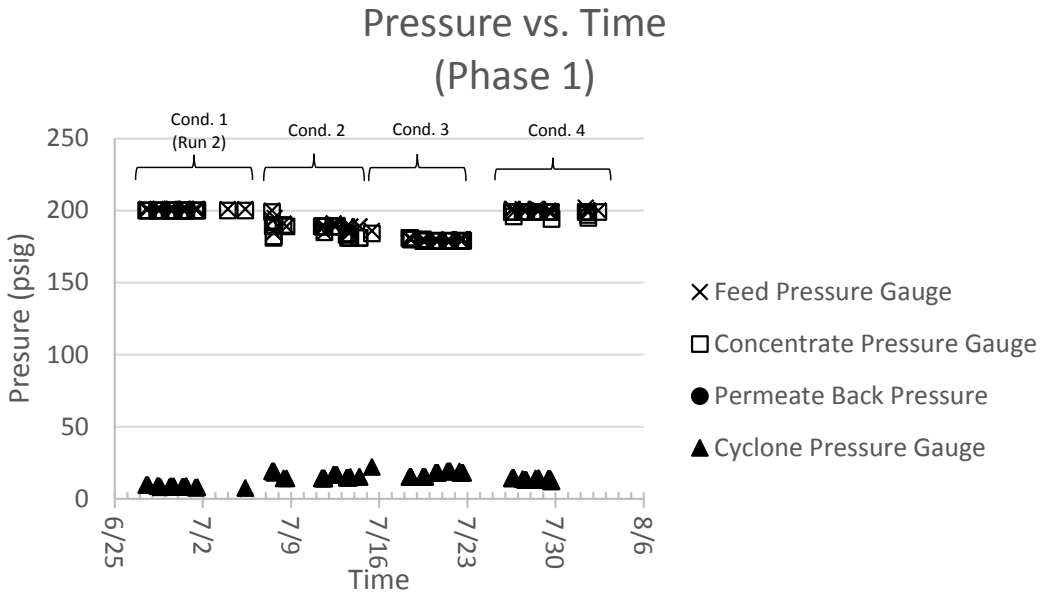

Figure 31. SPARRO system pressure vs. time (Phase 1).

Figure 32 shows a plot of the normalized permeate flow (NPF) for the conditions in which the seed concentration was 10 g/L (Condition 1 and Condition 2) for both the TFC and CA membranes. This graph illustrates the challenges with trying to control the TFC permeate flux with a manual back pressure valve. As can be seen t the TFC membrane has periods of inconsistent data, whereas the CA membrane data shows for less variability.

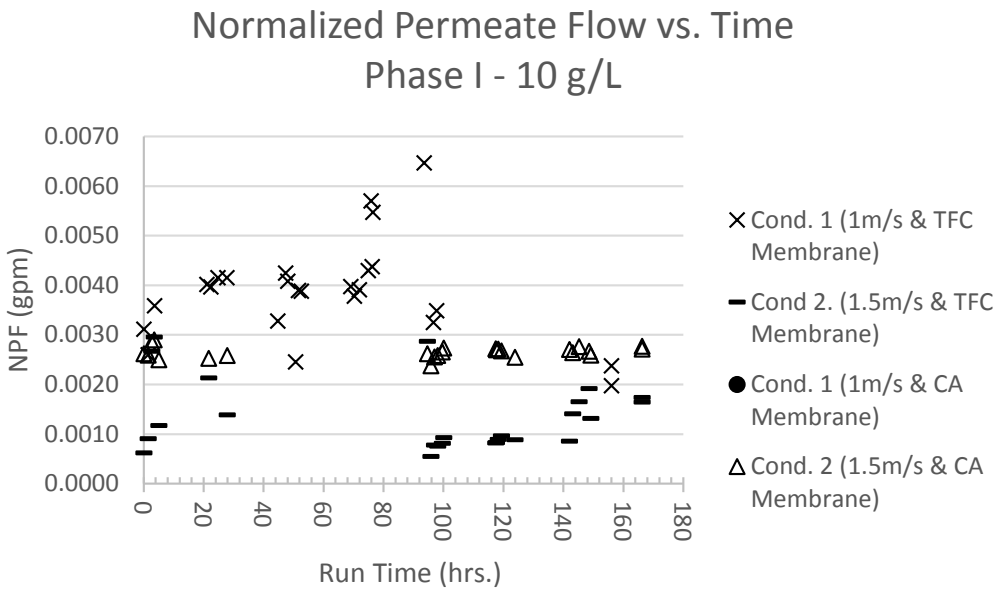

Figure 32. TFC and CA normalized permeate flow vs. time (Condition 1 and 2).

Similar plots were obtained for the NPF for the other conditions evaluated. They are included in Appendix D.

4.1.6 Membrane Performance

Table 11 presents the average water quality data for all samples collected during Phase 1. Samples for which parameters were below the detection limit were assumed to be at the detection limit for calculating the average value.

The EMWD TSS values were multiplied by 1.199 to account for the waters of hydration that were lost when drying the samples at 105°C. The 1.199 multiplier was based on the assumption that the solids were 95 percent gypsum (CaSO4.2H2O), which was the purity of the solids sample measured during testing, and discussed further below.

Figure 33 presents the conductivity variations for the feed, product and concentrate streams, as measured in the Laboratory.

Table 11. Average SPARRO Water Quality Analyzed by EMWD –Phase 1[1]

Stream No.			1	2	3	4	5	6
Stream Name		# of Samples	Train C Brine (SPARRO Feed)	Feed Tank	TFC Permeate	CA Permeate	Cyclone Overflow / SPARRO Concentrate	Cyclone Underflow
Parameter	**Units**							
pH	-	9	7.7	5.7	4.4	4.7	4.5	
ORP	-	9	-	166	-	-	-	
Conductivity	µS/cm	9	6,152	11,926	3,432	3,413	12,860	
Hardness	mg/L	9	3,079	3,058	60	231	3,062	
Alkalinity	mg/L	9	1,663	16[2]	4.2[3]	4.8[6]	4.3[6]	
TDS	mg/L	9	5,333	10,489	1,429	1,856	10,733	
TSS	mg/L	9	<5.4	9,612[7]	-	-	1,820[7]	22,224[7]
Sulfate	mg/L	9	1,166	4,537	73	230	4,353	
Sodium	mg/L	9	706	2,370	499	570	2,401	
Calcium	mg/L	9	756	529	12.8[4]	45	537	
Magnesium	mg/L	9	288	421	8[5]	29	416	
Chloride	mg/L	9	896	2,056	717	708	2,056	
Total Silica	mg/L	9	223	293	95	85	292	

(1) Parameters for which the values were reported as below the detection limit were assumed to be at the detection limit for calculating the average.
(2) 2 out of 9 feed tank samples were below the detection limit of 4 mg/L of alkalinity.
(3) 7 out of 9 TFC permeate samples were below the detection limit of 4 mg/L of alkalinity.
(4) 2 out of 9 TFC permeate samples were below the detection limit of 1 mg/L of calcium.
(5) 3 out of 9 TFC permeate samples were below the detection limit of 1 mg/L of magnesium.
(6) 8 out of 9 CA permeate and SPARRO concentrate samples were below the detection limit of 4 mg/L of alkalinity.
(7) The EMWD TSS results were all multiplied by a factor of 1.199 to account for the waters of hydration (attached to Calcium Sulfate Dihydrate) that were lost when drying the seed samples at 105°C (221 degrees Fahrenheit [°F] or 378.15 degrees Kelvin [°K])

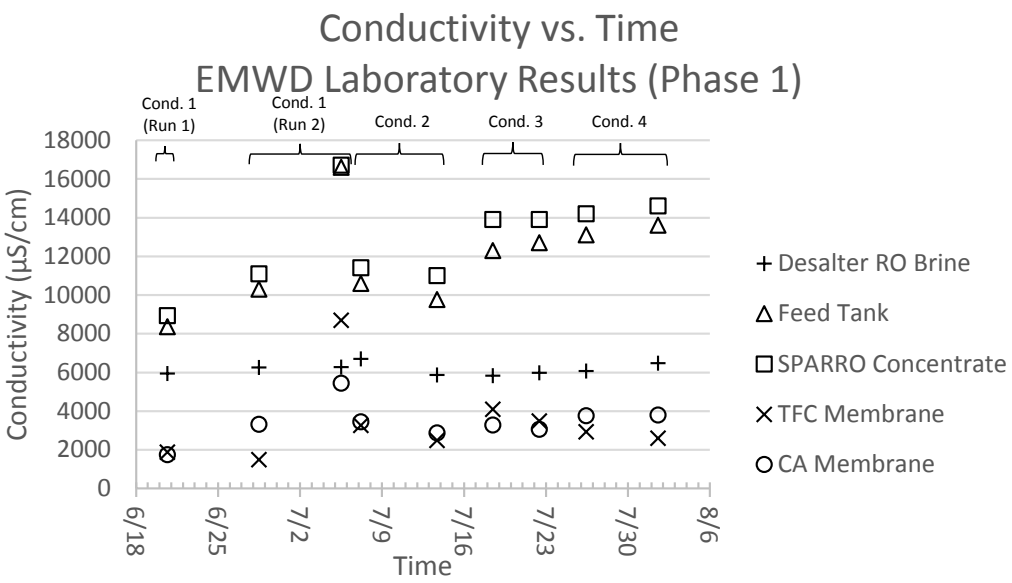

Figure 33. Phase 1 Conductivity vs. time (measured by EMWD).

As shown, while the Train C brine to the SPARRO unit remained constant around 6,000 µS/cm, the feed tank conductivity increased over Phase 1's six-week period, from around 8,000 µS/cm to almost 14,000 µS/cm as the system reached steady state. This resulted in an increase in the permeate conductivity of the membranes from around 2,000 µS/cm to between 3,000 and 4,000 µS/cm.

Figure 34 shows the on-site conductivity measurements. Again the consistency of the Train C brine is evident, as is the change in the feed tank conductivity. The change in feed tank conductivity occurred at the start of Condition 3 when the seed concentration was increased from 10 g/L to 18 g/L. This change was due to the residual salts that were added to the system along with the seed material.

Figure 35 shows that there was significant variability of pH during Conditions 1 and 2, but installing a pH controller towards the end of Condition 2 addressed this.

Figure 36 shows the variation in solids concentration for the four Conditions tested in Phase 1 as measured on site with the pycnometer. Condition 3 and 4 had the highest level of recirculating solids, around 18 g/L as expected. The cyclone underflow solids was measured at between 45 and 50 g/L during these Conditions, almost double what it was for Conditions 1 and 2.

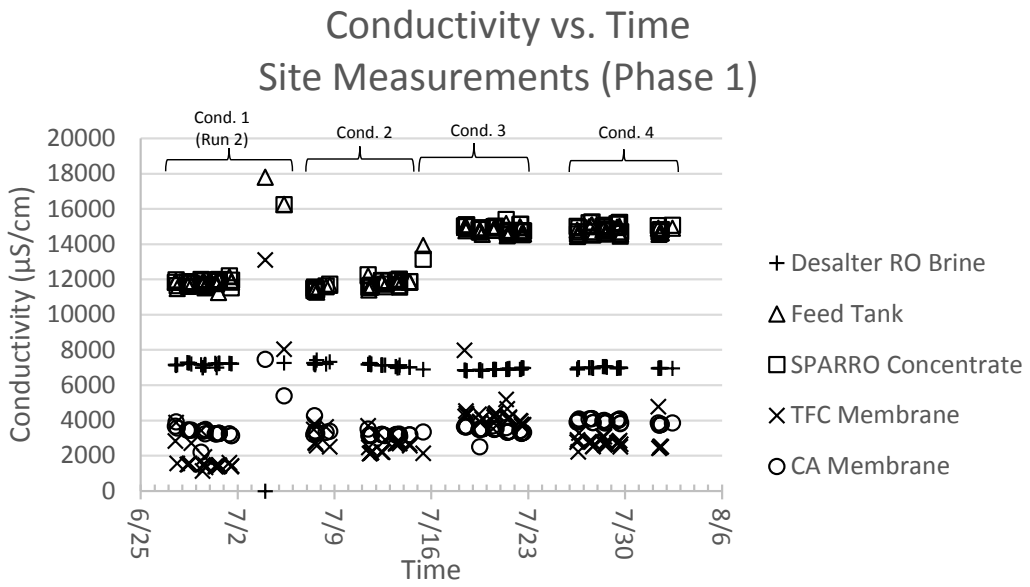

Figure 34. Phase 1 Conductivity vs. Time (Site Measurements)

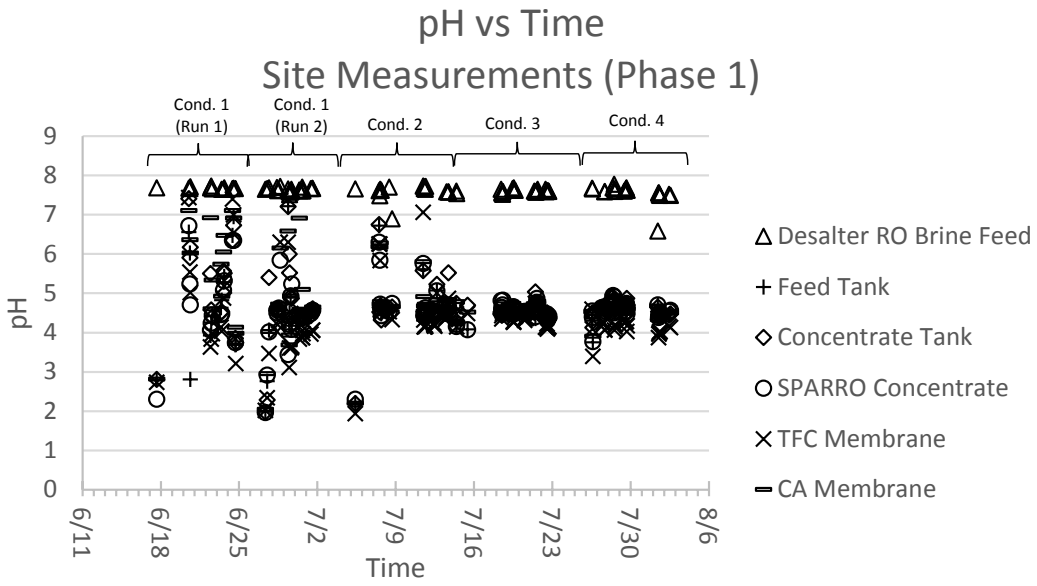

Figure 35. pH vs. time for Phase 1.

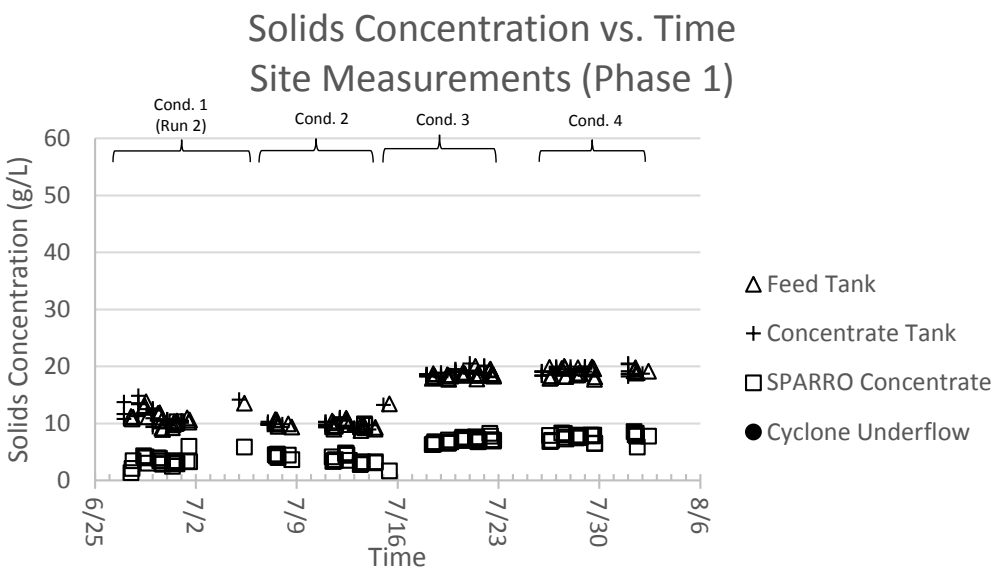

Figure 36. Phase 1 solids concentration vs. time (site measurements).

4.1.7 Phase 1 Discussion

Overall, the system performed very well during Phase 1. Controlling the pH of the feed tank was one of two technical issues that were encountered. Once a pH controller was installed, there were no further pH issues. Controlling the flux of the TFC membrane was a bit tricky because of the small flows involved and adjustments had to be done manually. This operation did not produce consistent results, as the data showed.

Nevertheless, the equipment operation was smooth during all four conditions that were tested and there were no signs of membrane blockages, membrane scouring, or any damage to the membrane. This was in spite of the fact that the system was operating with seed crystals that had rod/needle-type morphology.

Both membranes performed well as can be seen by the quality of the two permeate streams shown in Table 11, and there were no clear improvements or decline in performance between the conditions that were tested; changing the velocity between 1.0 and 1.5 m/s; adjusting the seed concentration between 10 g/L and 18 g/L; or between the performance of the TFC and CA membranes. There was an increase in the membrane permeate TDS of both membranes when operating at the higher seed concentration, but this was due to the resulting higher TDS of the feed solution.

4.2 SPARRO Performance Results - Phase 2

The TFC was selected for Phase 2 operation for three main reasons. Firstly, the TFC membrane was most readily available from the supplier (whereas the CA membrane would need to be manufactured). Secondly, the TFC operates at a lower pressure and would therefore result in a more energy efficient system. Thirdly, the permeate conductivity of the TFC membrane tended to be lower than that of the CA membrane.

It was decided to keep the single-tube elements in operation during Phase 2 with the same membranes that were installed at the end of Condition 4. This provided an opportunity to operate a CA membrane throughout Phase 2 and obtain additional long term performance data for this membrane as well.

As there was no discernable difference in the performance of the two membranes at different seed concentrations or tail-end tube velocities, it was decided to operate at a seed concentration of between 15 and 18 g/L and a tail-end velocity of around 1.5 m/s but no less than 1.0 m/s.

4.2.1 Phase 2 Timeline and Operation

A timeline for the operational period for Phase 2 is shown on Figure 37. As discussed earlier, the Phase 2 goal was to achieve a runtime of 700 hours while operating at one set of conditions. Therefore, the purpose of this timeline is to help visualize when and why the pilot stopped running. The achieved runtime (in hours) was incorporated into this timeline at the end of each pilot shutdown. Similar to Phase 1, each tic interval represents a day starting at 8:00 a.m. and is shaded according to how long the pilot ran.

In contrast to the very smooth operation during Phase 1, Phase 2 had several operational issues—as indicated by the white periods on the timeline in Figure 37. The membranes were loaded for Phase 2 operation on August 26, 2016. Data collection began on September 1, 2016, but the pilot was shut down shortly thereafter for the Labor Day weekend. After re-starting, it was shut down again because the new batch of sulfuric acid had not arrived. Almost two weeks were lost during this period. Before each shutdown, the pilot plant was flushed with RO permeate from the desalter and then placed into “permeate recycle mode,” in which permeate was continually pumped through the membranes in a recirculation mode.

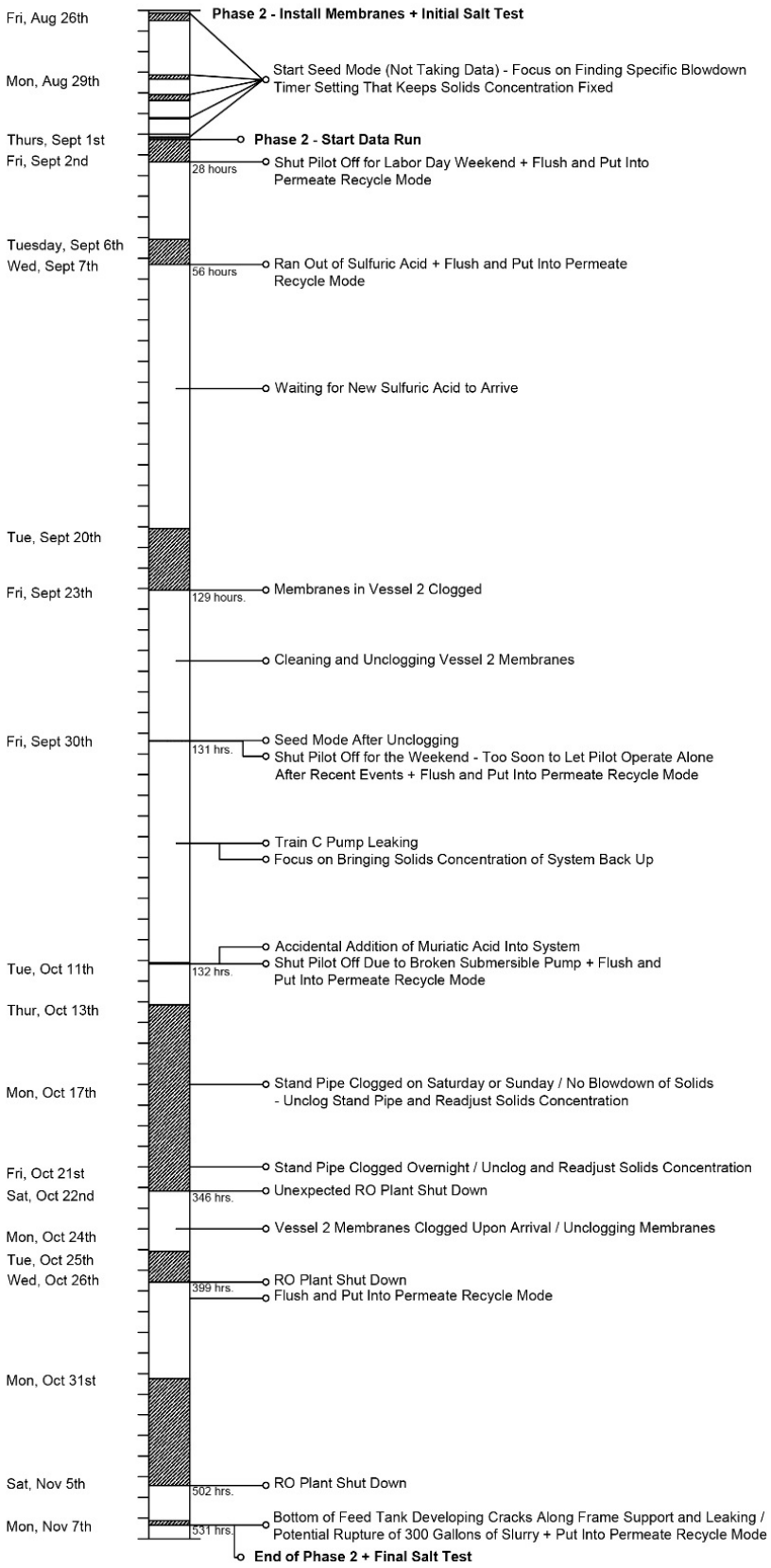

Figure 37. Timeline of Phase II Operation

The unit was re-started on feed solution on September 20, 2016 after acid was obtained, and it ran for 3 days until a blockage occurred in the system somewhere. Investigation revealed that several tubes in the second pressure vessel were blocked with solids. Some of the solids were collected and analyzed by EMWD. The results are discussed later. Unfortunately, during the unclogging, some of the membrane tubes became damaged due to the abrasive action of the solids material and kinking of the membrane tubes during removal and/or insertion (Figure 38). The impact of the damage was only evident after the plant was restarted on October 13, 2016. The shutdown was longer than anticipated due to the need to shut down Train C of the desalter to fix a leak. After re-starting, the plant ran for 9 consecutive days and then shut down due to an unexpected shut down of the desalter. Upon start-up, a second blockage occurred, also found to be in the second membrane vessel.

After cleaning and flushing the blocked membrane—and probably damaging the membrane further—the plant operation continued until November 7. At that point, 531 hours had been achieved, but a preliminary review of the results indicated fairly poor membrane performance. In addition, the feed tank was now leaking from a crack in the cone section of the tank. Thus, it was decided to end the Phase 2 operation.

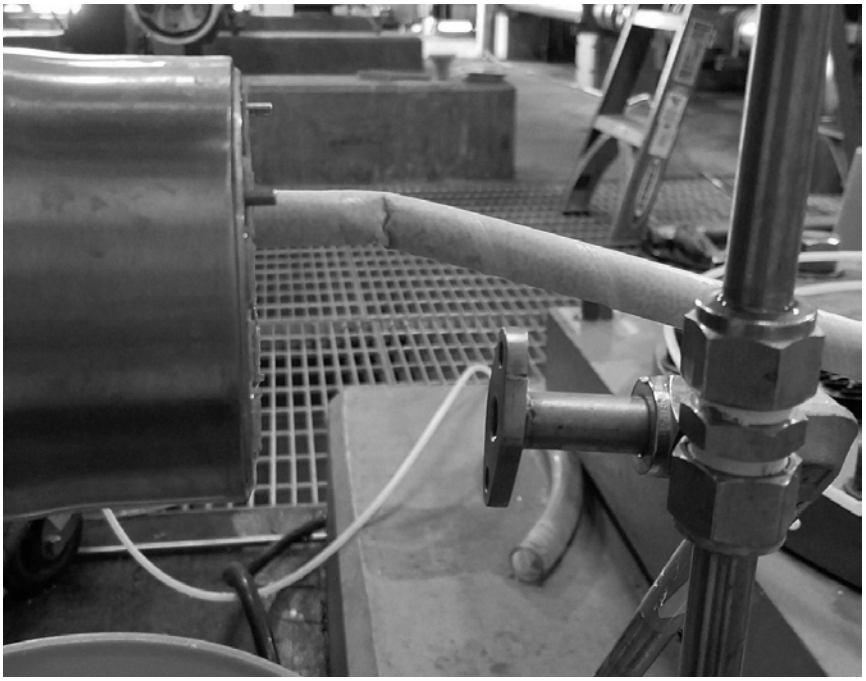

Figure 38. Kinked membrane during removal for cleaning after blockage on September 23.

4.2.2 SPARRO Start-Up

For Phase 2 start-up, a clean-in-place (CIP) was performed on the large membrane vessels on August 24. These vessels were flushed and recycled with

RO permeate and citric acid as the vessels had not been used since the 2013 Pilot Testing.

As shown in the Phase 2 Timeline, the SPARRO pilot unit began seed mode on August 26. However, the official runtime was not started until the first data-run was taken. The first data-run was taken once the timer setting on the seed blowdown system was determined. Note that, although this timer setting kept the feed tank seed concentration reasonably fixed, a small decrease or increase in solids concentration would be significant over time because of how often solids were being wasted from the underflow (every 33 minutes) and the periodic blockages of the stand pipe in the blowdown bucket.

On August 25, the initial salt test was performed. The conductivity of the salt test tank was set to 4,299 µS/cm and had an initial temperature of 25.1°C. The salt rejection curves for the combined vessels, top vessel, and bottom vessel are shown in Figure 39. The salt test data carried out at the end of Phase 2 on November 9, 2016 are also included in Figure 39.

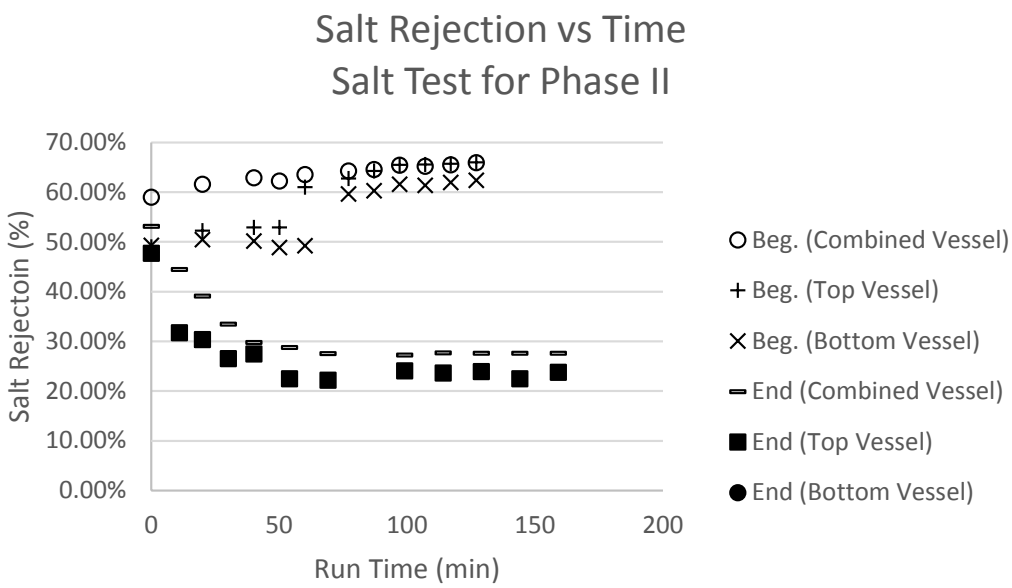

Figure 39. Salt rejection vs. time for beginning and end of Phase 2

As shown, the initial salt rejection stabilized at about 65 percent for the product from both membrane vessels similar to what was obtained in Phase 1. The second membrane vessel (bottom) showed a slightly lower salt rejection than the first. This is thought to be due to a slightly lower permeate flow from the second vessel.

The results for the final salt test at the end of Phase 2 are obviously very different to the initial values; with the salt rejection of the combined vessels being around 28 percent. The bottom vessel had a rejection of only 10 percent; confirming that the membranes were badly damaged. Since the solids blockage occurred only in the bottom vessel, it was surprising that the rejection in the top vessel was also

poor; around 25 percent, but this indicates that the membranes in the top vessel had also been damaged as a result of the blockages. It is not clear why the rejection of the combined vessels was greater than that of the top vessel; but this may have been due to the hydraulic impact of the permeate lines being connected.

4.2.3 Feed Water Quality

For Phase 2, EMWD collected and analyzed grab samples three times a week. Table 12 includes the average values for the individual feedwater quality parameters measured during Phase 2 and the number of samples that were factored into this average. Similar to Phase 1, the desalter's RO concentrate had a moderate salinity (5,180 mg/L TDS) as well as high levels of alkalinity, calcium, and silica. SPARRO feedwater quality results for 10 out of 11 samples collected were very consistent. However, samples collected on November 2, 2016, yielded much lower values than the consistent values and thus were excluded from this average (except for TSS and pH). The TSS value on September 9, 2016, was inconsistent, and, therefore, this value was removed from the data set.

Table 12. Average SPARRO Feedwater Quality – Phase 2

Parameter	Units	# of Samples	Average[(1)]
Alkalinity	mg/L	10	1,641
Calcium	mg/L	10	750
Chloride	mg/L	10	840
Conductivity	µS/cm	10	6,839
Hardness	mg/L	10	3,052
Magnesium	mg/L	10	287
pH	-	11	7.8
Sulfate	mg/L	10	1,103
Sodium	mg/L	10	714
TDS	mg/L	10	5,180
Total Silica	mg/L	10	209
TSS	mg/L	10	<4,2

Figure 40 below includes all 11 feedwater samples analyzed for Phase 2. The analyses indicate a fairly consistent feedwater quality during Phase 2 (with the exception of September 9 and November 2). This is highlighted by the flat, fairly consistent pattern of the TDS, pH, and conductivity data displayed on Figure 40. However, Phase 2 feedwater quality was not as consistent as Phase 1 feedwater quality.

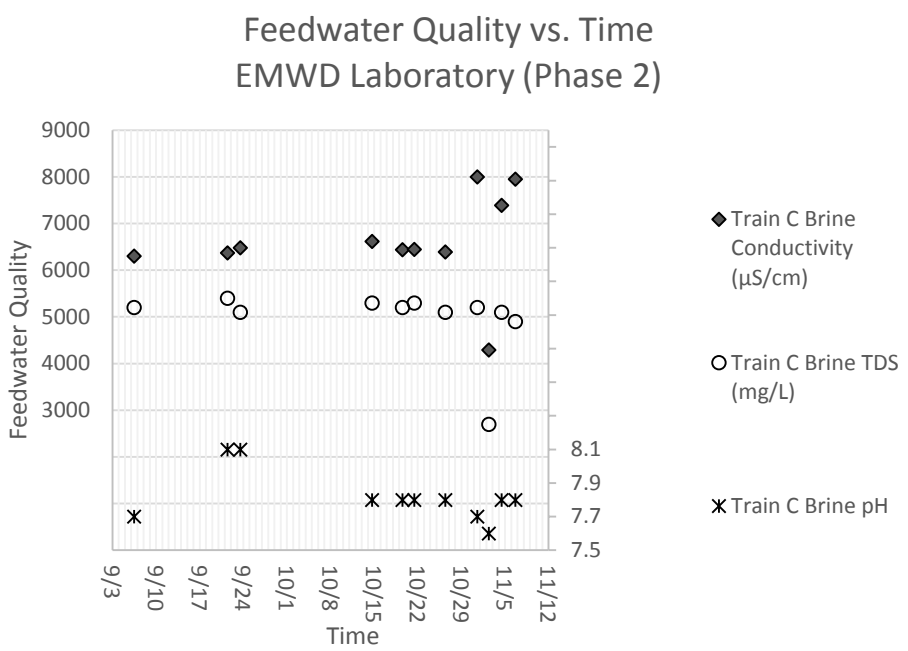

Figure 40. SPARRO feedwater quality for Phase 2 (EMWD).

4.2.4 Hydraulic Performance

Figure 41 presents the variation of the TFC permeate flow for Phase 2. After the damage caused to the membranes during the procedure to unclog the solids on September 23, there was significantly more variability in the permeate flow, which reached 0.6 gpm at times.

The Phase 2 normalized permeate flow (NPF) is plotted on Figure 42. It appears that the NPF dropped significantly just before the blockage in the bottom membrane vessel was discovered, which is understandable given that a portion of the membrane tube would no longer be producing flow, and the feed pressure was increasing, see Figure 43.

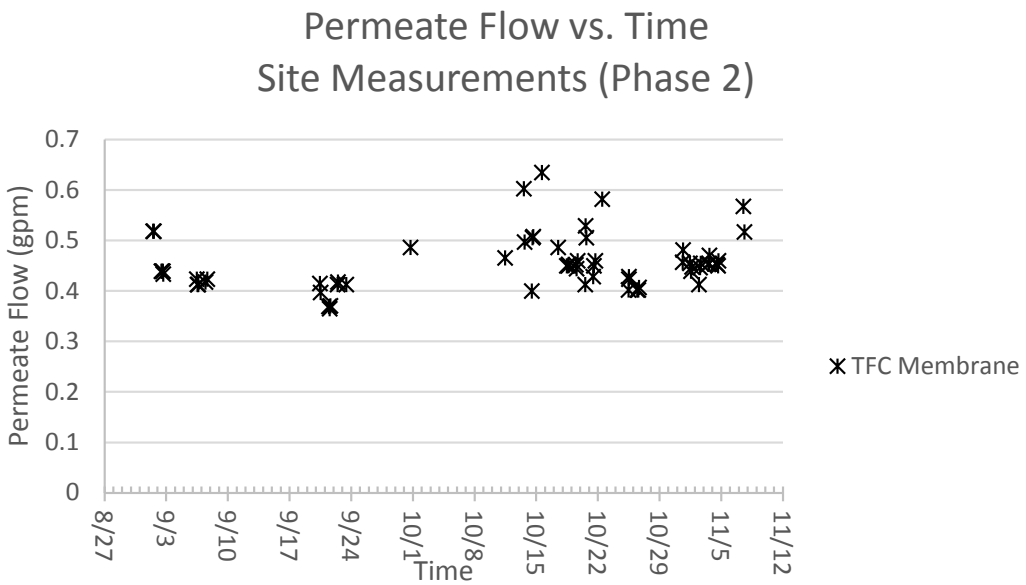

Figure 41. TFC permeate flow vs time for Phase 2.

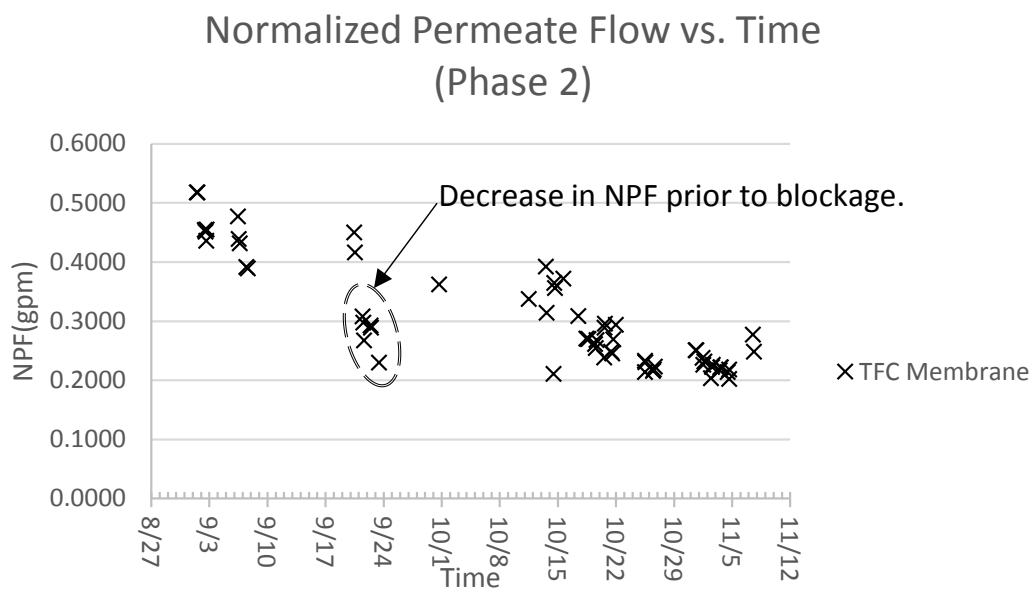

Figure 42. TFC normalized permeate flow vs. time (Phase 2).

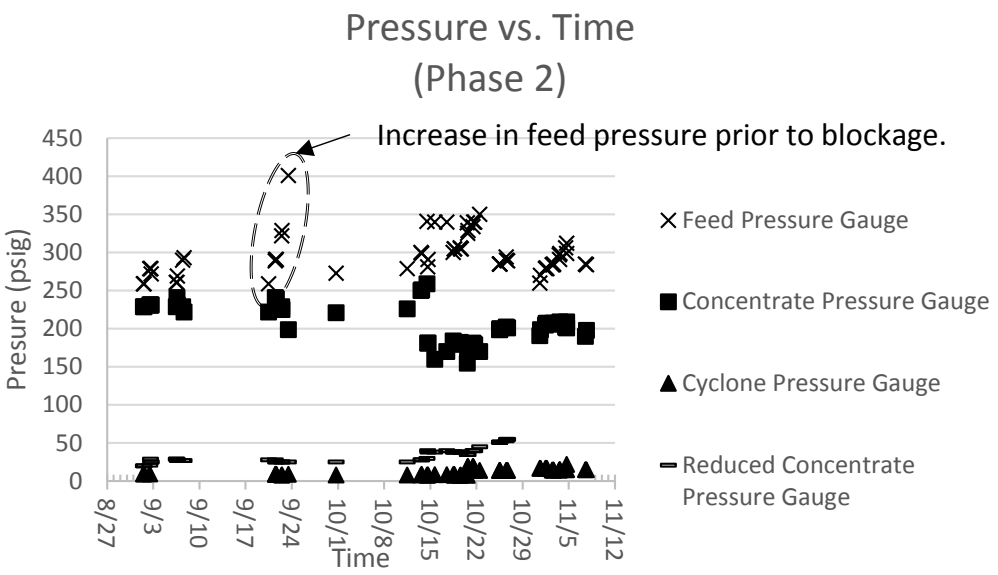

Figure 43. SPARRO system pressure vs. time (Phase 2).

4.2.5 Membrane Performance

Table 13 presents the water quality data for all samples collected during Phase 2. A striking point about the data presented in Table 13 is that the average feed tank suspended solids concentration (TSS) reported by the laboratory was less than 3,000 mg/L. This is less than a third of average values measured during Phase 1, which is discussed in more detail later. Other parameters are reasonably comparable apart from silica, which had an average concentration of 451 mg/L in Phase 2, significantly higher than the average of 293 mg/L in Phase 1.

Figure 44 shows the variation in system pH during Phase 2. As shown, the Train C brine pH was consistently in the range of about 7.5, as it was during Phase 1. The SPARRO system pHs were also stable throughout Phase 2, indicating that the pH controller worked well.

Table 13. Average SPARRO Water Quality Analyzed by EMWD –Phase 2[1]

Stream No.			1	2	3	4	5	6
Stream Name		# of Samples	Train C Brine (SPARRO Feed)	Feed Tank	CA & TFC Permeate (Single Tube Testers)[2]	TFC Permeate (Vessels 1 and 2)[11]	Cyclone Overflow / SPARRO Concentrate	Cyclone Underflow
Parameter	**Units**							
pH	-	11	7.8	5.3	4.8	4.5	4.6	
ORP	-	11	-	-	-	-	-	
Conductivity	µS/cm	11	6,607	12,537	7,689	4,196	14,082	
Hardness	mg/L	11	2,912	6,005	2,219	1,012	6,290	
Alkalinity	mg/L	11	1,577	18[4]	5[6]	4[7]	4.3[9]	
TDS	mg/L	11	4,955	11,673	5,570	2,627	13,164	
TSS	mg/L	11	<4.2[3]	2,867[10]	-	-	740[10]	10,396[10]
Turbidity	NTU				0.45	0.11[8]		
Sulfate	mg/L	11	1,052	4,676	1,960	715	5,275	
Sodium	mg/L	11	683	1,637	1,026	533	1,844	
Calcium	mg/L	11	715	894	317	141	778	
Magnesium	mg/L	11	274	916	347	159	1,055	
Chloride	mg/L	11	801	1,717[5]	1,179	677	1,826[5]	
Total Silica	mg/L	11	201	451	263	148	501	

(1) Parameters for which the values were reported as below the detection limit were assumed to be at the detection limit for calculating the average.
(2) Sample of the CA stream is missing for the date 9/23 due to the blockage event that interrupted the sampling. Thus, 10 CA samples were collected in total. Also, the CA and TFC permeate from the Single-Tube-testers was collected in the same sample bottle.
(3) 4 out of 11 train C brine samples were below the detection limit of 3 mg/L of TSS.
(4) 1 out of 11 feed tank samples were below the detection limit of 4 mg/L of alkalinity.
(5) 7 out of 11 feed tank and concentrate samples were below the detection limit of 1,512 mg/L of chloride.
(6) 9 out of 10 CA permeate samples were below the detection limit of 4 mg/L of alkalinity.
(7) 11 out of 11 TFC permeate samples were below the detection limit of 4 mg/L of alkalinity.
(8) 5 out of 11 TFC permeate samples were below the detection limit of 0.1 NTU of turbidity.
(9) 9 out of 11 concentrate samples were below the detection limit of 4 mg/L of alkalinity.
(10) The EMWD TSS results were all multiplied by a factor of 1.199 to account for the waters of hydration (attached to Calcium Sulfate Dihydrate) that were lost when drying the seed samples at 105°C (221 °F or 378.15 K)
(11) The combined permeate stream of both membrane vessels was collected in the same sample bottle.

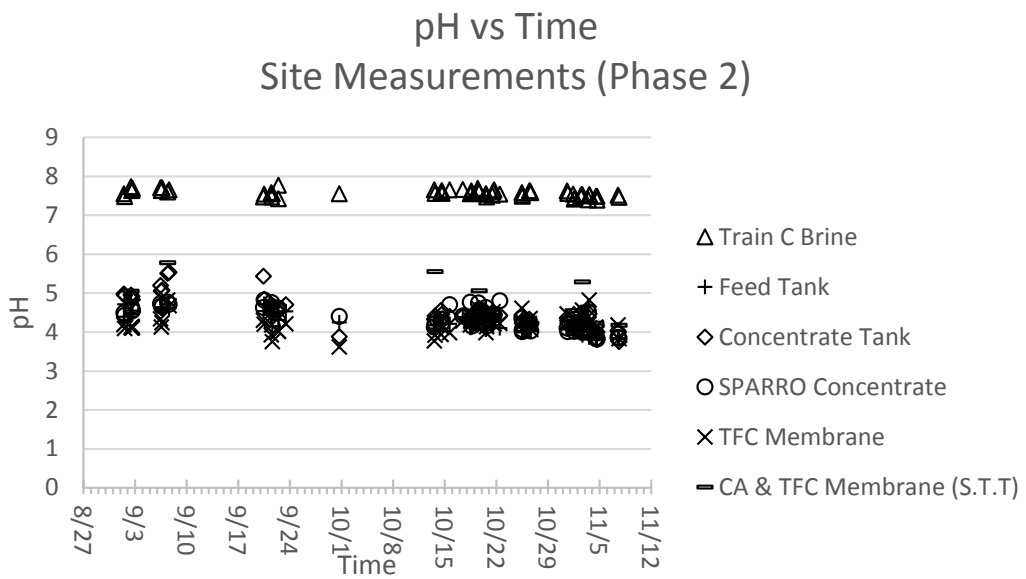

Figure 44. pH vs. time (Phase 2).

Figure 45 shows the variation of TDS with time for several sampling points for Phase 1 and 2. From the Phase 2 data, it can be seen that the TFC membrane permeate TDS increase with time. More striking is the large variation in feed tank and concentrate TDS. These were both very high at the start of Phase 2: the feed tank was about 16,000 mg/L and the concentrate was about 18,000 mg/L. In contrast, the maximum concentration in Phase 1 was around 12,000 mg/L. Although the feed tank and concentrate values started high, they began to decrease from about October 15 and continued this trend all the way to the end of Phase 2—ending around 8,000 mg/L. Other parameters such as conductivity, sodium, sulfate, and silica show similar trends. Graphs showing the variations in these parameters are included in Appendix D, except for silica, which is shown on Figure 46.

The feed and concentrate values of silica shown for Phase 2 in Figure 46 were about double the concentrations encountered in Phase 1. The concentrate stream had a silica concentration of over 600 mg/L on at least two occasions. This is about 3 times the saturation limit. Towards the end of Phase 2, the concentrations were more in line with the values in Phase 1. It is not clear how the silica concentrations got as high as they did during Phase 2.

The normalized salt passage (NSP) for the TFC membranes is shown in Figure 47. It can clearly be seen how the salt passage increased after the first blockage that occurred on September 23.

Figure 48 shows the variation in solids concentration in samples analyzed by EMWD laboratory, and Figure 49 shows the solids concentration estimates made on the site using the pycnometer flask.

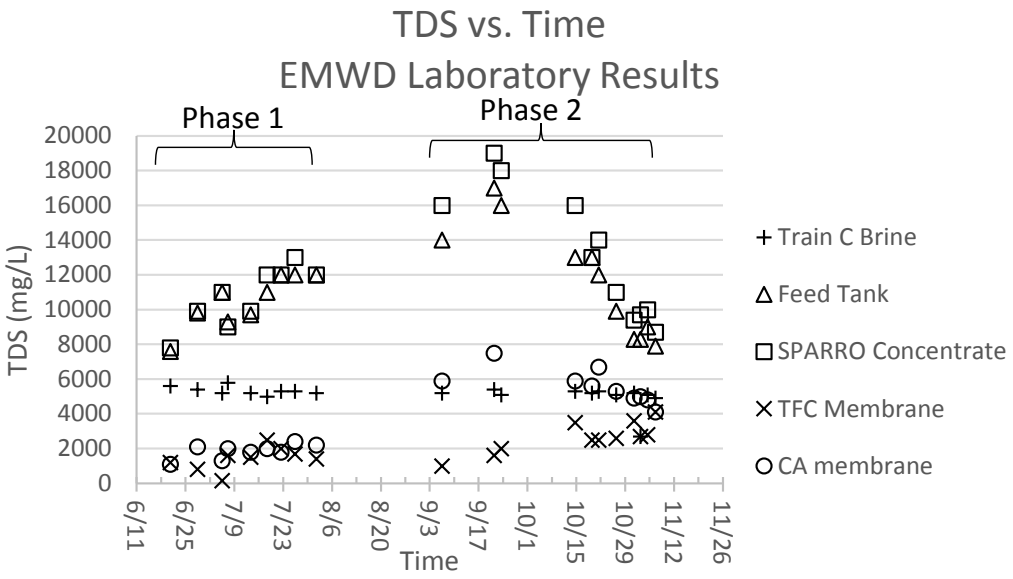

Figure 45. TDS vs. time (Phase 1 and 2).

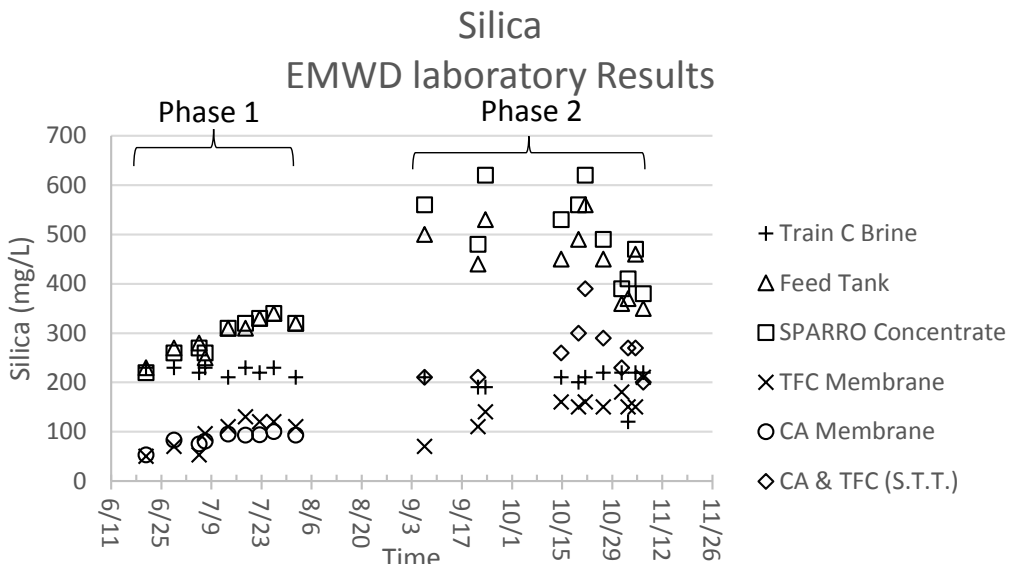

Figure 46. Silica vs. time (Phase 1 and 2).

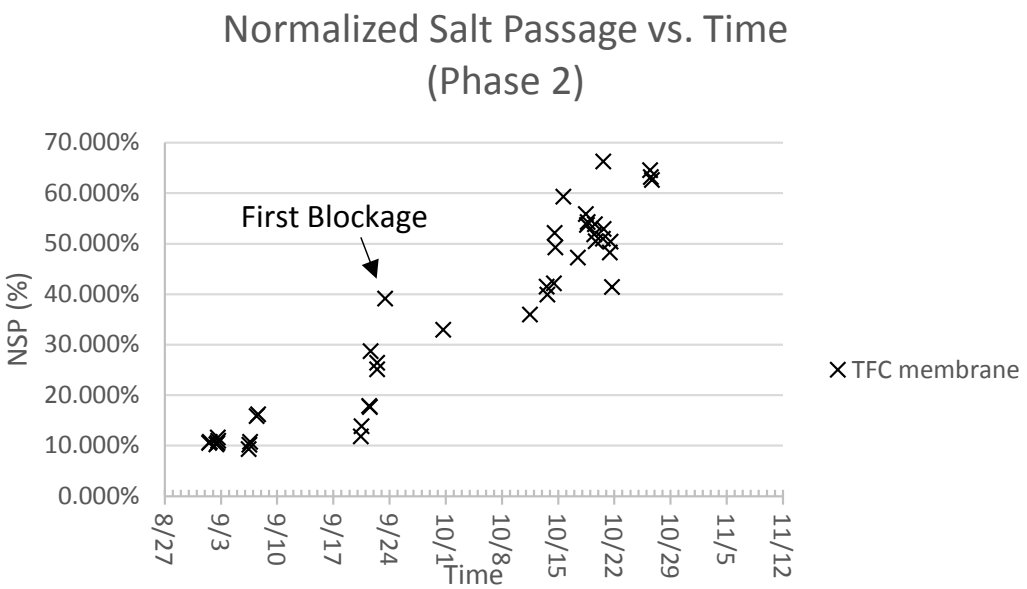

Figure 47. Normalized salt passage vs. time (Phase 2).

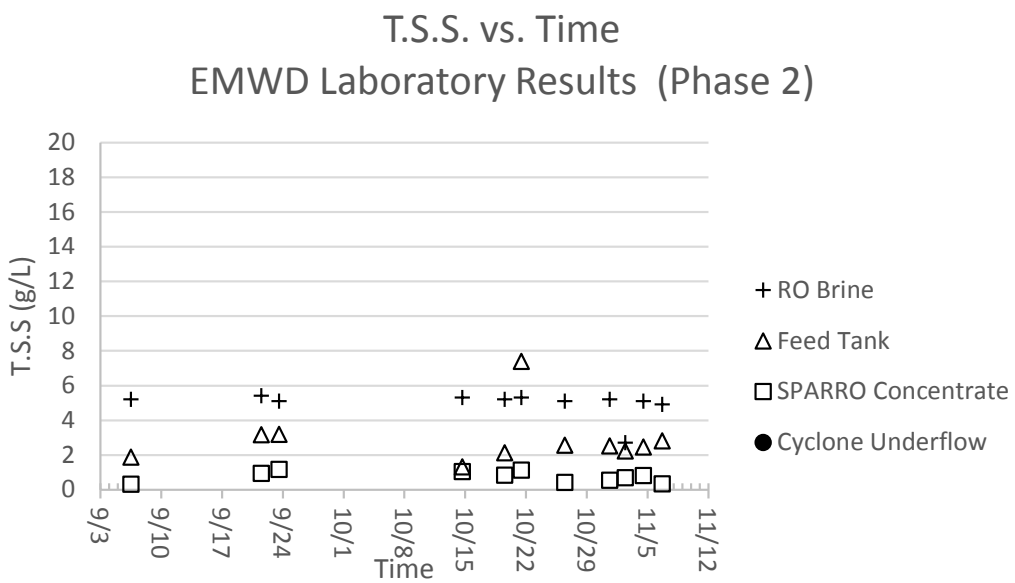

Figure 48. Total suspended solids vs. time for Phase 2 (measured by EMWD).

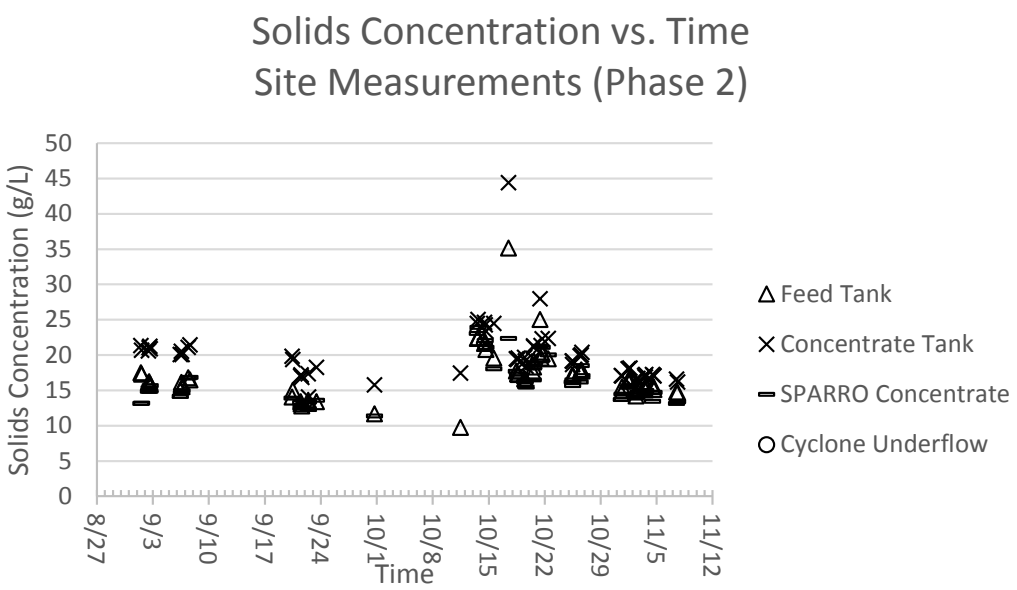

Figure 49. Solids concentration vs. time for Phase 2 (site measurements).

The on-site measurements show the feed tank concentration just above 15 g/L at the start of Phase 2 and around 12.5 g/L when the first clogging event occurred (September 23). The lowest value recorded was 10 g/L, and the highest recorded was 22 g/L. In contrast, the laboratory data shows the feed tank solids concentration at the start of Phase 2 at less than 2 g/L, and only between 2 and 3 g/L at the time of the clogging incident. The cyclone underflow values measured in the laboratory are proportionally lower as well, and are in the range of where the feed tank concentration should have been.

Figure 50 presents a comparison of the solids concentration laboratory data (shaded symbol) and the field measurements (open symbol) for Phase 1. As shown, the field measurements are consistently higher than the laboratory values, for all samples shown, but for the most part, the values are reasonably close particularly for the first 5 sample sets, when the feed tank TSS values were around 10 g/L. There was more deviation when the feed tank TSS concentration was increased to 18 g/L. The results indicate that the site measurement method of using the pycnometer provided a reasonable estimate of the feed tank solids concentrations during Conditions 1 and 2 of Phase 1. At higher concentrations, (Condition 3 and 4), the method provided less accurate results.

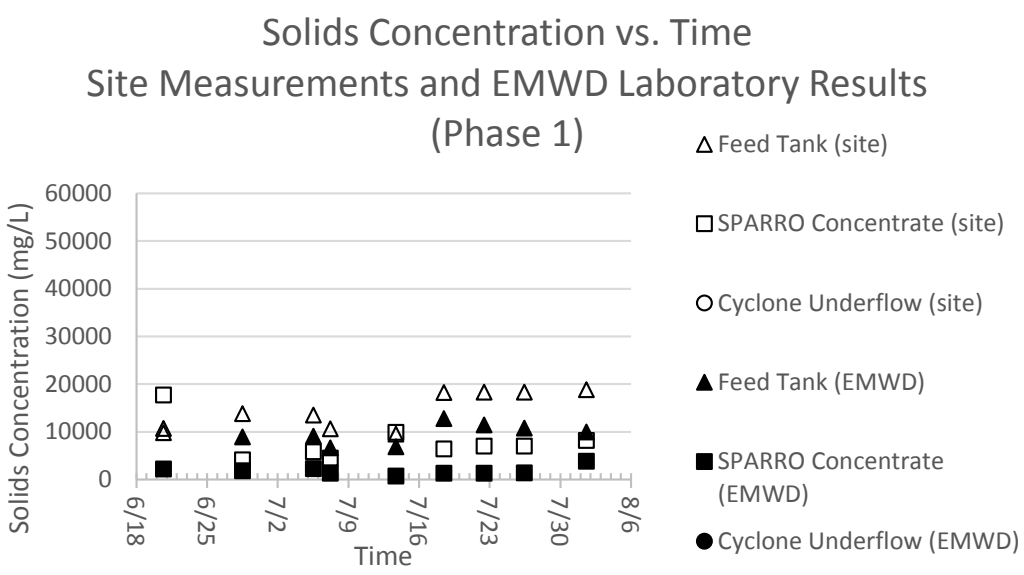

Figure 50. Comparison of on-site measurements and EMWD laboratory solids concentration values

The day-to-day operations of the SPARRO pilot plant were based on the on-site measurements for solids. However, if these values were wrong and the EMWD laboratory values were correct, then during Phase 2 the plant was operated with dangerously low seed concentrations, which may have contributed to the membrane tube plugging. Calculations show that at a seed concentration of around 2 g/L, the surface area of the seeds would only be about double that of the membrane area (assuming an average seed crystal length of 20 µm). This surface area size makes the probability of precipitation on the system pipework or membrane surface much greater. Unfortunately, by the time the Phase 2 lab data was obtained for the samples collected in September, the blockage had already occurred and it was too late to correct the situation.

The pycnometer calculations used to obtain solids concentration rely on an estimate of the solution SG value. This value was kept constant for all calculations. The significantly higher salinity values in the feed tank at the start of Phase 2 and even the latter part of Phase 1 are thought to have increased the SG enough to produce a significant underestimation of the seed concentration during that period.

Because the membrane performance declined so severely after the first blockage that occurred on September 23, it was decided to focus the performance evaluation on the period leading up to the blockage to try to determine the cause of the blockage. During this period, three sets of samples were collected and analyzed by EMWD's laboratory. Figure 51 shows a plot of the membrane rejection for each parameter measured.

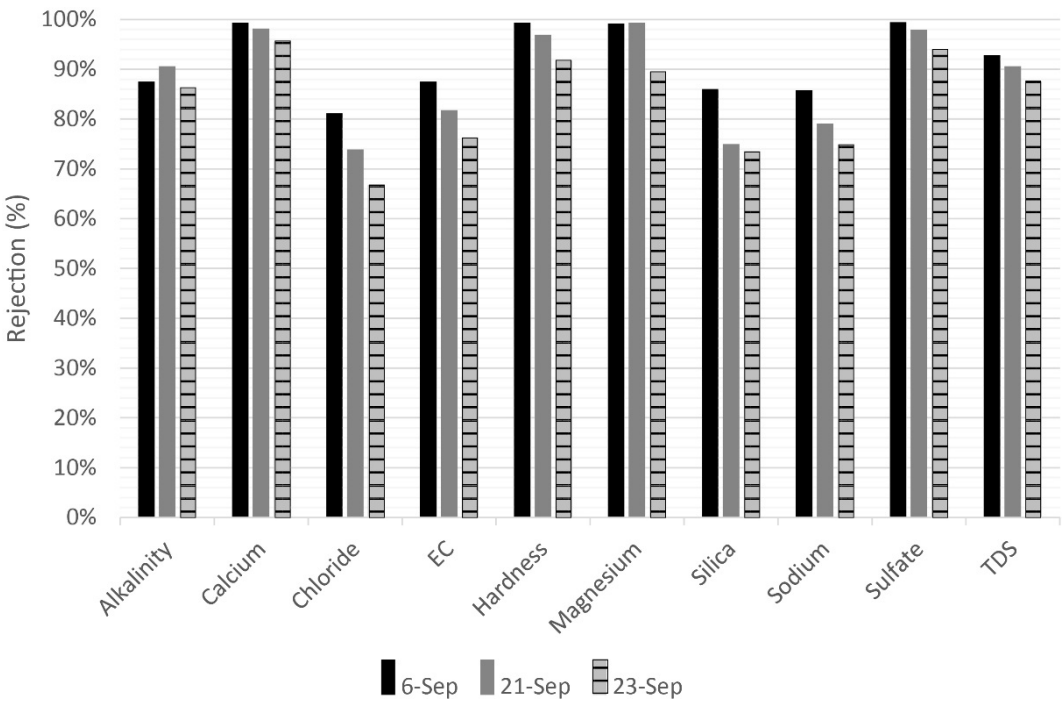

Figure 51. Membrane rejection for each parameter measured before blockage.

As can be seen, the salt rejection declined between each successive sample analysis for almost all the parameters. The same trend was also true for the rejection of the two membrane tubes (one TFC and one CA) in the single-tube testing units. The overall salt rejection for the two full-scale modules containing TFC membranes declined from 93 percent on September 6 (after about 35 hours of run time), to 91 percent on September 21 (after about 84 hours of run time), and then to 88 percent on September 23 (after about 128 hours of run time). These salt rejection results suggest an almost immediate decline in performance from the start of Phase 2 operation.

An evaluation of the water quality results obtained on September 6 showed that the calcium sulfate saturation level in the SPARRO Feed Tank was 247 percent, highly supersaturated. The saturation level in the concentrate stream was calculated to be 136 percent, close to equilibrium saturation. This implies a significant change in the chemistry from the feed tank through the membrane vessels. Evaluation of the results showed that the calcium concentration declined from 1,420 mg/L in the feed tank to 650 mg/L in the concentrate stream. Such a change in calcium concentration would have resulted in formation of 37.6 g/min of gypsum solids, or a change in solids concentration of about 4,400 mg/L. Solids formed in the system were measured by the change in TSS value between the Feed Tank and the solids in the Cyclone Overflow and Underflow Streams.
A mass balance on the solids showed that 18.7 g/min of solids were present in the feed stream to the membranes, while 52.8 g/min of solids were leaving the system; and increase of 34.1 g/min. This compares well to the 37.6 g/min of solids formed based on the change in calcium concentrations; being within 10 percent of each other. These values are summarized in Table 14.

Table 14. Mass Balance Based on Laboratory Data for September 6, 2016

Description	Membrane Feed	Concentrate Stream	Change
Calcium Concentration, mg/L	1,420	650	770
Calculated Amount of Gypsum Formed, g/min	-	37.6	-
Calculated Amount of Gypsum Formed, mg/L	-	4,400	-
TSS Concentration, mg/L	1,858	6,207	4,349
Measured Amount of Solids Formed, g/min	-	34.1	-

(-) Data not shown are not relevant for this discussion.

The results in Table 14 indicate that 90 percent of the solids formed, as measured by the change in calcium concentration, were accounted for by the measured change in TSS concentration. What happened to the remaining 10 percent? It is possible that given the very low feed tank TSS value (1,858 mg/L) that solids was already starting to precipitate on the internal pipework and parts of the membrane due to the relatively low seed surface area available for precipitation.

A similar analysis was carried out for the laboratory results obtained on September 21, and the results are summarized in Table 15. In this case, the calcium sulfate saturation level went from 204 percent in the feed tank to 136 percent in the concentrate stream. As shown in Table 15, the formation of gypsum based on the change in calcium concentration was lower than on September 6, at 24.0 g/min or a total of 2,823 mg/L of new solids. The measured TSS values in this case only increased by 12.8 g/min, indicating that only about 53 percent of the formed solids were accounted for in the TSS measurements. Thus, in two weeks, the percent of missing solids grew from 10 percent to 47%. This could mean that the unaccounted-for solids were continuing to precipitate and accumulate in other parts of the system.

Table 15. Mass Balance Based on Laboratory Data for September 21, 2016

Description	Membrane Feed	Concentrate Stream	Change
Calcium Concentration, mg/L	1,210	770	440
Calculated Amount of Gypsum Formed, g/min	24.0	-	-
Calculated Amount of Gypsum Formed, mg/L	2,823	-	-
TSS Concentration, mg/L	3,153	5,174	2,021
Measured Amount of Solids Formed, g/min	12.8	-	-

(-) Data not shown are not relevant for this discussion.

The third set of data from September 23 showed very similar values to the above and the measured TSS only accounted for about 55 percent of the solids formed in this case.

Once solids begin to precipitate in areas other than on the recirculating seed crystals, the process is in trouble because those sites are now available for future precipitation to occur. What is likely to have happened during the first 120 hours of operation is that solids began to precipitate in other parts of the system from the first day of operation due to the lack of seed crystal area (the seed concentration was more than 5 times lower than expected). The values in Table 14 indicate that this may have been about 10 percent of the solids formed. Over time, the solids in these areas grew larger. The values in Table 15 indicated that later almost half of the solids formed were not being accounted for by the change in TSS concentration. Eventually, pieces of the solids formed on the pipework and elsewhere could have broken off and travelled through the membrane tubes, damaging them and reaching a point where they accumulate. From there, the solids began to build up until a complete blockage occurred.

4.2.6 Solids Morphology and Production

4.2.6.1 Phase 1 Operation

During Phase 1 of the project, the amount of solids that precipitated was minimal, as expected. New feed water entering the system was limited to only 10.8 gallons per day. Evaluation of the feed tank chemistry showed that the feed water to the membranes was only marginally above saturation levels for calcium sulfate—indicating minimal seed growth potential. This was confirmed in the SEM images of the seed collected during Phase 1, see Figure 52 and Figure 53.

Figure 52 shows the morphology of the seed crystals at the start of Condition 3 after a new batch of seed was added to the feed tank to increase the seed concentration from 10 to 18 g/L. The sharpness of the crystal edges can be seen clearly. Figure 53 shows a mixture of seed that was collected from the system over a three-week period after the start of Phase 1. This shows a very similar rod-like morphology to the crystals in Figure 52, except that the crystals have a slightly rounded shape on the edges. A sample of seed was not collected at the start of Phase 1 but it can be assumed that it would have had the same morphology of that shown in Figure 52 because the same recipe (0.6 M solutions) was used to make it. The seed sample in Figure 53 shows very little evidence of new crystal growth, but does show evidence of some "crystal wear" due to the action of pumping and mixing.

There was no evidence of any damage to the membranes as a result of the presence of the seed crystals at the concentration of around 10 g/L during Phase 1, despite their rod-like morphology.

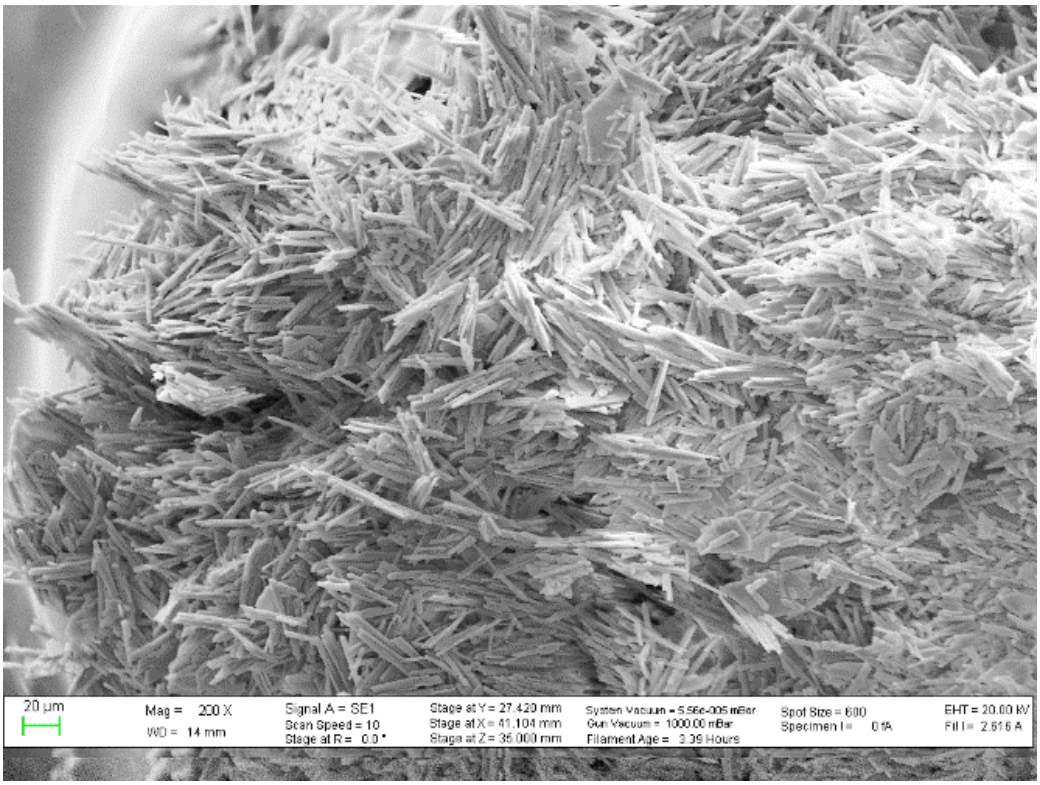

Figure 52. New batch of seed crystals at start of Condition 3.

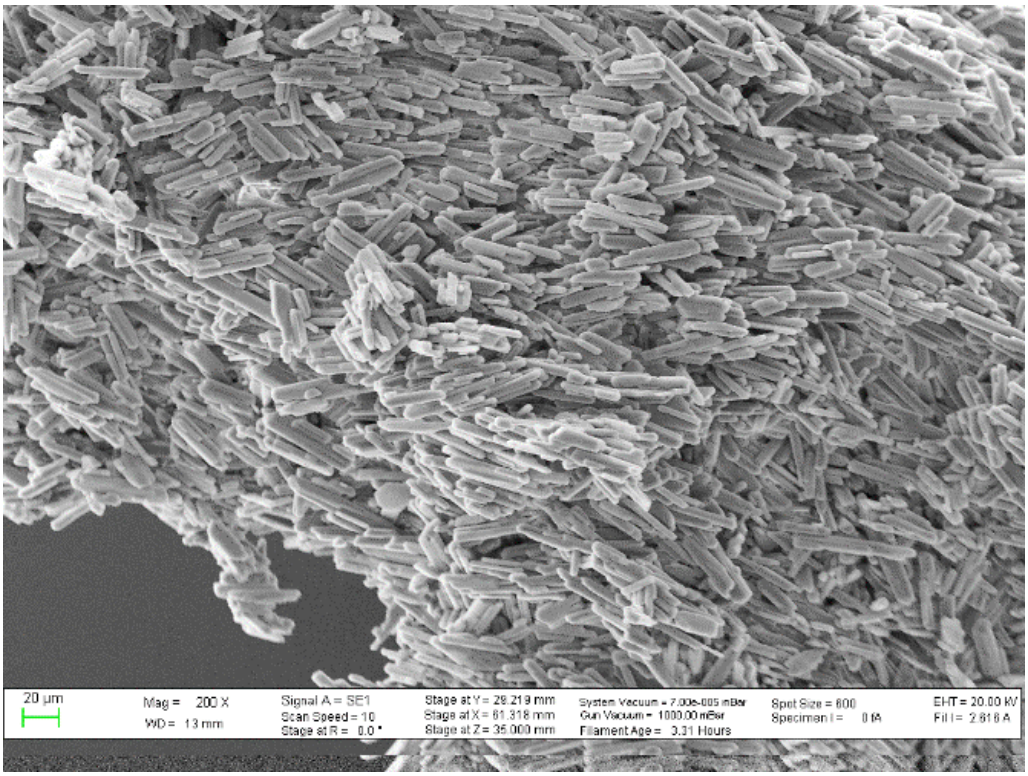

Figure 53. Combined seed sample after three weeks of operation from the start of Phase 1.

4.2.6.2 Phase 2 Operation

At the start of Phase 2, some seed material was removed from the system to reduce the seed concentration into the range of about 15 g/L, as described previously. However, as also described previously, the on-site method used to determine the seed concentration (using the pycnometer) had an error in the calculation which overestimated the solids concentration. This resulted in significantly more seed material being removed from the system than desired. The result was very low concentrations of seed in the feed tank at the start of Phase 2 (around 1.9 g/L). In fact, the seed levels were so low that evidence of "seed dissolving" can be seen in a sample of the seed material taken from the feed tank at the start of Phase 2 (Figure 54). The morphology of the crystals in Figure 54 is very different to that in Phase 1, as shown in Figure 52 and Figure 53. All the solids are more rounded, and the smaller crystals have agglomerated. Again, there is no evidence of new crystal growth.

Figure 54. Sample of feed tank seed at start of Phase 2.

On October 17, 2016, a sample of seed from the feed tank was collected for SEM analysis (Figure 55). At this point, Phase 2 had already been operating for about 230 hours. However, the first blockage of the membranes had already taken place, which had impacted the degree of supersaturation experienced across the membranes.

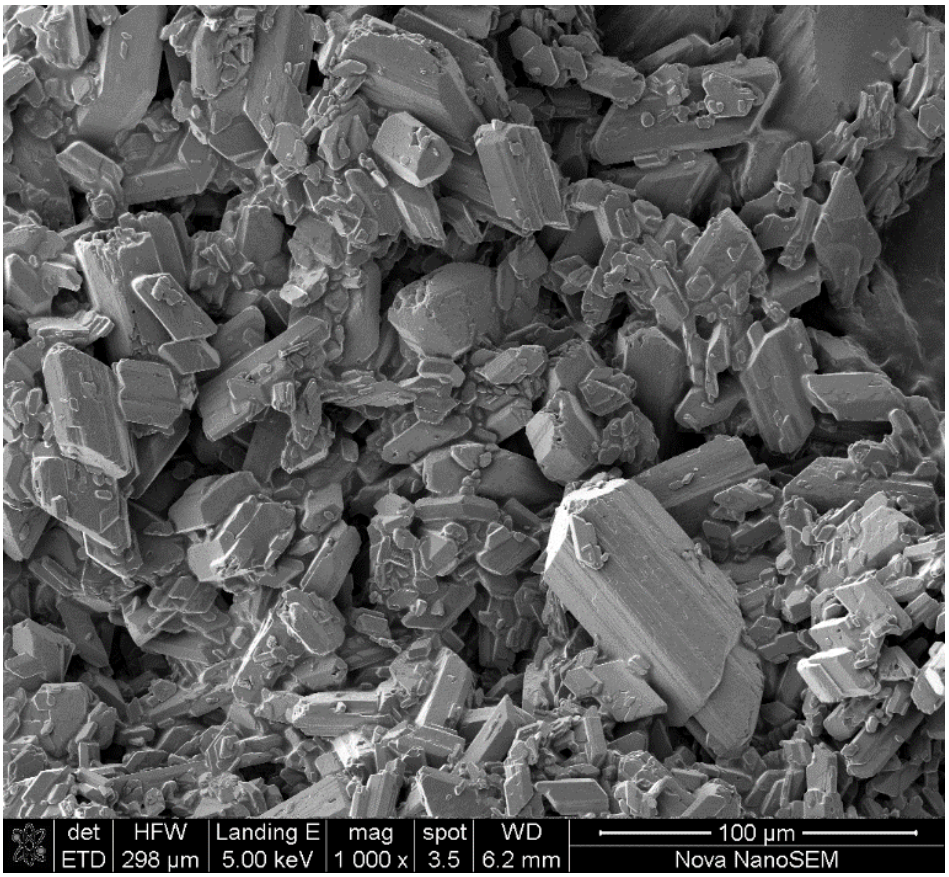

Figure 55. Sample of solids from feed tank after 230 hours of operation.

As shown in Figure 55, there is now evidence of new crystal growth and the solids have taken on more of a crystal shape and have generally grown in size. UCT's assessment of these solids was that the crystals show signs of irregular growth and evidence of macrosteps, which is symptomatic of higher supersaturation levels and faster growth rates. This supports the earlier discussion about the high levels of calcium sulfate supersaturation at the start of Phase 2 and the relatively low seed surface area available for precipitation. Mass balance calculations for three laboratory analyses done before the first membrane blockage showed that the gypsum production was 5.0, 3.2, and 3.5 lbs/h (2.3, 1.4, and 1.6 kg/h). At the start of Phase 2 the total mass of seed material in the entire system was only 5.0 lb (2.3 kg). Thus, the seed concentration would be doubling every hour to keep up with the precipitation rates.

During the latter part of the Phase 2 operation, when the membrane performance had declined, the amount of solids precipitation also declined, because more calcium was leaving the system through the membrane permeate stream. During this period, the average gypsum production was calculated to be around 0.5 lb/h (0.2 kg/h). A sample of seed material from the feed tank at the end of Phase 2 was also sent for SEM analysis. Figure 56 shows an image of the material, which shows a slightly modified morphology compared with that shown in Figure 55.

Here there seems to be a mixed morphology of platelet and rod-type crystals, with a wide range of particle size.

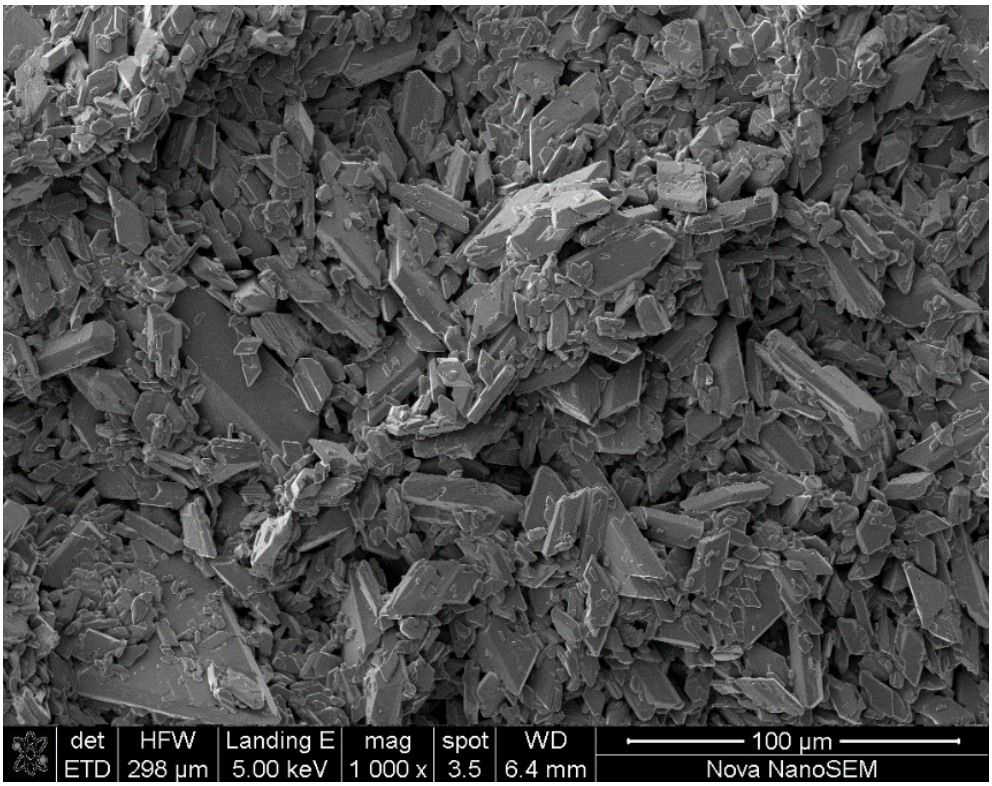

Figure 56.Sample of seed material from the feed tank taken at the end of Phase 2

4.2.6.3 Summary

The highest formation rate of gypsum calculated during Phase 2 was in the range of 5.0 lb/h (2.3 kh/h), occurring when the system had the lowest seed concentration, around 1.9 g/L—almost 8 times lower than intended. It is highly probable that the low seed concentrations in the feed tank, coupled with the high precipitation rate, are the reason that the system experienced uncontrolled solids precipitation that resulted in blocking the second membrane vessel on September 23, 2016.

The crystal morphology analysis has shown that although the system started with small rod-type crystals and maintained that shape during Phase 1 when the precipitation rate was very low, the crystal morphology changed when the mass of gypsum precipitation increased at the start of Phase 2. The lack of crystal surface area for precipitation may have led to higher localized rates of crystal growth than would have occurred if the seed concentration had been in the desired range of 15 g/L. Later in Phase 2 when the crystal growth rate was lower, there was evidence of mixed morphology developing and the formation of platelet-type crystals.

4.2.6.4 Solids Quality

4.2.6.4.1 Solids Composition Analyzed by OMYA

A combined sample of wasted solids from the process over Phase 2 was collected on November 16 and sent to Omya Inc. for a full composition analysis. See Appendix E for full report.

The sample was dried at 80°C and then the minerology and composition was determined using x-ray diffraction (XRD), x-ray fluorescence (XRF), and thermogravimetric (TGA) analysis.

The XRD analysis determined that the material consisted of about 95 percent gypsum and about 4 percent calcite. This was cross-checked against the XRF results. Small concentrations of silica and strontium (less than 0.1 percent) were also detected, along with some other metals such as barium, iron, potassium, and manganese at very low levels.

4.2.6.4.2 Solids Composition Analyzed by EMWD

Solid samples were filtered and then dried at 103 °C. After that, a measured mass of solids was digested in acid and the resulting solution was analyzed using ion chromatography for all metals. Table 16 shows the results for metals that were measured with a concentration greater than 0.001 percent of the total sample mass. As can be seen, there are not many of them. As expected, the dominant metal is calcium, with very small amounts of boron, barium, iron, phosphorous, silica, and strontium. Silica and strontium were present in the highest concentrations in the sample collected from the blocked membrane tubes on September 26, 2016. The concentration of these two metals was significantly lower in the sample of wasted solids collected on November 17, 2016. This may have something to do with the fact that precipitation rates were lower after the first sample was collected on September 26, 2016.

Table 16. Solids Samples Analyzed by EMWD for Metals

	E161209020		E161209021	
	SOLIDS WASTED-SPARRO 09/26/16[1]		SOLIDS WASTED-SPARRO 11/17/16[2]	
Total Solids	42%		53%	
	Solid Portion	Dissolved Metals	Solid Portion	Dissolved Metals
Metals[3]	Percent	µg/L	Percent	µg/L
B	<0.002%	300	<0.002%	1600
Ba	0.0056%	79	0.0055%	408
Ca	31.8%	670,000	29.2%	660,000
Fe	0.0052%	540	0.0014%	440

Table 16. Solids Samples Analyzed by EMWD for Metals

	E161209020		E161209021	
	SOLIDS WASTED-SPARRO 09/26/16(1)		SOLIDS WASTED-SPARRO 11/17/16(2)	
Total Solids	42%		53%	
	Solid Portion	Dissolved Metals	Solid Portion	Dissolved Metals
Metals(3)	Percent	µg/L	Percent	µg/L
K	<0.009%	4,500	<0.009%	55,000
Mg	0.005%	74,000	0.010%	1,200,000
Na	0.04%	140,000	<0.03%	2,100,000
P	<0.07%	740	<0.07%	5,300
Si	0.29%	81,000	<0.02%	140,000
Sr	0.20%	6,300	0.082%	13,000

(1) Solids recovered from the blocked membrane tube.
(2) Solids collected from the solids-blowdown tank.
(3) Only metals with proportion > 0.001% shown.

4.2.7 Membrane Autopsy

A membrane tube from the top (first in series) vessel, which contained the least damaged membranes, was removed and sent to American Water Chemicals (AWC) for a full autopsy at the end of the pilot testing. A summary of the autopsy results are presented below. The full autopsy report can be found in Appendix F.

AWC refers to this membrane as the "fouled" membrane. In addition, membrane Specialists LLC provided AWC with a virgin TFC membrane to use as a comparison and reference point for the salt rejection and dye test results.

The first test that was performed was a regular inspection of both the fouled membrane and the virgin membrane. On the feed side of both membranes, sporadic brown spots were found as shown on Figure 57. It is not clear what these spots represent. Upon inspection of the permeate side of the fouled membrane, a brown, green, and yellow deposit was found along the seams of the membrane while the virgin membrane did not contain these yellow bands as shown on Figure 57. AWC determined the organics to be humic in nature. When performing the Loss on Ignition (LOI) test, the foulant from the fouled membrane consisted of 27.1 percent organic matter and 72.9 percent inorganic matter. The organic content of the Train C RO brine was not measured, but is typically not very high.

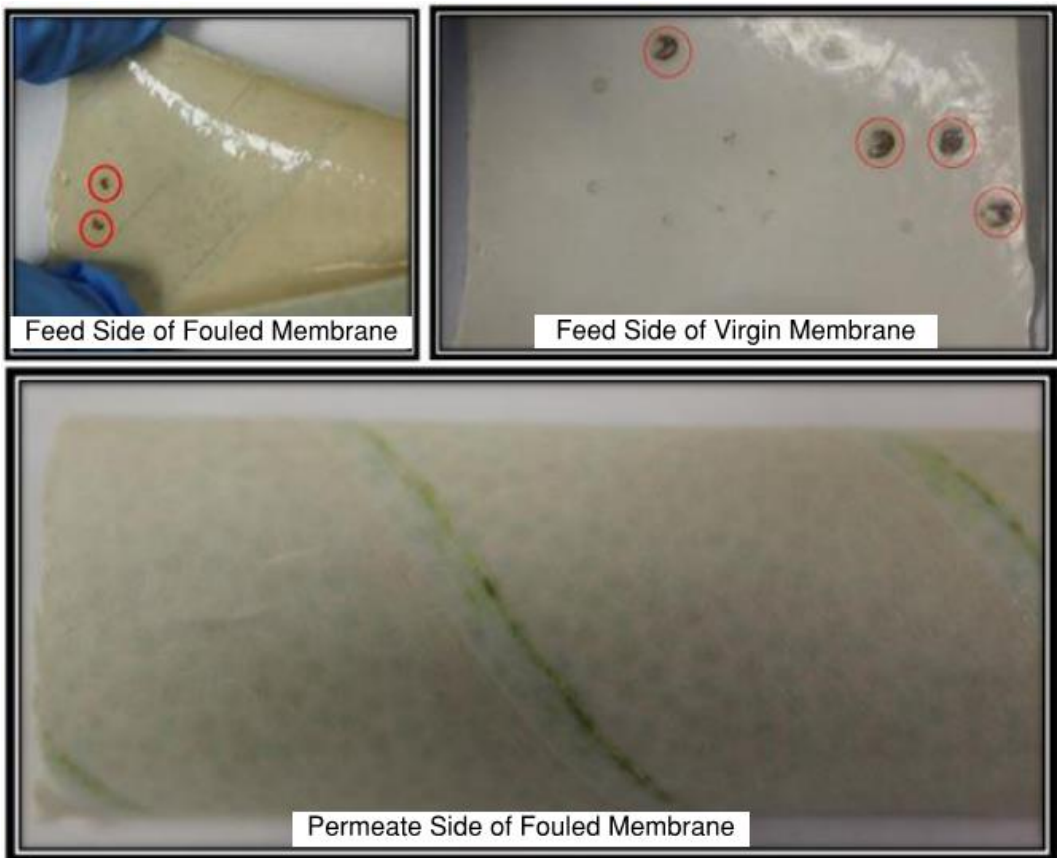

Figure 57. Inspection of feed and permeate side of fouled and virgin membrane that shows brown foulant (top left), sporadic brown spots (top right), and brown, green, and yellow deposit along seam (bottom).

A cell test was performed to determine the performance of the membrane. First, the salt rejection and flux of the virgin membrane was determined to be 90.28 percent and 24.99 gallons per day per square foot (gfd), respectively. Next, the fouled membrane was tested after soaking in distilled water (DI) for 24 hours, and the resulting salt rejection and flux was 78.8 percent and 25.5 gfd, respectively. The fouled membrane was cleaned using a high pH (10.2) solution (2 percent C-239) for 6 hours, and the resulting salt rejection became worse—28.4 percent lower than the virgin membrane—and the resulting flux was 46.4 percent higher. Finally, the membranes were cleaned using a low pH solution (1.8) (2 percent C-234) for 2 hours. This resulted in a salt rejection that was 24.3 percent lower than the virgin membrane and flux that was 26.4 percent higher. This indicated that the membrane integrity had been severely compromised.

After cleaning the membrane during the cell test, a dye penetration test was performed to check for any mechanical or chemical damage to the membrane. Dye penetration testing on the fouled membrane showed very light penetration to the permeate side of the membrane as well as heavy penetration marks that correlate to the location of the brown spots as shown on Figure 58. It was noted

by AWC that the pattern of the dye penetration suggested surface abrasion. The virgin membrane was also included in this test and showed no significant dye penetration to the permeate side except for the location of the membrane that corresponds to the brown spots on the feed side of the membrane.

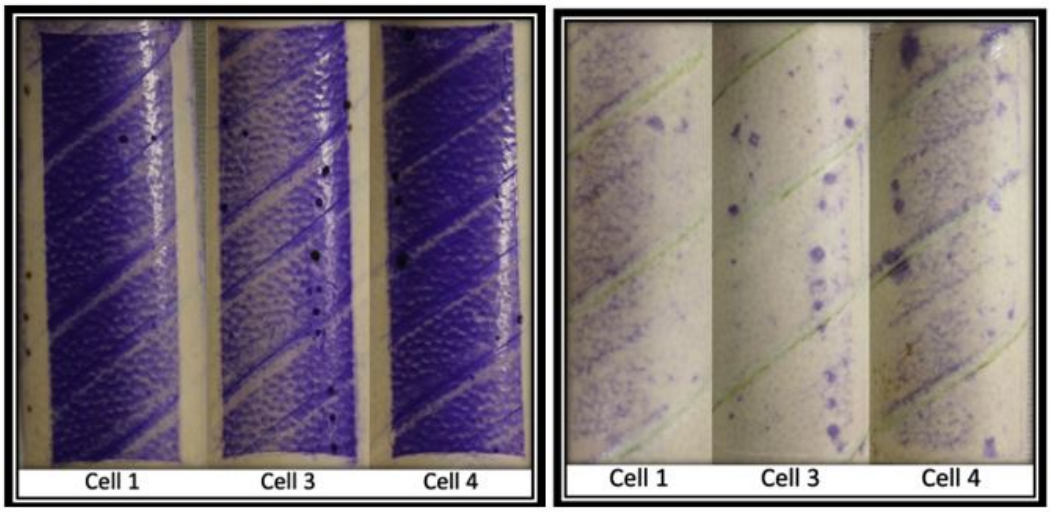

Figure 58. Dye test of fouled membrane that shows feed (left) and permeate (right) sides after dye penetration.

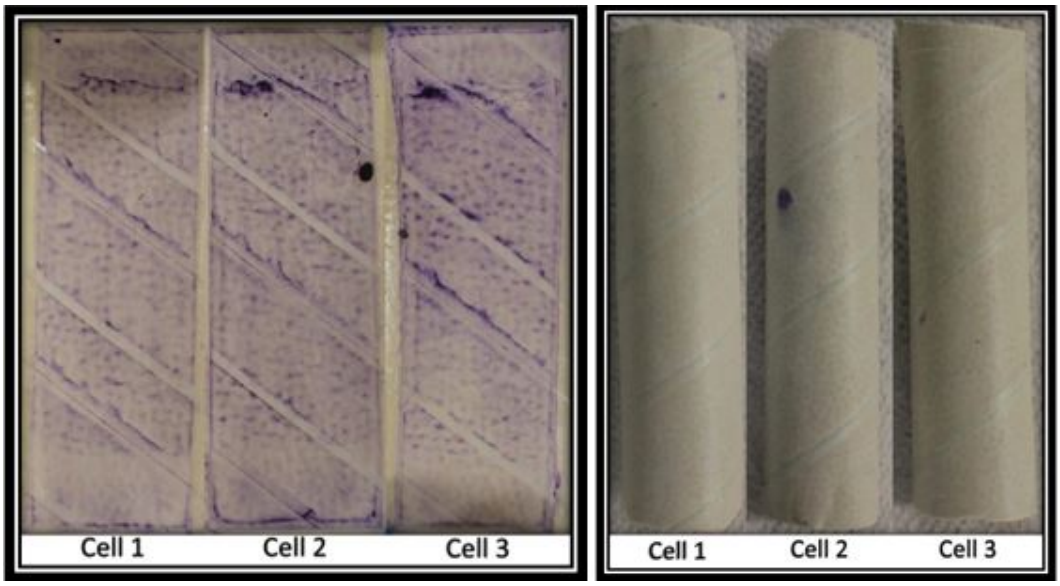

Figure 59. Dye test of virgin membrane showing feed (left) and permeate (right) sides.

Samples collected from the membrane surface as well as the LOI residue were tested for solubility in concentrated acid and caustic solution. Both of the samples collected from the membrane surface as well as the LOI residue were found to be insoluble in 50 percent NaOH and 37 percent HCI. In addition, when adding acid to both the foulant and the LOI residue, no effervescence was observed. This indicated that no carbonate salts were present.

AWC concluded that the major foulant on the membrane surface was barium sulfate, and there was evidence of silica fouling as well (Figure 60).

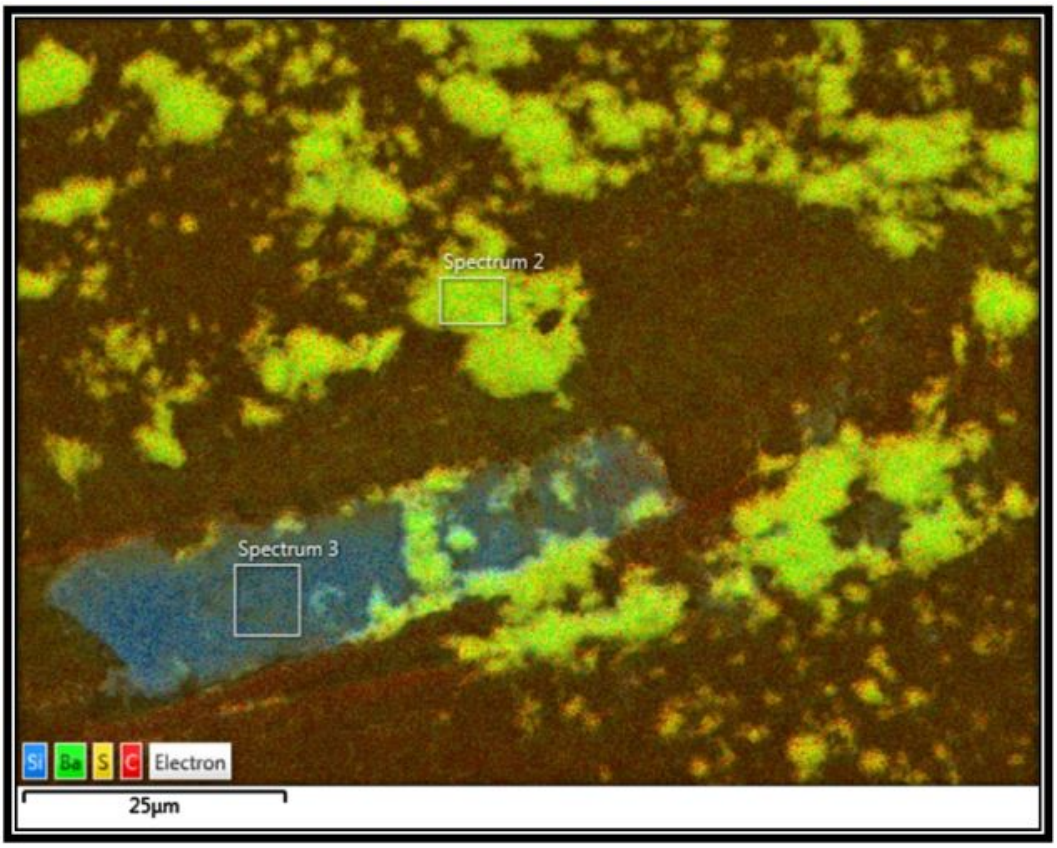

Figure 60. Superimposed elemental imaging (SEI) of barium sulfate, calcium sulfate, and amorphous silica.

Very few calcium sulfates were found on the membrane surface as a foulant. AWC also noted membrane surface damage (Figure 61), which shows what appears to be a scratch or gash in the membrane surface, which seems to be over 100 µm long and about 40-50 µm wide. This damaged area is significantly larger than most of the seed material. But we do know that bigger chucks of solids formed and created the blockages, and it is quite plausible that these much larger solids came into contact with the membrane surface and caused the observed damage.

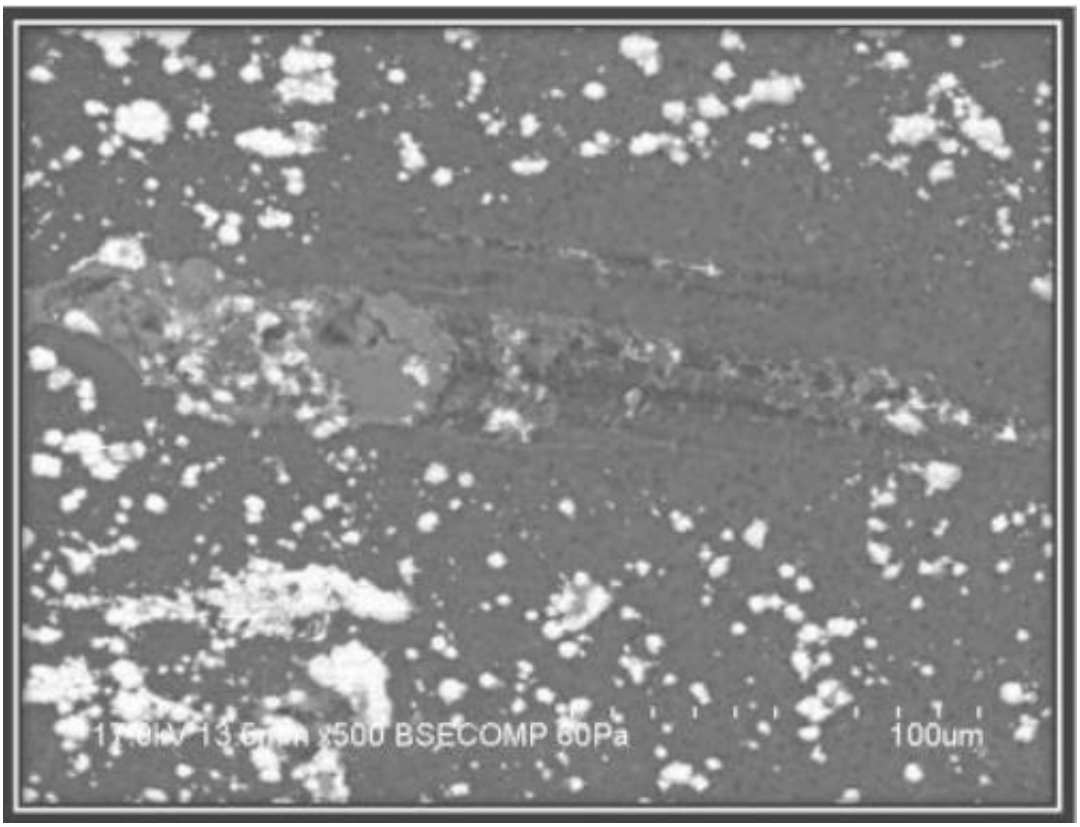

Figure 61. Electron micrograph of the membrane surface damage at 500 times magnification.

5.0 Summary and Conclusions

5.1 Progress with Respect to Project Goals

This section lists goals and conclusions based on the analysis of the results obtained during the Phase 1 and Phase 2 operations.

Goal 1. Establish whether there is a difference in performance between the TFC and CA membrane.

A direct comparison of the membrane performance was carried out in Phase 1. Both membranes performed well, with no sign of damage or loss of rejection due to the presence of the circulating rod-like seed crystals. The only noticeable difference between the two membrane types was that the flux of the CA membrane was lower than that of the TFC membrane for a given feed pressure. Also the salt rejection of the TFC membrane was slightly greater than that of the CA membrane.

Goal 2. Establish whether operating at different gypsum seed concentrations impacts membrane performance/life.

The objective was to operate the system at a seed concentration of between 10 g/L, on the low side, and 18 g/L on the high side. During Phase 1, the laboratory measurements showed that the feed tank seed concentration was between about 8 and 12 g/L, with an average of 9.6 g/L. The actual range during Phase 1 was lower than anticipated, due to an error in the method used on site to measure the feed tank solids concentration and make adjustments to the system conditions. The variation in seed concentration during Phase 1 did not appear to have any impact on membrane performance.

At the start of Phase 2, the seed concentration was reduced to 1.9 g/L by mistake. This period also coincided with the highest precipitation rates experienced during the study, around 5 lb/h (2.3 kg/h). The results showed that operating the system at a very low seed concentration of 1.9 g/L in the high gypsum precipitation environment resulted the high rates of crystal growth on the seed material and possible crystal growth in other parts of the system, which lead to a system blockage within 129 hours of operation.

Goal 3. Establish whether operating at different feed water velocities impact membrane performance/life.

During Phase 1, the feed water velocity was adjusted from 1.0 m/s (3.3 ft/s) to 1.5 m/s (4.9 ft/s). There was no evidence to suggest that the change in velocity impacted the performance of either membrane type. The duration of the testing was not long enough to enable a conclusion to be drawn regarding the impact on membrane life.

Goal 4. Operate the pilot plant with the selected membrane type, seed concentration **and feed velocity, and achieve 700 hours of operation.**

Phase 1 of the project went very smoothly. Although there were no significant performance differences between the TFC and CA membrane, the TFC membrane was selected for Phase 2 operation; at a seed concentration of 15 – 18 g/L and a brine velocity of 1.3 m/s (4.2 ft/sec). Only 530 hours of operation was achieved, short of the 700 hour goal. Moreover, much of the 530 hours of operation was for periods in which the membrane performance had already declined due to damaged caused by one or both blockages that occurred.

5.2 Additional Conclusions and Observations

1. The Phase 1 operation was very smooth, and there was no evidence of declining performance for either of the membranes tested—and certainly no evidence of membrane damage caused by the recirculating rod-shaped seed crystals at an average concentration of 9.6 g/L. This is a very positive

conclusion. It should be noted that there was very little precipitation of gypsum occurring across the membranes during Phase 1.

2. Using a pycnometer to estimate the concentration of seed in the feed tank and elsewhere in the system appeared to be a reasonably accurate method when compared to the laboratory results for the first half of Phase 1. However, changes in solution SG impacted the calculations and resulted in erroneous feed tank seed concentrations for the latter half of Phase 1 and for Phase 2. Unfortunately, this error went unnoticed and the system was operated at the start of Phase 2 with an exceptionally low feed tank seed level of 1.9 g/L. The gypsum formation rate at this point was calculated to be 37.6 grams per minute (g/min), which proved to be more than could be supported by 1.9 g/L of circulating seed crystals. During this period, the gypsum was precipitating at a rate that would have doubled the seed concentration in the system during the first hour of operation. The seed blowdown system worked quite well to remove excess solids from the system, which in this case exacerbated the situation by keeping the system seed concentration levels too low.

   Mass balance calculations showed that the change in seed concentration at the start of Phase 2 only accounted for about 90 percent of the gypsum that precipitated. This suggests that the absolute minimum seed concentration for operation under those conditions would be around 2.5 g/L—without any safety factor applied.

3. Following the successful performance during Phase 1, it appeared that there was a high probability of achieving 700 hours of operation during Phase 2. Unfortunately, the error regarding the feed tank seed concentration at the start of Phase 2 led to conditions that blocked and damaged the membranes.

4. The membrane autopsy concluded that primarily barium sulfate scale had formed on the membrane. There was also evidence of some silica scale formation. Notably, there was minimal calcium sulfate scale on the membrane surface. This is a very positive conclusion and indicates that the presence of the seed crystals behaved as expected. However, their concentrations were too low to sustain the high growth environment.

5. The solids analysis confirmed that wasted solids consisted mainly of calcium sulfate. Neither silica nor barium sulfate appeared to precipitate on the gypsum seed crystals in significant amounts. Controlling these two precipitates will require a different strategy.

6. If future work is to be pursued with this process, then the on-site measurement of seed concentration needs to be confirmed and checked against laboratory analyses. In addition, repairs to the pilot plant will be needed. Future work should also consider adding small glass beads and barium sulfate crystals to the feed tank to provide precipitation sites for the silica and barium sulfate, respectively.

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Appendix A - Phase 1: Master Field Data Sheet

Run Time Calculation									Flow					Conductivity						Solids Concentration				Pressure				pH					
Date	Time	Date/Time	Stop Pilot? (Y or Blank)	Run Time	Condition	SLURRY Pump Speed	Seed Feed Tank Level	Feed Tank Temperature	SPARRO Feed	Concentrate	Concentrate Removed	TFC Permeate	CA Permeate	Feed	Seed Feed Tank	Concentrate Tank	Blowdown	TFC Permeate	CA Permeate	Seed Feed Tank	Concentrate Tank	Blowdown	Underflow	Feed	Concentrate	Cyclone Feed	TFC Permeate	Feed	Feed Tank	Concentrate Tank	Blowdown	TFC Permeate	CA Permeate
				min		%	in.	°C	gpm	gpm	gpm	gpm	gpm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	g/L	g/L	g/L	g/L	psig	psig	psig	psig	unitless	unitless	unitless	unitless	unitless	unitless
Column1	**Column2**						**Column21**							**Cf**		**Ccon**	**Cblow**										**Ppa2**	**Ppa29**	**Ppa28**	**Ppa27**	**Ppa272**	**Ppa26**	**Ppa23**
Monday, June 27, 2016	12:00 PM	6/27/16 12:00 PM		0	1	33	7 3/4	29.1		2	0.00275	0.003434	0.00317	7,177	11,890	12,890	11,850	2,841	3,692	11.2	11.6	1.3	32.1	201	200	9.5	65.0	7.7	2.76	2.28	2.91	2.34	2.95
Monday, June 27, 2016	1:26 PM	6/27/16 1:26 PM		86	1	33	7 1/4	29.9		2.1	0.00275	0.003381	0.003276	7,121	11,900	12,090	11,990	3,881	3,935	10.8	10.8	2.1	30.6	201	200	9.5	65.0	7.7	2.60	2.57	2.73	2.15	2.65
Monday, June 27, 2016	3:34 PM	6/27/16 3:34 PM		214	1	33	7 3/5	30		2	0.00275	0.003593	0.00317	7,170	11,500	11,400	11,660	1,564	3,579	11.1	13.7	3.5	31.1	201	200	9.5	65.0	7.7	4.06	5.40	4.01	3.46	4.02
Tuesday, June 28, 2016	9:03 AM	6/28/16 9:03 AM		1,263	1	33	9 3/4	27.8		2.1	0.00198	0.003117	0.003064	7,281	11,720	11,870	11,860	1,506	3,449	12.8	13.5	4.3	33.5	201	200	8.8	70.0	7.7	4.63	4.56	4.50	4.02	4.58
Tuesday, June 28, 2016	10:26 AM	6/28/16 10:26 AM		1,346	1	33	10 1/16	28.1		2.1	0.00198	0.003117	0.003012	7,276	11,700	11,820	11,610	1,511	3,466	13.1	14.9	4.0	33.1	201	200	8.8	70.0	7.6	4.58	4.58	4.56	4.20	4.63
Tuesday, June 28, 2016	12:42 PM	6/28/16 12:42 PM		1,482	1	33	10 15/16	28.7		2.1	0.00198	0.002959	0.003012	7,270	11,880	11,850	11,890	1,567	3,457	13.8	13.4	4.2	35.3	201	200	8.8	72.0	7.6	4.64	4.59	4.62	4.30	4.72
Tuesday, June 28, 2016	3:41 PM	6/28/16 3:41 PM		1,661	1	33	9	31.1		2.1	0.00198	0.002747	0.002959	7,215	11,650	11,847	11,787	2,725	3,452	11.1	11.3	3.0	28.4	201	200	8.0	85.0	7.7			5.84	6.30	6.15
Wednesday, June 29, 2016	8:40 AM	6/29/16 8:40 AM		2,680	1	33	9 7/16	27.9		2.1	0.00308	0.002589	0.002959	7,177	11,750	11,750	12,010	3,434	2,198	11.8	12.3	4.0	29.4	201	200	8.3	82.0	7.7	7.21	7.20	3.44	6.30	6.58
Wednesday, June 29, 2016	11:20 AM	6/29/16 11:20 AM		2,840	1	33	9 5/8	27.9		2	0.00308	0.002853	0.002906	7,013	11,820	11,900	11,920	1,145	3,425	11.8	12.5	3.9	30.4	201	200	8.8	71.0	7.6	4.17	5.99	4.21	3.11	3.68
Wednesday, June 29, 2016	12:01 PM	6/29/16 12:01 PM		2,881	1	33	9 7/10	28		2.1	0.00308	0.002853	0.002959	7,013	11,890	11,910	11,940	1,480	3,423	11.8	12.6	3.5	29.6	201	200	8.3	71.5	7.5	4.50	5.52	4.53	3.60	3.93
Wednesday, June 29, 2016	2:40 PM	6/29/16 2:40 PM		3,040	1	33	10 7/8	28.9		2	0.00308	0.001427	0.002959	7,157	11,870	11,890	11,960	1,944	3,413	10.4	9.4	3.4	25.6	201	200	8.3	80.0	7.6	4.90	4.92	4.93	4.48	4.92
Wednesday, June 29, 2016	3:33 PM	6/29/16 3:33 PM		3,093	1	33	7 1/4	28.3		2	0.00308	0.003012	0.003012	7,192	11,540	11,700	11,620	1,491	3,250	9.2	9.8	3.0	23.5	201	200	8.3	72.0	7.6	4.08	4.87	4.08	3.61	4.29
Wednesday, June 29, 2016	4:33 PM	6/29/16 4:33 PM		3,153	1	33	7	28.7		2.1	0.00308	0.002959	0.002959	7,140	11,610	11,640	11,720	1,336	3,507	9.0	10.9	2.8	23.9	201	200	8.8	71.0	7.6	4.24	4.38	5.23	3.65	4.30
Thursday, June 30, 2016	9:06 AM	6/30/16 9:06 AM		4,146	1	33	7 15/16	29.5		2	0.00198	0.003064	0.003012	7,252	11,780	11,840	11,950	1,412	3,248	9.2	9.3	2.5	24.5	201	200	8.3	70.0	7.6	4.38	4.38	4.43	3.83	6.91
Thursday, June 30, 2016	10:13 AM	6/30/16 10:13 AM		4,213	1	33	8 1/16	29.4		2	0.00198	0.003012	0.003012	7,197	11,810	11,840	11,890	1,389	3,254	9.7	9.7	3.0	25.6	201	200	8.3	68.5	7.6	4.38	4.35	4.43	4.21	4.59
Thursday, June 30, 2016	11:58 AM	6/30/16 11:58 AM		4,318	1	33	8 5/16	29.5		2	0.00198	0.00317	0.003012	7,013	11,780	11,900	11,964	1,427	3,256	10.2	10.6	3.5	25.8	201	200	8.3	68.5	7.7	4.43	4.35	4.40	3.87	5.10
Thursday, June 30, 2016	2:52 PM	6/30/16 2:52 PM		4,492	1	33	8 13/16	29.5		2.1	0.00198	0.003064	0.003012	7,224	11,270	11,910	11,980	1,407	3,270	10.0	10.7	3.0	25.6	201	200	8.5	77.0	7.6	4.37	4.36	4.38	3.97	4.49
Thursday, June 30, 2016	4:25 PM	6/30/16 4:25 PM		4,585	1	33		29.7		2	0.00198	0.003064	0.003012	7,247	11,930	11,900	11,980	1,422	3,276	10.4	10.3	2.9	26.5	201	200	8.5	77.0	7.6	4.39	4.38	4.39	3.87	4.45
Thursday, June 30, 2016	3:49 PM	6/30/16 3:49 PM		4,549	1	33	8 7/8	29.4		2.1	0.00198	0.00317	0.002985	7,243	11,960	11,950	12,000	1,454	3,271	10.2	10.1	3.2	26.1	201	200	8.5	77.0	7.6	4.40	4.37	4.38	4.05	4.46
Thursday, June 30, 2016	4:14 PM	6/30/16 4:14 PM		4,574	1	33	9	29.7		2	0.00198	0.003012	0.003012	7,240	11,930	11,900	11,970	1,461	3,267	10.1	10.6	10.3	26.6	201	200	8.8	72.3	7.7	4.46	4.43	4.48	3.96	4.49
Friday, July 01, 2016	9:31 AM	7/1/16 9:31 AM		5,611	1	33	10 7/16	29.3		2	0.00396	0.002959	0.002959	7,245	12,160	12,150	12,220	1,604	3,258	11.0	10.1	3.4	27.2	201	200	7.8	80.0	7.7	4.54	4.55	4.56	4.05	4.60
Friday, July 01, 2016	12:35 PM	7/1/16 12:35 PM		5,795	1	33	7 9/16	28.9		2	0.00396	0.003117	0.002959	7,231	11,880	11,860	11,530	1,383	3,150	10.2	10.4	6.0	24.7	201	200	7.8	61.0	7.7	4.59	4.60	4.56	4.06	4.65
Friday, July 01, 2016	1:45 PM	7/1/16 1:45 PM		5,865	1	33	9 1/16	28.7		2.05	0.00396	0.003276	0.002906	7,221	11,870	11,910	11,960	1,423	3,156	10.6	10.5	3.2	26.0	201	200	8.0	62.0	7.7	2.20	2.19	2.30	1.93	2.20
Monday, July 04, 2016		7/4/16 12:00 AM		9,360	1	33		29		2	0.00367	0.003276	0.002853	7,221	17,800	18,200	16,240		7,480					201	200		56.0	7.6	6.72	6.75	6.30	6.25	6.19
Tuesday, July 05, 2016	8:50 AM	7/5/16 8:50 AM	Y	9,360	1	33	9 7/8	28.1		2.2	0.00083	0.00243	0.002536	7,269	16,270	16,230	16,240	8,052	5,406	13.5	14.2	5.9	30.6	201	200	7.5	61.0	7.5	4.65	4.52	5.84	6.25	6.17
Thursday, July 07, 2016	11:58 AM	7/7/16 11:58 AM		0	2	45	8 1/16	24.6		3	0.00000	0.003064	0.002959	7,277	11,400	11,520	11,490	3,494	3,215	10.6	9.7	4.5	24.0	200	199	19.0	83.0	7.6	4.65	4.64	4.72	5.83	6.28
Thursday, July 07, 2016	1:24 PM	7/7/16 1:24 PM		86	2	45	8 5/16	25.1		2.9	0.00000	0.002959	0.002906	7,195	11,470	11,450	11,570	3,815	4,270	10.1	9.8	4.4	23.3	193	189	19.0	88.0	7.6	4.70	4.68	4.63	4.57	4.78
Thursday, July 07, 2016	2:35 PM	7/7/16 2:35 PM		157	2	45	8 7/16	25.7		2.9	0.00000	0.002959	0.002853	7,159	11,480	11,470	11,320	2,753	3,413	10.6	10.3	4.2	22.4	185	181	19.0	88.0	7.6	4.47	4.32	4.43	4.53	4.72
Thursday, July 07, 2016	3:27 PM	7/7/16 3:27 PM		209	2	45	8 7/16	25.6		3	0.00000	0.002959	0.002906	7,270	11,470	11,490	11,540	2,702	3,347	9.9	10.0	4.7	24.0	185	182	19.0	89.0	7.7	4.62	4.62	4.53	4.53	4.64
Thursday, July 07, 2016	4:59 PM	7/7/16 4:59 PM		301	2	45	7 3/16	26.9		3	0.00000	0.002695	0.002853	7,442	11,290	11,440	11,440	2,570	3,278	9.5	9.9	4.0	22.8	195	190	18.0	90.0	6.9	4.55	4.65	4.74	4.33	4.66
Friday, July 08, 2016	9:38 AM	7/8/16 9:38 AM		1,300	2	45	8 7/16	26.6		3	0.00000	0.00243	0.002747	7,216	11,600	11,590	11,640	3,644	3,343	9.9	9.9	4.4	22.8	191	190	14.0	100.0	7.7	5.61	5.57	5.76	7.06	5.80
Friday, July 08, 2016	3:46 PM	7/8/16 3:46 PM		1,668	2	45		27.8		3	0.00000	0.002906	0.002853	7,331	11,680	11,700	11,730	2,521	3,403	9.4	9.4	3.7	23.4	189	189	14.0	84.0	7.7	4.30	4.53	4.43	4.32	4.91
Monday, July 11, 2016	10:37 AM	7/11/16 10:37 AM		5,679	2	45	12 7/8	28.9		3	0.00587	0.002589	0.002853	7,179	12,220	12,200	12,280	3,710	3,513	10.4	10.2	4.2	24.8	189	189	14.0	94.5	7.7	4.39	4.43	4.43	4.14	4.54
Monday, July 11, 2016	11:47 AM	7/11/16 11:47 AM		5,749	2	45	6	27.8		3	0.00587	0.002536	0.002642	7,195	11,420	11,730	11,550	2,481	3,142	9.4	10.3	3.3	22.0	189	189	14.0	70.0	7.7	4.45	4.44	4.44	4.14	4.67
Monday, July 11, 2016	1:00 PM	7/11/16 1:00 PM		5,822	2	45	6 1/8	29		3	0.00587	0.003064	0.002906	7,265	11,560	11,580	11,630	2,121	3,174	10.1	9.4	3.4	23.4	189	189	14.0	71.0	7.6	4.40	4.48	4.63	4.18	4.71
Monday, July 11, 2016	2:01 PM	7/11/16 2:01 PM		5,883	2	45	6 1/4	28.1		3	0.00587	0.002906	0.002853	7,247	11,600	11,590	11,630	2,143	3,171	9.0	9.7	3.5	23.2	189	189	14.0	71.0	7.7	4.44	4.53	4.46	4.15	4.72
Monday, July 11, 2016	3:30 PM	7/11/16 3:30 PM		5,972	2	45	6 3/8	28.1		3	0.00587	0.003276	0.002932	7,162	11,600	11,600	11,680	2,180	3,172	9.6	9.8	3.5	22.9	189	189	14.0	70.0	shut down	4.59	4.53	4.55	4.23	4.63
Monday, July 11, 2016	4:00 PM	7/11/16 4:00 PM		6,002	2	45	6 3/8	28.1		3	0.00587	0.00317	0.002906	7,207	11,600	11,610	11,660	2,183	3,172	9.5	9.3	3.7	23.4	185	185	14.0	70.0	shut down	4.51	4.52	4.54	4.20	4,57
Tuesday, July 12, 2016	9:20 AM	7/12/16 9:20 AM		7,042	2	45	8 3/4	26.7		2.9	0.00198	0.002853	0.002853	7,148	11,870	11,860	11,930	2,228	3,201	10.4	10.8	4.8	26.3	191	189	16.6	72.0	shut down	4.49	4.50	4.48	4.17	4.55
Tuesday, July 12, 2016	9:40 AM	7/12/16 9:40 AM		7,062	2	45	8 13/16	26.3		3	0.00198	0.002853	0.0028	7,148	11,880	11,860	11,930	2,227	3,204	10.6	10.9	4.4	25.9	191	189	16.6	72.0	shut down	4.48	4.47	4.48	4.16	4.60
Tuesday, July 12, 2016	10:14 AM	7/12/16 10:14 AM		7,096	2	45	8 7/8	26.1		3	0.00198	0.003012	0.0028	7,148	11,850	11,920	11,940	2,225	3,210	10.9	11.1	4.7	25.8	190	189	16.6	72.0	6885 using other train	5.07	5.22	5.06	5.00	4.83
Tuesday, July 12, 2016	11:14 AM	7/12/16 11:14 AM		7,156	2	45	8 15/16	26.2		3	0.00198	0.003012	0.002747	7,148	11,880	11,890	11,940	2,214	3,217	10.6	10.8	4.4	25.8	189	189	16.6	73.0	7.56, using other train	4.51	4.48	4.72	4.33	4.80
Tuesday, July 12, 2016	3:48 PM	7/12/16 3:48 PM		7,430	2	45	9 1/2	27.1		3	0.00198	0.002747	0.002747	7,148	11,600	11,670	11,730	2,895	3,147	9.8	10.5	3.5	25.0	190	189	16.6	81.0	7.48, using other train	4.51	4.52	4.53	4.36	4.58
Wednesday, July 13, 2016	9:56 AM	7/13/16 9:56 AM		8,518	2	45	7 5/8	27.7		3	0.00281	0.003117	0.0028	7,059	11,890	11,830	11,930	2,669	3,197	9.4	9.1	2.8	24.0	189	183	14.6	70.0	7.6	4.55	4.55	4.68	4.39	4.64
Wednesday, July 13, 2016	11:02 AM	7/13/16 11:02 AM		8,584	2	45	9 3/16	27.7		3	0.00281	0.002747	0.002747	7,059	11,880	11,870	11,940	2,735	3,202	8.7	9.0	3.0	23.5	189	184	14.5	82.0	7.6	4.58	4.54	4.65	4.42	4.65
Wednesday, July 13, 2016	1:11 PM	7/13/16 1:11 PM		8,713	2	45	9 9/16	28		3	0.00281	0.002853	0.0028	6,989	11,870	11,900	11,960	2,724	3,208	9.4	9.2	3.2	24.5	185	181	14.5	80.0	7.6	4.50	5.52	4.63	4.87	4.84
Wednesday, July 13, 2016	4:27 PM	7/13/16 4:27 PM		8,909	2	45	10 1/8	28.7		3	0.00281	0.002747	0.002747	7,008	11,920	11,940	12,020	2,812	3,227	9.5	9.1	9.9	24.3	185	181	14.5	82.0	7.6	4.18	4.74	4.15	4.47	4.78
Wednesday, July 13, 2016	5:04 PM	7/13/16 5:04 PM		8,946	2	45	5 5/8	28.2		3	0.00281	0.0028	0.002747	7,142	11,580	11,720	11,650	2,701	3,101	9.2	8.7	9.7	21.8	189	181	15.0	82.0	7.5	4.24	4.44	4.21	4.14	4.25
Thursday, July 14, 2016	10:10 AM	7/14/16 10:10 AM		9,972	2	45	7 9/16	27.3		2.9	0.00450	0.002747	0.002747	7,034	11,870	11,820	11,890	2,674	3,185	9.0	9.0	3.1	25.1	189	181	15.0	82.0		4.08	4.69	4.07	4.48	4.52
Thursday, July 14, 2016	10:35 AM	7/14/16 10:35 AM	Y	9,972	2	45	7 9/16	27.2		3	0.00450	0.002747	0.0028	7,017	11,860	11,830	11,890	2,568	3,181	9.3	9.7	3.2	24.8	189	181	15.0	82.0	7.6	4.46	4.47	4.81	4.62	4.49
Friday, July 15, 2016	10:12 AM	7/15/16 10:12 AM		0	3	45	8 1/8	25.8		3	0.00000	0.00243	0.002061	6,901	13,940	15,690	13,150	2,141	3,360	13.5	13.2	1.7	43.7	186	184	22.0	57.0	7.6	4.56	4.46	4.47	4.43	4.55
Monday, July 18, 2016	9:49 AM	7/18/16 9:49 AM		4,297	3	45	10	28.1		3	0.00083	0.000528	0.002061	6,860	14,960	14,960	15,040	7,990	3,668	17.9	18.3	6.3	46.9	181	181	15.0	160.0	7.5	4.46	4.44	4.64	4.34	4.59
Monday, July 18, 2016	11:04 AM	7/18/16 11:04 AM		4,372	3	45	9 7/16	28		3	0.00083	0.002272	0.002166	6,862	15,000	14,860	14,990	4,237	3,648	18.7	18.2	6.3	47.0	181	181	15.0	65.0	7.5	4.47	4.45	4.70	4.47	4.64
Monday, July 18, 2016	11:49 AM	7/18/16 11:49 AM		4,417	3	45	9 15/16	28.2		3	0.00083	0.001691	0.001955	6,837	14,780	14,870	15,070	4,542	3,673	18.2	18.6	6.4	47.4	180	180	15.0	86.0	7.6	4.57	4.53	4.82	4.50	4.73
Monday, July 18, 2016	12:44 PM	7/18/16 12:44 PM		4,472	3	45	10 1/8	28.3		3	0.00083	0.001796	0.002219	6,835	14,990	14,880	15,090	4,403	3,651	18.2	18.5	6.5	46.8	180	180	15.0	83.0	7.7	4.48	4.44	4.64	4.49	4.74
Monday, July 18, 2016	1:32 PM	7/18/16 1:32 PM		4,520	3	45	10 1/8	28.2		3	0.00083	0.002113	0.002113	6,829	14,880	14,960	15,090	4,308	3,664	18.3	18.7	6.8	47.8	180	180	15.0	75.0	7.6	4.54	4.44	4.66	4.28	4.47
Tuesday, July 19, 2016	10:53 AM	7/19/16 10:53 AM		5,801	3	45	8	27.4		3	0.00198	0.001479	0.002008	6,868	14,730	14,690	14,840	4,357	3,489	18.5	18.8	6.6	48.2	180	180	15.0	93.0	7.6	4.45	4.45	4.63	4.26	4.50
Tuesday, July 19, 2016	11:58 AM	7/19/16 11:58 AM		5,866	3	45	8 1/8	27.4		3	0.00198	0.00214	0.002113	6,876	14,690	14,800	14,860	3,946	2,514	17.9	18.4	6.6	47.8	179	179	15.0	68.0	7.7	4.52	4.43	4.47	4.26	4.50
Tuesday, July 19, 2016	12:32 PM	7/19/16 12:32 PM		5,900	3	45	8 13/16	27.7		3	0.00198	0.002219	0.002113	6,867	14,790	14,710	14,920	3,902	3,511	18.4	18.9	7.1	47.6	179	179	15.0	66.5	7.6	4.54	4.49	4.55	4.41	4.68
Tuesday, July 19, 2016	1:12 PM	7/19/16 1:12 PM		5,940	3	45	8 7/8	27.5		2.9	0.00198	0.002113	0.002166	6,873	14,740	14,780	14,860	3,907	3,512	17.8	18.1	6.6	47.1	179	179	15.0	66.5	ALL TRAINS SHUT DOWN	4.51	4.50	4.53	4.34	4.60
Tuesday, July 19, 2016	4:20 PM	7/19/16 4:20 PM		6,128	3	45	9 3/8	28.2		3	0.00198	0.002113	0.002113	6,829	14,560	14,880	14,930	4,097	3,527	18.3	18.3	6.8	47.0	179	179	15.0	70.5	ALL TRAINS SHUT DOWN	4.50	4.50	4.51	4.31	4.52
Wednesday, July 20, 2016	11:08 AM	7/20/16 11:08 AM		7,256	3	45	9 1/4	27		2.9	0.00198	0.002589	0.001849	6,901	14,790	14,880	14,950	3,546	3,694	18.5	19.4	7.3	49.2	180	179	18.0	50.0	ALL TRAINS SHUT DOWN	4.48	4.49	4.54	4.37	4.57
Wednesday, July 20, 2016	12:09 PM	7/20/16 12:09 PM		7,317	3	45	9 7/17	27.2		2.9	0.00198	0.002219	0.002034	6,901	14,810	14,850	14,940	3,877	3,510	18.5	19.0	7.6	48.9	180	179	18.0	64.0	ALL TRAINS SHUT DOWN	4.49	4.49	4.51	4.36	4.59
Wednesday, July 20, 2016	1:02 PM	7/20/16 1:02 PM		7,370	3	45	9 1/2	27.6		2.9	0.00198	0.001902	0.002034	6,901	14,800	14,940	14,990	4,197	3,507	18.9	19.5	7.2	49.2	179	179	18.0	74.0	ALL TRAINS SHUT DOWN	4.51	4.49	4.53	4.35	4.50
Wednesday, July 20, 2016	1:57 PM	7/20/16 1:57 PM		7,425	3	45	9 11/16	27.9		3	0.00198	0.001902	0.002061	6,901	14,960	14,850	14,990	4,281	3,532	18.5	19.0	7.0	49.6	179	179	18.0	76.0	ALL TRAINS SHUT DOWN	4.50	4.51	4.52	4.37	4.51
Wednesday, July 20, 2016	3:07 PM	7/20/16 3:07 PM		7,495	3	45	10 3/8	28.3		2.9	0.00198	0.001902	0.002113	6,901	14,970	14,880	15,020	4,383	3,545	18.7	19.0	7.5	48.6	179	179	18.0	76.0	7.6	4.54	4.51	4.55	4.49	4.73
Wednesday, July 20, 2016	4:10 PM	7/20/16 4:10 PM		7,558	3	45	10 1/2	28.5		3	0.00198	0.001902	0.002113	6,901	14,980	14,900	15,020	4,415	3,537	18.7	19.0	7.0	49.6	179	179	18.0	76.0	7.6	4.35	5.03	4.40	4.74	4.73
Thursday, July 21, 2016	9:30 AM	7/21/16 9:30 AM		8,598	3	45	12 9/16	27.3		2.9	0.00198	0.001374	0.001796	6,899	15,190	15,300	15,400	5,204	3,607	20.0	20.5	7.6	52.0	179	179	19.0	94.5	7.6	4.71	4.71	4.63	4.44	4.60
Thursday, July 21, 2016	11:35 AM	7/21/16 11:35 AM		8,723	3	45	7 3/16	27.2		3	0.00198	0.001691	0.001902	6,905	14,480	14,590	14,690	4,661	3,340	17.8	19.0	7.4	48.1	179	179	19.0	87.5	7.6	4.72	4.74	4.77	4.54	4.73
Thursday, July 21, 2016	12:37 PM	7/21/16 12:37 PM		8,785	3	45	7 13/16	27.3		3	0.00198	0.001955	0.002087	6,932	14,590	14,610	14,690	4,080	3,362	18.5	19.3	7.3	47.8	179	179	19.0	75.5	7.6	4.73	4.73	4.87	4.59	4.69
Thursday, July 21, 2016	1:49 PM	7/21/16 1:49 PM		8,857	3	45	8 1/16	27.7		3	0.00198	0.002113	0.002113	6,903	14,590	14,610	14,740	4,112	3,380	18.5	18.9	6.8	48.0	179	179	19.0	69.0	7.6	4.75	4.74	4.75	4.62	4.79
Thursday, July 21, 2016	2:36 PM	7/21/16 2:36 PM		8,904	3	45	8 1/16	27.9		3	0.00198	0.002113	0.002113	6,907	14,590	14,610	14,800	4,141	3,382	18.7	19.1	6.8	48.5	179	179	19.0	69.5	7.6	4.38	4.36	4.43	4.13	4.34

Run Time Calculation									Flow					Conductivity						Solids Concentration				Pressure				pH					
Date	Time	Date/Time	Stop Pilot? (Y or Blank)	Run Time	Condition	SLURRY Pump Speed	Seed Feed Tank Level	Feed Tank Temperature	SPARRO Feed	Concentrate	Concentrate Removed	TFC Permeate	CA Permeate	Feed	Seed Feed Tank	Concentrate Tank	Blowdown	TFC Permeate	CA Permeate	Seed Feed Tank	Concentrate Tank	Blowdown	Underflow	Feed	Concentrate	Cyclone Feed	TFC Permeate	Feed	Feed Tank	Concentrate Tank	Blowdown	TFC Permeate	CA Permeate
				min		%	in.	˚C	gpm	gpm	gpm	gpm	gpm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	g/L	g/L	g/L	g/L	psig	psig	psig	psig	unitless	unitless	unitless	unitless	unitless	unitless
Column1	**Column2**						**Column21**							**Cf**		**Ccon**	**Cblow**										**Ppa2**	**Ppa29**	**Ppa28**	**Ppa27**	**Ppa272**	**Ppa26**	**Ppa23**
Thursday, July 21, 2016	3:09 PM	7/21/16 3:09 PM		8,937	3	45	8 1/4	27.9		3	0.00198	0.002166	0.002113	6,965	14,600	14,600	14,730	4,200	3,386	18.4	18.7	7.1	48.7	179	179	19.0	69.5	7.6	4.35	4.36	4.37	4.13	4.36
Friday, July 22, 2016	9:30 AM	7/22/16 9:30 AM		10,038	3	45	10 3/8	27.4		3	0.00281	0.002008	0.001796	6,894	15,000	14,930	15,120	3,985	3,442	19.4	20.0	8.2	49.8	180	179	19.0	68.0	7.6	4.45	4.50	4.47	4.22	4.44
Friday, July 22, 2016	10:48 AM	7/22/16 10:48 AM		10,116	3	45	10 9/16	27.3		3	0.00281	0.002061	0.002061	6,906	14,940	14,930	15,140	3,966	3,437	19.5	20.1	7.8	50.2	180	179	18.0	68.0	7.6	4.30	4.40	4.31	4.09	4.35
Friday, July 22, 2016	12:02 PM	7/22/16 12:02 PM		10,190	3	45	7 3/16	27.2		3	0.00281	0.002113	0.002034	6,917	14,570	14,590	14,720	3,783	3,281	18.5	18.6	7.0	45.9	180	179	18.0	67.0	7.6	4.37	4.37	4.39	4.11	4.33
Friday, July 22, 2016	1:00 PM	7/22/16 1:00 PM		10,248	3	45	8	27.3		3	0.00281	0.00214	0.002061	7,000	14,590	14,580	14,750	3,705	3,299	18.7	18.5	7.1	47.6	180	179	18.0	65.0	7.6	4.38	4.37	4.37	4.13	4.36
Friday, July 22, 2016	2:00 PM	7/22/16 2:00 PM		10,308	3	45	8 3/16	27.6		3	0.00281	0.002113	0.002034	6,988	14,550	14,600	14,710	3,709	3,320	18.6	18.8	7.1	48.2	180	179	18.0	65.0	7.6	4.36	4.36	4.43	4.14	4.37
Friday, July 22, 2016	3:00 PM	7/22/16 3:00 PM		10,368	3	45	8 1/4	27.8		3	0.00281	0.002166	0.002087	6,986	14,630	14,630	14,770	3,751	3,317	18.5	18.9	6.9	48.5	180	179	18.0	65.0	7.7	4.30	4.48	4.55	4.59	4.54
Friday, July 22, 2016	4:00 PM	7/22/16 4:00 PM	Y	10,368	3	45	8 3/8	27.8		3	0.00281	0.002113	0.002061	6,988	14,590	14,620	14,760	3,760	3,332	18.3	18.8	7.0	48.5	180	179	18.0	64.5	7.7	4.35	4.50	4.38	4.09	4.41
Tuesday, July 26, 2016	12:40 PM	7/26/16 12:40 PM		0	4	33	8 15/16	27.3		2	0.00281	0.002325	0.002642	6,923	14,820	14,780	15,010	2,787	3,899	19.8	19.1	7.9	46.9	201	199	14.2	75.0	7.7	3.75	4.12	3.77	3.39	3.90
Tuesday, July 26, 2016	1:40 PM	7/26/16 1:40 PM		60	4	33	6 3/4	27.8		2	0.00281	0.001902	0.002589	6,906	14,440	14,620	14,580	2,903	3,991	17.9	19.2	6.9	44.0	201	199	14.2	94.5	7.7	4.98	5.09	5.03	4.66	4.86
Tuesday, July 26, 2016	2:40 PM	7/26/16 2:40 PM		120	4	33	6 7/8	28.2		2	0.00281	0.002589	0.002636	7,001	14,530	14,580	14,710	2,229	4,009	18.0	18.4	6.8	44.5	201	199	14.5	66.0	pH controller problem	4.59	4.62	4.63	4.24	4.66
Tuesday, July 26, 2016	4:20 PM	7/26/16 4:20 PM		220	4	33	6 15/16	28.8		2	0.00281	0.002615	0.002642	7,001	14,710	14,840	14,930	3,285	4,090	18.4	18.4	7.0	44.7	199	196	14.5	78.0	pH controller problem	4.60	4.61	4.65	4.23	4.62
Wednesday, July 27, 2016	9:30 AM	7/27/16 9:30 AM		1,250	4	33	9 1/16	27.5		2	0.00198	0.00243	0.002589	7,001	15,000	15,030	15,220	2,801	4,089	19.7	19.5	8.3	46.5	201	199	13.5	74.0	Train C Shut Down	4.60	4.60	4.63	4.24	4.63
Wednesday, July 27, 2016	1:38 PM	7/27/16 1:38 PM		1,498	4	33	9 1/2	27.9		2	0.00198	0.002457	0.002536	7,001	15,070	15,070	15,250	2,820	4,111	20.0	19.8	8.2	46.6	200	199	13.0	72.0	Train C Shut Down	4.46	4.68	4.49	4.06	4.50
Wednesday, July 27, 2016	2:45 PM	7/27/16 2:45 PM		1,565	4	33	9 5/8	28		2	0.00198	0.00243	0.002536	7,001	15,100	15,110	15,270	2,830	4,112	19.8	20.0	8.0	47.5	200	199	13.0	72.0	Train C Shut Down	4.52	4.64	4.55	4.07	4.48
Wednesday, July 27, 2016	4:00 PM	7/27/16 4:00 PM		1,640	4	33	5 15/16	27.9		2	0.00198	0.002531	0.002562	6,984	14,520	14,700	14,680	2,543	3,879	18.2	19.0	7.6	43.7	200	199	13.0	74.0	7.7	4.91	4.90	4.94	4.58	4.93
Wednesday, July 27, 2016	4:26 PM	7/27/16 4:26 PM		1,666	4	33	6	27.9		2	0.00198	0.00243	0.002536	6,968	14,560	14,660	14,720	2,541	3,891	18.3	19.1	7.3	44.3	200	199	13.0	74.0	7.8	4.85	4.84	4.91	4.56	4.89
Thursday, July 28, 2016	9:50 AM	7/28/16 9:50 AM		2,710	4	33	7 7/8	27.3		2	0.00198	0.002325	0.002536	7,060	14,820	14,840	15,000	3,079	4,000	18.5	18.5	7.5	44.2	201	199	14.0	70.0	7.7	4.49	4.60	4.50	4.06	4.49
Thursday, July 28, 2016	12:00 PM	7/28/16 12:00 PM		2,840	4	33	8 1/16	27.5		2	0.00198	0.002325	0.002536	7,063	14,890	14,900	15,070	3,092	4,010	19.8	19.9	8.0	46.9	201	199	13.0	70.0	7.6	4.52	4.56	4.55	4.14	4.54
Thursday, July 28, 2016	1:00 PM	7/28/16 1:00 PM		2,900	4	33	6 7/16	27.5		2	0.00198	0.002325	0.002536	7,056	14,590	14,670	14,750	2,612	3,872	18.7	19.5	7.8	46.0	201	199	13.0	78.0	7.6	4.57	4.58	4.62	4.20	4.61
Thursday, July 28, 2016	2:04 PM	7/28/16 2:04 PM		2,964	4	33	6 9/16	27.7		2	0.00198	0.002325	0.002536	7,060	14,600	14,640	14,780	2,687	3,893	18.7	19.1	7.7	45.4	201	199	13.0	79.0	7.6	4.61	4.61	4.64	4.21	4.62
Thursday, July 28, 2016	3:00 PM	7/28/16 3:00 PM		3,020	4	33	6 5/8	27.9		2	0.00198	0.002325	0.002536	7,060	14,640	14,660	14,870	2,802	3,908	18.8	19.2	7.5	45.7	200	199	14.0	79.0	7.6	4.61	4.61	4.64	4.21	4.62
Thursday, July 28, 2016	4:13 PM	7/28/16 4:13 PM		3,093	4	33	6 3/4	28.2		2	0.00198	0.002589	0.002562	7,032	14,650	14,660	14,850	2,643	3,923	18.8	19.2	7.6	45.8	200	199	14.0	71.0	7.6	4.63	4.62	4.68	4.35	4.65
Friday, July 29, 2016	9:55 AM	7/29/16 9:55 AM		4,155	4	33	8 9/16	27.9		2	0.00396	0.002536	0.00243	6,960	14,970	14,990	15,160	2,736	4,007	19.5	19.7	8.0	47.5	200	199	13.8	70.0	7.6	4.66	4.67	4.68	4.26	4.66
Friday, July 29, 2016	11:30 AM	7/29/16 11:30 AM		4,250	4	33	8 11/16	28.2		2	0.00396	0.002536	0.002536	6,992	14,960	14,980	15,150	2,745	4,011	19.9	19.9	7.8	47.6	199	199	13.8	69.0	7.6	4.68	4.68	4.70	4.27	4.68
Friday, July 29, 2016	1:00 PM	7/29/16 1:00 PM		4,340	4	33	10 1/4	28.6		2	0.00396	0.002589	0.002536	6,982	14,980	15,010	15,200	2,792	4,028	19.8	19.6	7.8	49.4	199	199	13.5	69.0	7.7	4.69	4.69	4.74	4.28	4.69
Friday, July 29, 2016	2:30 PM	7/29/16 2:30 PM		4,430	4	33	10 1/2	29.1		2	0.00396	0.002589	0.002536	6,997	15,010	15,020	15,250	2,871	4,083	19.6	19.9	8.0	48.6	199	199	13.5	70.0	7.6	4.45	4.87	4.46	4.02	4.49
Friday, July 29, 2016	3:26 PM	7/29/16 3:26 PM		4,486	4	33	6 1/16	29.1		2	0.00396	0.002562	0.002589	6,999	14,470	14,720	14,600	2,515	3,824	17.8	19.1	6.6	44.4	199	199	12.0	71.0	7.6	4.62	4.70	4.64	4.17	4.59
Friday, July 29, 2016	4:30 PM	7/29/16 4:30 PM		4,550	4	33	6 3/16	29.4		2	0.00396	0.002536	0.002642	6,980	14,560	14,610	14,710	2,654	3,860	18.2	18.4	6.5	44.8	199	194	12.0	72.0	6.6	4.69	4.65	4.70	4.51	4.67
Monday, August 01, 2016	9:40 AM	8/1/16 9:40 AM		8,460	4	33	7 3/4	28		2	0.00396	0.001004	0.002483	6,953	14,910	14,910	15,050	4,783	3,877	19.2	20.4	8.6	48.3	202	199	Problem With Gauge	126.0	7.6	4.36	4.53	4.38	3.87	4.33
Monday, August 01, 2016	11:15 AM	8/1/16 11:15 AM		8,555	4	33	6 1/16	27.8		2	0.00396	0.002536	0.00251	6,977	14,570	14,690	14,720	2,425	3,742	19.6	20.5	8.0	45.7	200	199	Problem With Gauge	68.5	7.6	4.40	4.46	4.43	3.96	4.39
Monday, August 01, 2016	12:20 PM	8/1/16 12:20 PM		8,620	4	33	7 13/16	28		2	0.00396	0.002483	0.002536	6,980	14,620	14,660	14,790	2,450	3,762	19.8	18.2	8.2	45.9	200	199	Problem With Gauge	68.0	7.5	4.45	4.43	4.49	3.99	4.42
Monday, August 01, 2016	1:00 PM	8/1/16 1:00 PM		8,660	4	33	6 5/16	28.2		2	0.00396	0.002483	0.002536	6,970	14,640	14,670	14,800	2,532	3,770	18.9	19.2	8.2	43.7	200	199	Problem With Gauge	71.0	7.5	4.46	4.46	4.49	4.01	4.45
Monday, August 01, 2016	2:00 PM	8/1/16 2:00 PM		8,720	4	33	6 5/8	28.4		2	0.00396	0.00243	0.002536	6,988	14,640	14,670	14,840	2,522	3,779	18.9	18.6	7.8	45.0	200	197	Problem With Gauge	71.0	7.5	4.47	4.47	4.50	4.03	4.46
Monday, August 01, 2016	2:50 PM	8/1/16 2:50 PM		8,770	4	33	6 13/16	28.6		2	0.00396	0.002642	0.002536	6,973	14,650	14,670	14,830	2,513	3,792	18.9	18.7	5.9	44.6	199	195	Problem With Gauge	66.0	7.5	4.45	4.44	4.54	4.16	4.54
Tuesday, August 02, 2016	10:00 AM	8/2/16 10:00 AM	Y	9,920	4	33	8 3/8	29.6		2	0.00198	0.002325	0.002536	6,961	14,920	14,930	15,070	2,915	3,858	19.2	18.7	7.8	45.6	200	199	Problem With Gauge	67.0	7.5	4.46	4.47	4.56	4.12	4.50

Appendix B - Phase 2: Master Field Data Sheet

Run Time Calculation										Timer					Flow						Conductivity								Solids Concentration				Pressure					pH							
Date	Time	Date/Time	Stop Pilot? (Y or Blank)	Stop Pilot Reason	Stop Pilot Time	Run Time Modifier (min)	Run Time (min)	Run Time (hr)	SLURRY Pump Speed	Open	Close	Seed Feed Tank Level	Feed Tank Temperature	SPARRO Feed	Concentrate	Concentrate Overflow	Concentrate Underflow	TFC Permeate	CA Permeate	Feed	Seed Feed Tank	Concentrate Tank	Blowdown	TFC Permeate	PV-1 TFC Permeate	PV-2 TFC Permeate	CA Permeate	Seed Feed Tank	Concentrate Tank	Blowdown	Underflow	Feed	Concentrate	Reduced Concentrate	Cyclone Feed	Permeate	Feed	Feed Tank	Concentrate Tank	Blowdown	TFC Permeate	PV-1 TFC Permeate	PV-2 TFC Permeate	CA Permeate
									%	min	min	in.	°C	gpm		gpm		gpm	gpm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	µS/cm	g/L	g/L	g/L	g/L	psig	psig	psig	psig	psig	unitless	unitless	unitless	unitless	unitless	unitless	unitless	unitless
Column1	Column2											Column21				Qsblow	Column10			Cf		Ccon	Cblow													Ppa2	Ppa29	Ppa28	Ppa27	Ppa272	Ppa26	Ppa25	Ppa24	Ppa23
Thursday, September 01, 2016	12:09	9/1/16 12:09 PM					0	0	43	3	30	9 15/16	27.7	2.3	2.25	1.5	0.7	0.52		6,967	15,320	17,420	18,020	1,861				17.5	21.3	13.1	40.4	259	229	20	10.1	0	7.55	4.39	4.98	4.49	4.19			
Thursday, September 01, 2016	14:12	9/1/16 2:12 PM					123	2	43	3	30	8 1/4	27.6	2.3	2.25	1.5	0.7	0.52		6,923	15,320	17,610	18,000	1,891				17.3	20.6	13.2	37.4	259	229	20	10.1	0	7.48	4.71	4.94	4.43	4.09			
Friday, September 02, 2016	10:43	9/2/16 10:43 AM					1,354	23	43	3	30	7 1/2	25.8	2.3	2.25	1.5	0.7	0.44	2.25	6,541	16,440	18,600	18,900	1,881			8,463	16.1	20.6	14.9	35.9	279	231	21	10.5	0	7.73	4.71	4.95	4.64	4.12			5.05
Friday, September 02, 2016	12:58	9/2/16 12:58 PM					1,489	25	43	3	30	7 1/2	26.0	2.3	2.25	1.5	0.8	0.44		6,587	16,470	18,600	18,940	1,933				16.2	21.0	15.4	35.4	279	231	29	broken	0	7.63	4.55	4.85	4.63	4.10			
Friday, September 02, 2016	14:57	9/2/16 2:57 PM					1,608	27	43	3	30	7 1/4	26.3	2.3	2.25	1.5	0.8	0.44		6,562	16,360	18,680	18,840	2,060				15.7	21.2	14.9	34.4	279	231	25	broken	0	7.64	4.49	4.91	4.57	4.15			
Friday, September 02, 2016	15:48	9/2/16 3:48 PM		Labor Day Weekend			1,659	28	43	3	30	7 1/4	26.5	2.3	2.25	1.5	0.7	0.43		6,612	16,520	18,810	18,940	2,084				15.9	20.9	15.6	35.2	272	231	25	broken	0	7.69	4.47	4.83	4.55	4.11			
Tuesday, September 06, 2016	11:00	9/6/16 11:00 AM	y		10:45 AM	15.00	1,674	28	43	3	30	7 9/16	27.1	2.3	2.25	1.6	0.7	0.42	2.25	6,990	16,440	18,350	18,830	1,931				15.0	20.1	14.2	33.6	261	229	29	broken	0	7.71	4.64	5.20	4.73	4.34			
Tuesday, September 06, 2016	13:20	9/6/16 1:20 PM					1,814	30	43	3	30	8 3/8	26.5	2.3	2.25	1.5	0.7	0.41		6,985	16,540	18,490	18,910	1,961	1,929	2,369		16.1	20.5	14.7	34.0	261	241	29	broken	0	7.63	4.60	5.05	4.67	4.13	4.20	4.10	
Tuesday, September 06, 2016	15:35	9/6/16 3:35 PM					1,949	32	43	3	30	7 1/2	26.5	2.3	2.25	1.6	0.7	0.41		6,989	16,390	18,610	18,840	2,020	1,995	2,480		15.5	20.1	14.9	33.1	269	231	27	broken	0	7.71	4.60	5.08	4.66	4.24	4.30	4.25	
Wednesday, September 07, 2016	10:30	9/7/16 10:30 AM					3,084	51	43	3	30	8 1/4	25.5	2.3	2.25	1.5	0.8	0.42		7,019	16,670	18,770	19,080	2,629	2,870	4,040	8,930	16.8	21.1	16.7	30.9	290	229	27	broken	0	7.60	4.70	5.51	4.77	4.82	4.78	4.93	5.78
Wednesday, September 07, 2016	15:30	9/7/16 3:30 PM		Waiting for Sulfuric Acid			3,384	56	43	3	30	8 1/2	26.5	2.3	2.25	1.5	0.7	0.42		6,989	16,580	18,770	19,020	2,706	2,878	4,200		16.5	21.4	16.8	30.9	293	222	27	broken	0	7.65	4.61	5.53	4.71	4.68	4.64	4.69	
Tuesday, September 20, 2016	10:30	9/20/16 10:30 AM	y		10:00 AM	30.00	3,414	57	43	3	30	7 1/4	28.0	2.3	2.25	1.5	0.7	0.41	1.4	7,022	16,320	18,530	18,510	2,393	2,314	3,533		14.0	19.8	13.9	30.6	259	222	28	10.5	0	7.47	4.54	5.43	4.63	4.30	4.23	4.46	
Tuesday, September 20, 2016	12:40	9/20/16 12:40 PM					3,544	59	43	3	30	7 1/4	27.3	2.3	2.25	1.5	0.7	0.40		6,945	16,290	18,420	18,460	2,645	2,514	3,873		15.0	19.4	-	-	-	-	-	-		7.54	4.72	4.84	4.82	4.20	4.35	4.29	
Wednesday, September 21, 2016	11:30	9/21/16 11:30 AM					4,914	82	43	3	30	7 1/4	26.3	2.3	2.25	1.6	0.7	0.37		6,953	16,520	18,180	18,440	2,661	2,481	4,973		13.4	17.0	13.3	26.9	289	241	28	11.1	0	7.58	4.45	4.53	4.66	3.93	3.97	4.10	
Wednesday, September 21, 2016	13:10	9/21/16 1:10 PM					5,014	84	43	3	30	7 1/4	26.6	2.3	2.25	1.6	0.7	0.36	2.1	6,910	16,360	18,120	18,170	2,567	2,765	5,498	9,499	13.1	17.2	12.7	27.0	291	240	25	11.1	0	7.47	4.69	4.69	4.76	4.18	4.47	4.39	4.77
Wednesday, September 21, 2016	15:33	9/21/16 3:33 PM					5,157	86	43	3	30	7 1/4	26.9	2.3	2.25	1.6	0.7	0.37		6,855	16,080	18,110	18,080	3,664	2,694	5,558		12.8	16.8	12.5	26.5	291	239	25	11	0	7.55	4.16	4.50	4.16	3.75	3.80	3.89	
Thursday, September 22, 2016	10:30	9/22/16 10:30 AM					6,294	105	43	3	30	7 1/4	26.0	2.3	2.25	1.5	0.7	0.41		6,811	16,000	17,880	18,060	3,081	2,690	6,894		13.6	17.3	12.4	26.4	322	229	25	10.7	0	7.42	4.52	4.54	4.61	4.02	4.10	4.30	
Thursday, September 22, 2016	11:17	9/22/16 11:17 AM					6,341	106	43	3	30	7 1/4	25.8	2.3	2.25	1.4	0.9	0.42		6,787	15,820	17,840	17,970	3,106	2,442	7,184		13.1	14.1	13.4	26.3	329	225	25	10.4	0	7.77	4.31	4.62	4.27	4.02	3.90	4.41	
Friday, September 23, 2016	10:48	9/23/16 10:48 AM		Membranes Clogged	1:00 PM		7,752	129	43	3	30	7 1/4	25.2	2.3	2.1	1.4	0.7	0.41		-	15,300	17,580	18,070	3,541	3,082	9,014		13.4	18.2	13.6	26.8	401	199	25	9.9	0	7.82	4.53	4.70		4.21		4.60	
Friday, September 30, 2016	17:00	9/30/16 5:00 PM	y	Shut Off For Weekend	4:30 PM	132.00	7,884	131	43	3	30	7 1/2	27.6	2.3	2.25	1.5	0.8	0.49		7,116	15,120	17,230	17,390	4,248	4,086	6,577		11.7	15.8	11.4	26.7	273	221	25	11	0	7.55	4.25	3.88	4.40	3.62	3.45	3.70	
Tuesday, October 11, 2016	11:25	10/11/16 11:25 AM	y		11:49 AM	30.00	7,914	132	43	3	30	7 1/2	25.5	2.3	2.25	1.5	0.7	0.46		-	-	-	-	-	-	-		9.8	17.4	-	29.6	279	226	25	11.9	0								
Thursday, October 13, 2016	13:56	10/13/16 1:56 PM	y			24.00	7,938	132	43	3	30	7 1/2	23.3	2.3	2.25	1.6	0.7	0.60	1.8	7,081	14,430	15,680	16,520	4,016	3,748	6,150		22.3	24.5	23.0	34.5	300	250	28	12.5	0	7.65	4.09	4.33	4.13	3.77	3.84	4.01	
Thursday, October 13, 2016	16:03	10/13/16 4:03 PM					8,065	134	43	3	30	7 1/2	24.0	2.3	2.25	1.6	0.7	0.50		7,033	14,340	16,070	16,300	3,735	3,973	6,014	5,910	22.4	25.0	23.9	30.3	299	251	28	12.5	0	7.56	4.17	4.41	4.22	3.92	4.06	4.20	5.55
Friday, October 14, 2016	11:52	10/14/16 11:52 AM					9,254	154	43	3	30	7 3/4	25.7	2.3	2.25	1.7	0.6	0.40	2.8	6,982	14,800	16,280	16,480	3,512	4,127	8,841		21.6	24.6	21.6	27.4	341	259	30	13.2	0	7.60	4.25	4.56	4.33	3.94	4.45	4.10	
Friday, October 14, 2016	14:03	10/14/16 2:03 PM					9,385	156	55	3	10	7 1/2	25.6	2.3	3.2	2.1	1.1	0.51	2.38	6,985	14,420	15,840	15,910	5,716	4,951	9,226		21.8	24.2	22.0	27.4	281	181	40	20	0	7.63	4.22	4.46	4.22	4.13	4.20	4.36	
Friday, October 14, 2016	15:51	10/14/16 3:51 PM					9,493	158	55	3	30	7 1/2	25.7	2.3	3.2	2.1	1.1	0.51	2	6,974	14,160	15,450	15,500	5,175	4,857	8,612		20.8	23.3	21.1	26.4	291	181	38	19.5	0	7.56	4.20	4.34	4.23	4.12	4.28	4.39	
Saturday, October 15, 2016	15:45	10/15/16 3:45 PM					10,927	182	55	3	25.5	9	25.9	2.3	3.2	2.1	1.1	0.63		6,964	12,870	13,950	14,220	4,839	4,200	8,670		19.6	24.5	18.0	35.1	340	160	38	18.5	0	7.65	4.21	4.40	4.70	3.98	4.00	4.25	
Monday, October 17, 2016	11:24	10/17/16 11:24 AM					13,546	226	55	3	25.5	8	26.4	2.0	3.2	2.2	1.0	0.49		7,016	14,580	15,550	16,060	4,709	4,772	8,012		35.1	44.4	22.3	87.8	340	170	40	19.5	0	7.66	4.38	4.41	4.41	4.28	4.48	4.52	
Tuesday, October 18, 2016	10:59	10/18/16 10:59 AM					14,961	249	55	3	30	7 1/2	25.1	2.0	3.2	2.3	0.9	0.45	1.6	6,945	12,030	13,230	13,190	4,181	4,111	6,508		17.7	19.4	17.7	25.6	300	184	38	20.5	0	7.55	4.11	4.26	4.77	4.18	4.33	4.35	
Tuesday, October 18, 2016	14:43	10/18/16 2:43 PM					15,185	253	55	3	30	7 1/2	25.3	2.0	3.2	2.2	1.0	0.45		6,952	12,090	12,970	13,160	4,049	4,447	6,446		17.3	19.4	17.3	24.2	305	182	38	20.5	0	7.62	4.26	4.39	4.27	4.30	4.46	4.38	
Tuesday, October 18, 2016	16:20	10/18/16 4:20 PM					15,282	255	55	3	30	7 1/2	25.3	2.0	3.2	2.2	1.0	0.45		6,930	11,950	12,890	13,010	4,013	4,147	6,639		17.2	19.6	16.9	26.0	305	182	38	20.5	0	7.59	4.12	4.37	4.16	4.43	4.35	4.41	
Wednesday, October 19, 2016	12:05	10/19/16 12:05 PM					16,467	274	55	3	30	7 1/2	26.3	2.0	3.25	2.1	1.2	0.45		6,945	11,810	12,700	12,920	3,789	3,783	6,265		16.6	19.6	16.2	24.7	306	182	38	20.9	0	7.69	4.18	4.29	4.24	4.15	4.26	4.48	
Wednesday, October 19, 2016	14:13	10/19/16 2:13 PM					16,595	277	55	3	30	7 1/2	26.6	2.0	3.2	2.1	1.1	0.44		6,944	11,750	12,730	12,910	3,911	3,904	6,340		16.4	19.1	16.2	25.0	305	180	38	20.5	0	7.62	4.59	4.59	4.75	4.43	4.55	4.48	
Wednesday, October 19, 2016	16:20	10/19/16 4:20 PM					16,722	279	55	3	30	7 1/2	26.8	2.0	3.1	2.1	1.0	0.46		6,954	11,880	12,750	13,060	3,798	3,967	6,345	7,215	16.4	18.4	15.5	25.4	305	180	38	20.8	0	7.60	4.50	4.61	4.58	4.59	4.66	4.51	5.06
Thursday, October 20, 2016	13:46	10/20/16 1:46 PM					18,008	300	55	3	30	7 1/2	25.7	2.0	3	1.9	1.1	0.41		6,995	11,740	12,610	12,830	3,634	3,774	6,544		17.5	19.5	-	26.1	339	155	35	17	0	7.55	4.06	4.26	4.23	3.98	4.07	4.23	
Thursday, October 20, 2016	14:45	10/20/16 2:45 PM					18,067	301	55	3	30	7 1/2	25.9	2.0	3.1	1.3	1.8	0.53	2	6,884	11,680	12,660	13,000	4,528	4,873	7,615		18.3	21.3	18.1	30.6	325	171	35	20.1	0	7.54	4.58	4.51	4.63	4.52	4.61	4.57	
Thursday, October 20, 2016	16:17	10/20/16 4:17 PM					18,159	303	55	3	30	7 1/2	26.3	2.0	3.1	1.6	1.5	0.51		7,001	12,820	12,770	13,050	4,283	4,448	7,437		19.1	21.1	18.8	29.9	329	173	35	10.5	0	7.47	4.10	4.43	4.16	4.14	4.21	4.32	
Friday, October 21, 2016	10:38	10/21/16 10:38 AM					19,260	321	55	3	30	7 1/2	26.7	2.0	3	2.1	0.9	0.43	2	6,923	13,340	14,380	14,620	4,040	2,895	7,069		25.0	27.9	21.2	46.5	334	181	40	22.1	0	7.51	4.38	4.35	4.43	4.23	4.28	4.33	
Friday, October 21, 2016	13:16	10/21/16 1:16 PM					19,418	324	55	30	0.3	7 1/2	26.6	2.0	3.1	2.1	1.0	0.45		6,870	12,450	13,980	13,740	3,704	4,236	6,901		19.6	21.3	19.1	28.4	340	180	40	22	0	7.61	4.17	4.51	4.30	4.52	4.76	4.56	
Friday, October 21, 2016	16:55	10/21/16 4:55 PM		Desalter shut down (Sunday)	12:00 p.m.		19,637	327	55	3	30	7 1/2	28.1	2.0	3.1	2.2	0.9	0.46		6,889	13,870	15,120	15,220	3,806	3,093	6,777		20.1	22.3	21.1	23.6	340	179	40	22	0	7.65	4.36	4.44	4.44	4.21	4.49	4.47	
Saturday, October 22, 2016	11:15	10/22/16 11:15 AM					20,737		55	3	25	7 1/2	26.0	2.0	3.1	2.2	0.9	0.58		6,940	12,230	14,190	13,680	5,377	5,330	9,892		19.4	22.3	20.0	27.4	350	170	45	25	0	7.54	4.10	4.43	4.80	4.22	4.50	4.50	
Tuesday, October 25, 2016	11:39	10/25/16 11:39 AM	y			1485.00	22,222	370	55	3	30	7 1/2	23.2	2.0	3.1	2.0	1.1	0.40		6,934	10,450	11,110	11,230	5,269	4,372	10,010		17.2	19.1	16.2	24.9	285	199	51	31.5	0	7.58	4.31	4.43	4.36	4.61	4.49	4.56	
Tuesday, October 25, 2016	12:09	10/25/16 12:09 PM					22,252	371	55	3	30	7 1/2	23.4	2.0	3.1	2.0	1.1	0.43	1.9	6,920	10,510	11,170	11,260	4,869	4,350	9,901		17.0	18.6	15.7	25.0	285	199	51	31.5	0	7.52	4.03	4.28	4.06	4.27	4.23	4.38	
Tuesday, October 25, 2016	12:50	10/25/16 12:50 PM					22,293	372	55	3	30	7 1/2	23.5	2.0	3.1	2.0	1.1	0.42		6,914	10,490	11,230	11,250	4,669	4,262	8,537		17.1	19.1	16.4	24.7	285	200	51	31.5	0	7.49	3.99	4.23	4.01	4.21	4.18	4.31	
Wednesday, October 26, 2016	11:11	10/26/16 11:11 AM					23,634	394	55	3	30	7 3/4	25.3	2.0	3.1	2.0	1.1	0.40	1.7	6,804	10,920	11,680	11,700	3,914	3,846	6,461		17.7	19.9	16.2	25.7	294	202	53	35.1	0	7.62	4.14	4.33	4.18	4.22	4.28	4.41	
Wednesday, October 26, 2016	13:31	10/26/16 1:31 PM					23,774	396	55	3	30	7 3/4	25.5	2.0	3.1	2.0	1.1	0.40		6,784	10,960	11,700	11,830	3,906	3,903	6,691		17.9	20.0	18.5	25.9	290	202	55	35.3	0	7.62	4.04	4.21	4.19	4.35	4.21	4.28	
Wednesday, October 26, 2016	16:11	10/26/16 4:11 PM		Desalter shut down (Wednesday)	10:00 PM		23,934	399	55	3	30	7 3/4	25.4	2.0	3.1	1.9	1.2	0.41		6,884	10,930	11,790	11,810	3,887	3,733	6,409	4,682	17.7	20.3	17.1	26.0	289	201	55	35.4	0	7.58	4.02	4.23	4.03	4.06	4.19	4.22	4.23
Monday, October 31, 2016	14:30	10/31/16 2:30 PM	y			348.96	24,283	405	55	3	30	7 3/4	24.1	2.0	3.1	1.9	1.2	0.46	2.05	6,922	9,060	9,755	9,685	4,399	4,635	6,377		14.6	17.1	13.7	21.2	260	191	-	25.5	0	7.62	4.08	4.36	4.10	4.47	5.08	4.51	
Monday, October 31, 2016	16:20	10/31/16 4:20 PM					24,393	407	55	3	30	7 3/4	23.8	2.0	3.1	1.9	1.2	0.48		6,946	9,217	9,793	9,896	4,772	4,737	6,528		15.5	17.0	14.5	22.5	270	199	-	26.3	0	7.56	4.06	4.24	4.01	4.22	4.43	4.27	
Tuesday, November 01, 2016	10:30	11/1/16 10:30 AM					25,483	425	55	3	30	7 3/4	23.7	2.8	3.1	1.9	1.2	0.45		6,777	9,809	10,460	10,490	4,618	4,600	6,631	5,751	16.3	18.0	15.5	22.8	279	205	-	27.5	0	7.54	4.04	4.20	4.11	4.14	4.22	4.25	4.55
Tuesday, November 01, 2016	13:13	11/1/16 1:13 PM					25,646	427	55	3	25.5	7 3/4	23.9	2.8	3.1	1.9	1.2	0.44		6,548	9,779	10,400	10,490	4,582	4,673	6,591		16.6	18.0	15.6	22.1	280	207	-	28	0	7.41	4.00	4.18	4.02	4.16	4.21	4.21	
Tuesday, November 01, 2016	16:00	11/1/16 4:00 PM					25,813	430	55	3	25.5	7 3/4	23.8	2.8	3.1	1.9	1.2	0.45		6,590	9,711	10,390	10,330	4,516	4,650	6,614		16.3	18.2	15.7	22.3	279	207	-	28	0	7.45	4.24	4.20	4.33	4.28	4.31	4.35	
Wednesday, November 02, 2016	10:59	11/2/16 10:59 AM					26,952	449	55	3	25.5	7 3/4	24.3	2.8	3.25	1.9	1.4	0.41	2	3,785	8,972	9,721	9,642	3,904	3,891	5,738	5,801	14.2	16.6	13.9	19.9	284	207	-	28.2	0	7.50	4.03	4.48	4.04	4.47	4.52	4.56	4.39
Wednesday, November 02, 2016	14:08	11/2/16 2:08 PM					27,141	452	55	3	25.5	8	24.5	2.8	3.1	1.9	1.2	0.45		6,579	9,182	9,777	9,871	3,961	3,924	5,799		15.0	16.4	14.4	19.9	284	207	-	28.2	0	7.53	4.18	4.19	4.22	4.26	4.33	4.36	
Wednesday, November 02, 2016	16:20	11/2/16 4:20 PM					27,273	455	55	3	25.5	8	24.5	2.8	3.1	1.8	1.3	0.45		6,599	9,209	9,856	9,874	3,966	4,044	5,925	5,564	15.3	16.7	14.7	20.2	285	207	-	28.2	0	7.52	3.92	4.35	3.99	4.57	4.47	4.50	5.29
Thursday, November 03, 2016	12:30	11/3/16 12:30 PM					28,483	475	55	3	25.5	8	25.4	2.8	3.25	1.7	1.6	0.45		6,639	9,611	10,210	10,140	4,033	4,060	6,225		15.3	17.1	14.7	19.6	297	206	-	29.4	0	7.40	4.68	4.38	4.51	4.40	4.59	4.47	
Thursday, November 03, 2016	14:20	11/3/16 2:20 PM					28,593	477	55	3	25.5	8	25.4	2.8	3.1	1.7	1.4	0.45		6,662	9,566	10,230	10,310	4,037	4,093	6,156		15.0	16.9	15.0	19.6	291	206	-	29.2		7.52	3.86	4.47	3.98	4.82	4.43	4.52	
Thursday, November 03, 2016	15:43	11/3/16 3:43 PM					28,676	478	55	3	25.5	8	25.4	2.8	3.1	1.6	1.5	0.47		6,611	9,562	10,280	10,240	4,099	4,054	6,208		15.7	17.2	15.0	20.2	299	209	-	29.4	0	7.52	4.09	4.11	4.04	4.11	4.20	4.14	
Friday, November 04, 2016	11:50	11/4/16 11:50 AM					29,883	498	55	3	25.5	7 1/4	24.8	2.5	3	1.5	1.5	0.45	1.9	6,590	9,597	10,270	10,260	4,432	4,251	7,163	5,681	15.6	17.2	13.4	19.5	306	202	-	31	0	7.49	3.82	3.99	3.84	4.13	4.06	4.13	4.23
Friday, November 04, 2016	15:20	11/4/16 3:20 PM					30,093	502	55	3	24	7 1/4	25.5	2.5	3.1	1.4	1.7	0.45		6,615	9,624	10,280	10,250	4,358	4,235	6,801		15.5	17.1	14.7	18.8	312	209	-	31.2	0	7.49	3.82	4.00	3.84	3.96	3.99	4.04	
Friday, November 04, 2016	16:00	11/4/16 4:00 PM		Desalter shut down (Saturday)	6:00 PM		30,133	502	55	3	24	7 1/4	25.4	2.5	3.1	1.4	1.7	0.46		6,616	9,575	10,270	10,270	4,416	4,295	6,994		15.1	17.0	14.7	19.1	299	201	-	30.7	0	7.39	3.79	3.81	3.82	4.00	4.05	4.02	
Monday, November 07, 2016	12:10	11/7/16 12:10 PM	y			1560.00	31,693	528	55	3	24	7 1/4	23.8	2.5	3.1	2.0	1.1	0.57	2	6,789	8,922	9,561	9,520	5,510	5,677	7,622		14.7	16.6	13.1	25.0	285	190	-	26.5	0	7.51	3.85	4.04	3.86	4.18	4.16	4.16	
Monday, November 07, 2016	15:21	11/7/16 3:21 PM					31,884	531	55	3	24	7 1/4	24.5	2.5	3.1	2.0	1.1	0.52		6,706	9,020	9,599	9,666	5,104	5,367	7,271	5,917	14.7	16.2	13.4	23.3	284	198	-	276	0	7.46	3.82	3.75	3.85	3.83	3.90	3.84	4.17

Appendix C - University of Cape Town – Gypsum Crystallization Particle Analysis

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Report for

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92626

Draft - February 2017

Tuesday, 24 May 2016

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Research Report
Gypsum Crystallization – Particle Analysis

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TABLE OF CONTENTS

1. Synopsis 1
2. Aims and Objectives 1
3. Seed samples 1
3.1 Particle Size Distributions 1
3.2 Scanning Electron Microscopy 2
- AC sample 3
- AC sample, washed 4
- PG sample 4
- PG sample, washed 5

4. Discussion 5
5. References 5

TABLE OF FIGURES

Figure 1: Particle Size Distribution of the seed samples AC and PG 2
Figure 2: SEM images of the seed sample AC 3
Figure 3: SEM images of the seed sample AC, washed 4
Figure 4: SEM images of the seed sample PG 4
Figure 5: SEM images of the seed sample PG, washed 5

TABLE OF TABLES

Table 1: Particle Size Distributions of the AC and PG samples 1

1. Synopsis

The overall aim was to provide an analysis of the gypsum crystals either produced or used in the membrane testing process.

Thus far, the analysis consists of two samples of gypsum seeds. These have been analysed using both SEM and PSD techniques.

2. Aims and Objectives

The aims of this project are to provide an analysis of the gypsum crystals either produced or used in the membrane testing process.

This initial project will consist of analysing **two** samples of gypsum seeds and **four** samples of produced product (ie. **six** samples in total) using a range of analytical equipment, including Scanning Electron Microscopy and a Particle Size distribution analysis (with either an electro-zone sensing method or a laser diffraction method).

3. Seed samples

Two seed samples were analysed: Sample AC and Sample PG.

3.1 Particle Size Distributions

The Particle Size Distributions of the two samples were analysed using a Malvern Mastersizer S Laser diffraction instrument and all distributions were measured five times for each sample. The relevant metrics of the two samples are given below in Table 1.

Table 1: Particle Size Distributions of the AC and PG samples

Sample Name	Span (µm)	D [4, 3] - Volume weighted mean (µm)	Specific surface area (m^2/g)	D [3, 2] - Surface weighted mean (µm)	d (0.1) (µm)	d (0.5) (µm)	d (0.9) (µm)
Sample AC	3.062	47.687	0.651	9.222	4.41	34.467	109.944
Sample PG	2.251	21.579	0.772	7.771	4.936	16.724	42.584

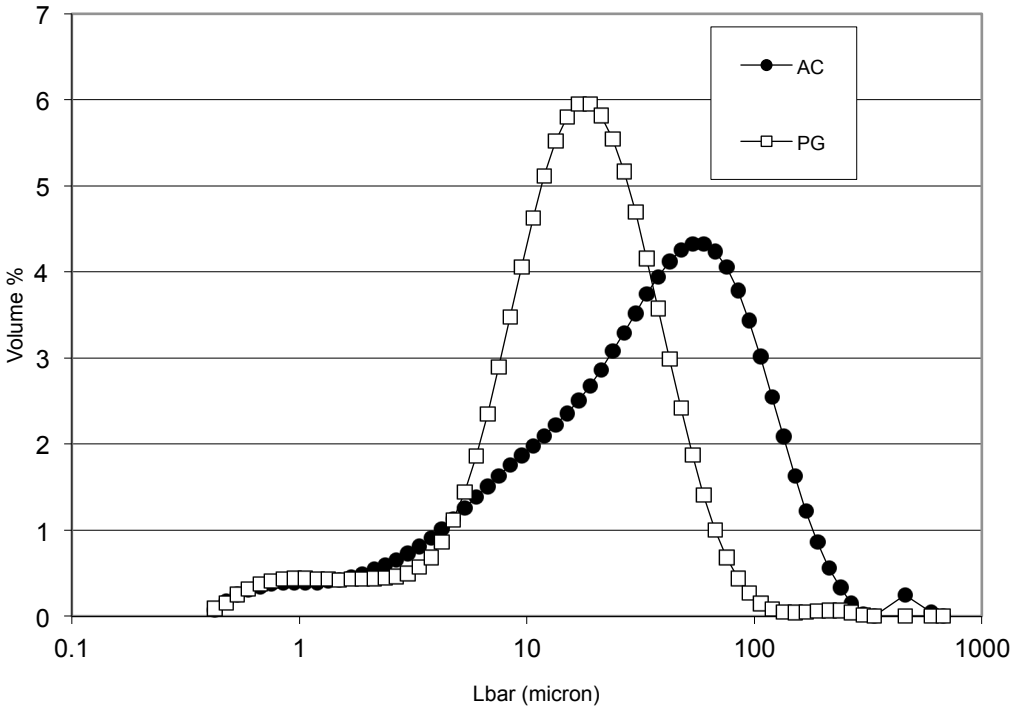

Figure 1: Particle Size Distribution of the seed samples AC and PG

3.2 Scanning Electron Microscopy

The two seed samples were analysed using Scanning Electron Microscopy The preparation protocol for the SEM images was as follows: the 10mm aluminium pin stubs were coated with carbon glue; a small amount of the sample was sprinkled/placed onto the stub, loose particles blown off with dust-off; the stub was sputter coated with gold palladium alloy and the stub was then placed in the scanning electron microscope (SEM). The SEM is a FEI Nova NanoSEM 230, with a field emission gun. The images were taken with the secondary detector. The supplementary information about kV, working distance, and magnification is on the data zone on each image.

- **AC sample**

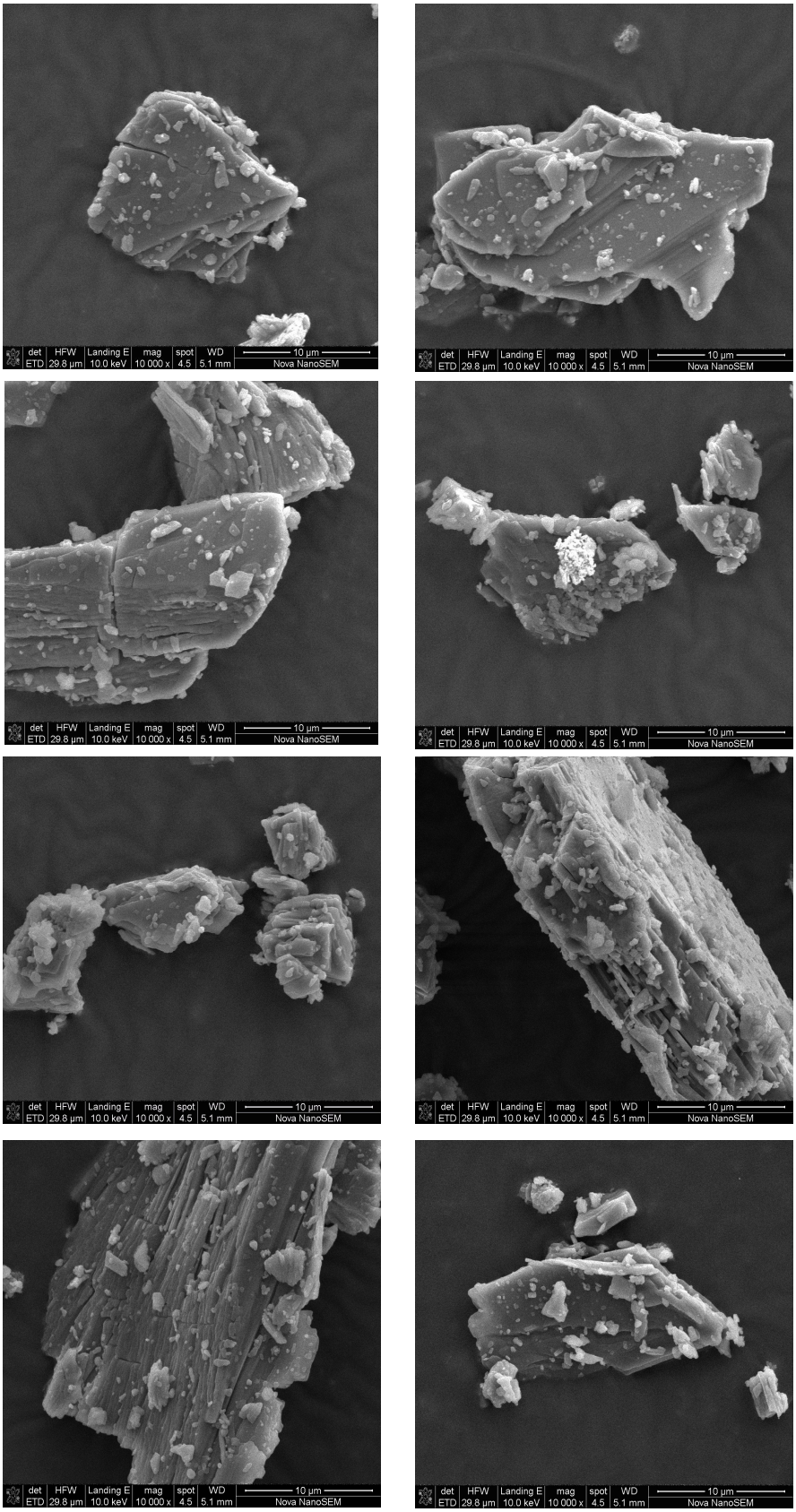

Figure 2: SEM images of the seed sample AC

- **AC sample, washed**

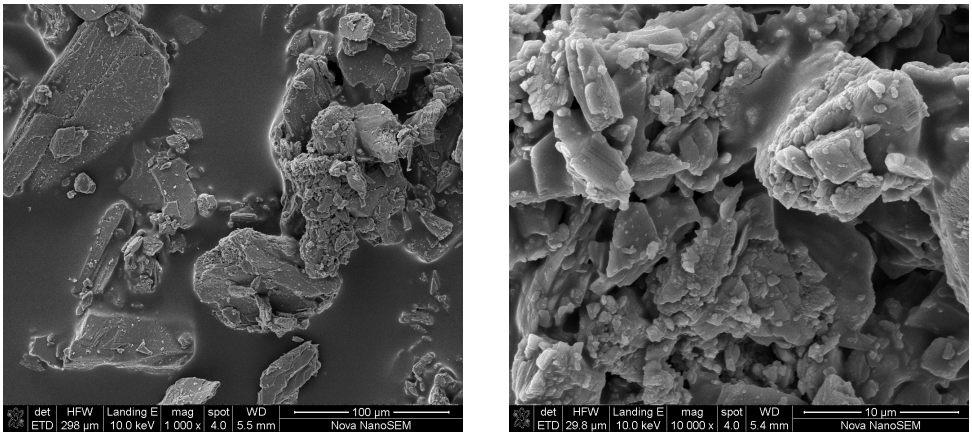

Figure 3: SEM images of the seed sample AC, washed

- **PG sample**

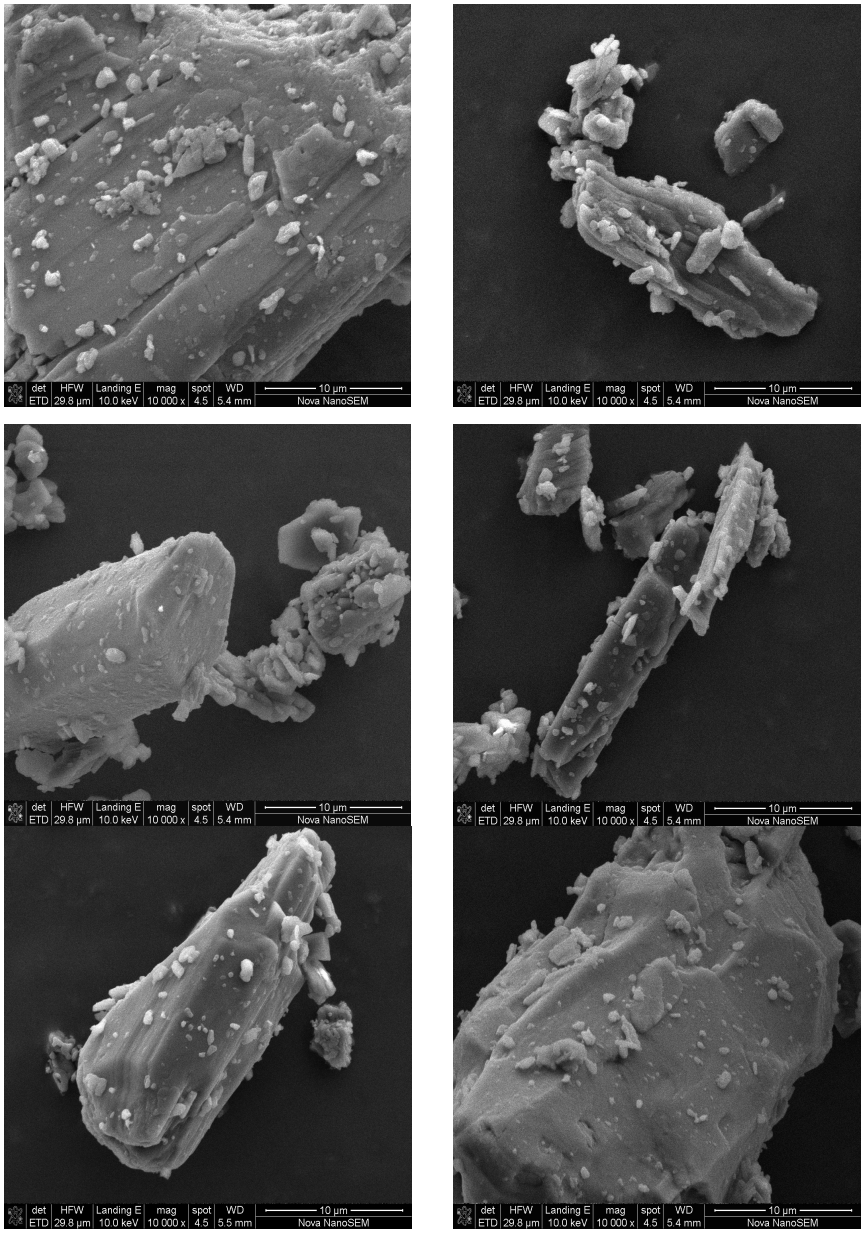

Figure 4: SEM images of the seed sample PG

- **PG sample, washed**

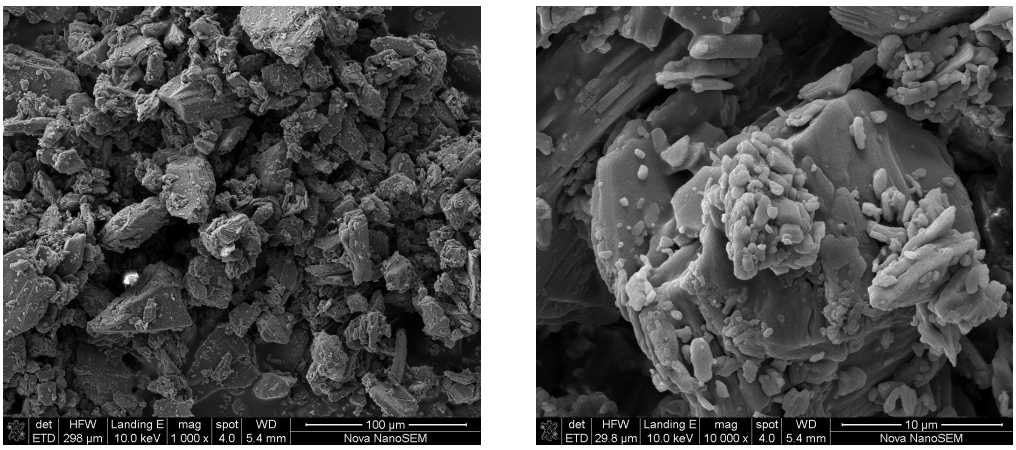

Figure 5: SEM images of the seed sample PG, washed

4. Discussion

From the PSD measurements, it is clear that sample AC is significantly larger than the sample PG, with a volume weighted mean size of 47.687µm, whereas the PG sample has a volume weighted mean size of 21.579 µm.

However, since neither sample has a normal distribution, there are some subtleties in the particle size distributions that are not immediately apparent from the characteristic metrics.

Sample PG, for example, has a significant volume % of particles in the very small size range, between 3 and 0.4 µm. This could be indicative of either attrition or nucleation combined with some growth. The results of primary nucleation would be evident ONLY in the very smallest size bin and therefore it can be deduced that this sample exhibits features of primary nucleation combined with growth (most likely) or attrition, which would account for the smaller fragments. These smaller fragments are most evident in the SEM pictures showing the washed samples. From the habit of the crystals in the SEM pictures, it appears that the smaller fragments are more likely to have arisen from nucleation combined with some growth than from attrition.

The sample AC, on the other hand, has a skewed normal distribution, with the peak skewed towards the larger sizes. It also has a small anomaly in the very largest size range at >450µm.

5. References

OLI Systems Inc (2015). OLI Studio 9.2, Stream Analyzer, 10-Jul-2015. Morris Plains, New Jersey, OLI Systems Inc.

Crystallization & Precipitation Unit

Wednesday, 10 August 2016

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Research Report
Gypsum Crystallization – Particle Analysis
Part 2: Homemade seeds sample and
Part 3: BC and EC seeds sample

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TABLE OF CONTENTS

1. Synopsis 1
2. Seed sample – Homemade Seed 1
2.1 Preparation method 1
2.2 Scanning Electron Microscopy 1
2.3 Discussion 1
3. Seed sample – BC and EC seeds 2
3.1 Preparation method 2
- BC sample 2
- EC sample 2
3.2 Scanning Electron Microscopy 2
- BC sample 3
- EC sample 3
3.3 Discussion - SEM 3
3.1 EDX 4
3.1 Discussion – EDX 4
4. References 4

TABLE OF FIGURES

Figure 1: SEM images of the homemade seed sample 1
Figure 2: SEM images of the BC seed sample 3
Figure 3: SEM images of the PG seed sample 3

TABLE OF TABLES

Table 1: EDX 4

1. Synopsis

The overall aim was to provide an analysis of the gypsum crystals either produced or used in the membrane testing process.

Part 2 consists of analysing homemade seeds using SEM.

Part 3 consists of analysing the BC and EC seed samples using SEM and EDX.

2. Seed sample – Homemade Seed

2.1 Preparation method

The homemade gypsum seeds were made using the UCT recipe. This sample was made using smaller volumes in the lab with 0.4 M solutions. Approximately 120g of seeds were made and the sample was not completely dried before being shipped.

2.2 Scanning Electron Microscopy

All seed samples were analysed using Scanning Electron Microscopy with the preparation protocol being the same as outlined in the previous report. A single sample of homemade seeds was analysed using SEM.

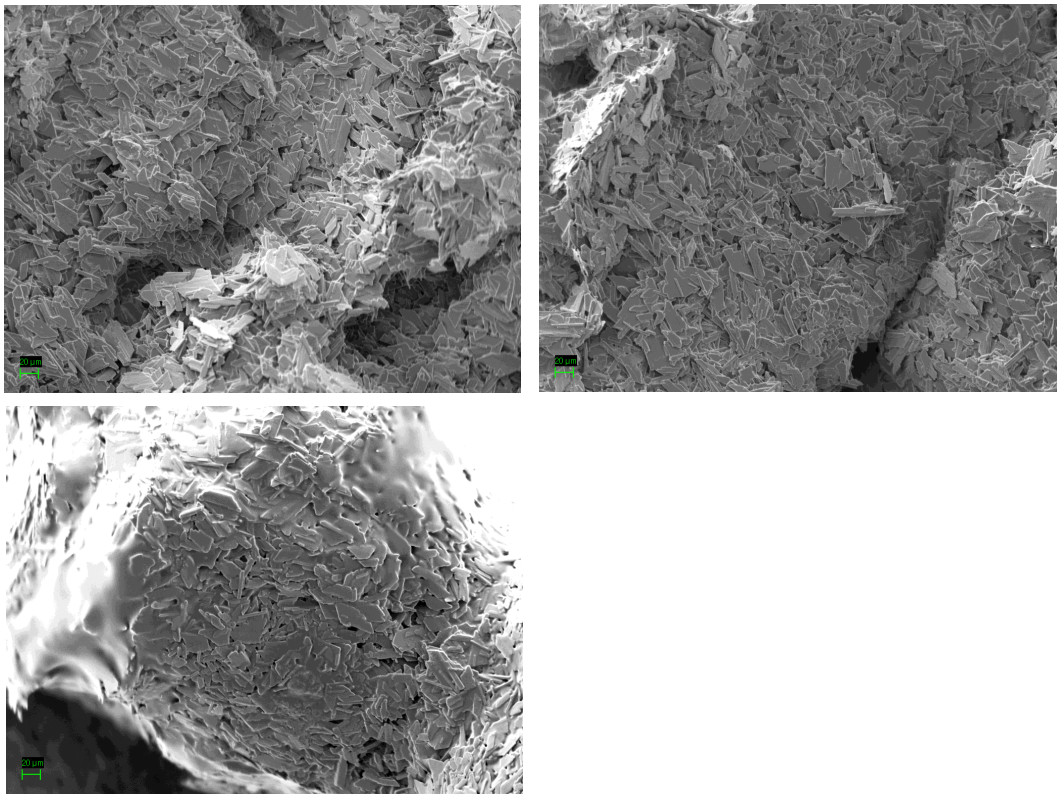

Figure 1: SEM images of the homemade seed sample

2.3 Discussion

The homemade seeds clearly consist of very small platelet morphology. The scale bar on the images is 20μm, and the images show that the primary platelet particles are in the size range 20μm. The general impression given by these samples is of a crystallization process that has occurred in a nucleation-dominated environment. This environment leads to the birth of large numbers of very small crystals. This relationship between supersaturation and a nucleation-dominated environment is illustrated in Figure 2.

In comparison to the other samples presented in this report, this is unexpected, since a lower concentration of reagent solutions (0.4M) was used for their preparation. Therefore, it is possible that the very high supersaturation necessary for the production of platelets was generated by inhomogeneities in the production process.

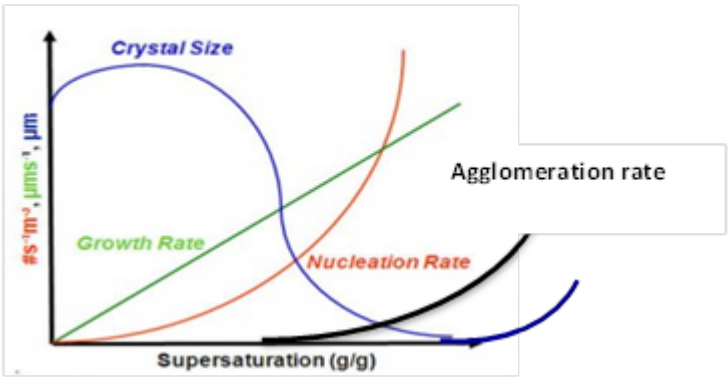

Figure 2: Relationship between supersaturation and crystallization mechanisms and crystal size (Lewis et al., 2015)

3. Seed sample – BC and EC seeds

3.1 Preparation method

- **BC sample**

Sample BC is a sample of freshly made seed using the UCT recipe, except that the concentration was increased to 0.6 M – because it was necessary to make about 12 kg.

- **EC sample**

Sample EC2 is a sample of seed taken after two to three weeks of operation. Unfortunately there is no sample of that seed at the time it was made, but it was made using the same method as that of Sample BC4.

3.2 Scanning Electron Microscopy

All seed samples were analysed using Scanning Electron Microscopy with the preparation protocol being the same as outlined in the previous report. The BC and EC seed samples were analysed using SEM and EDX.

- **BC sample**

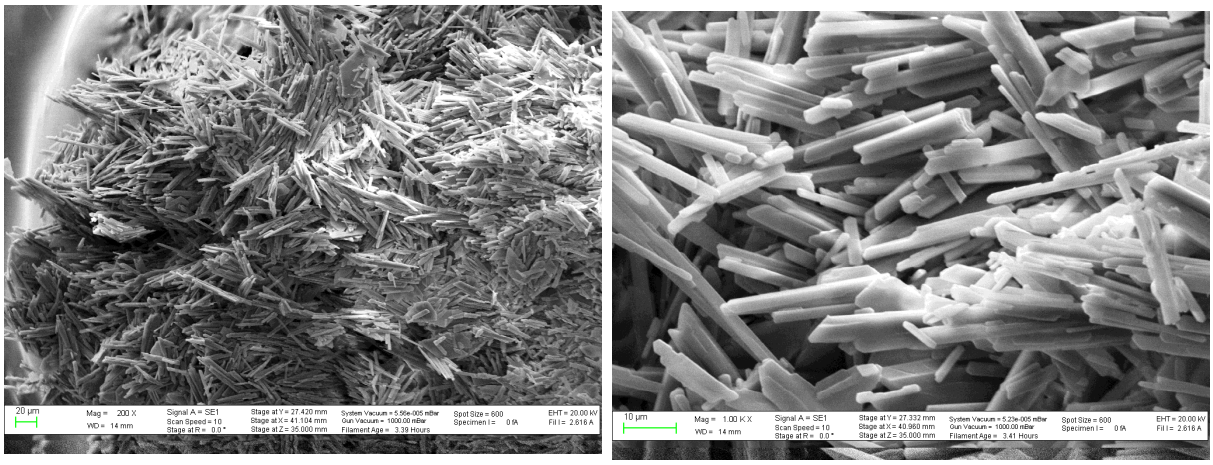

Figure 3: SEM images of the BC seed sample

- **EC sample**

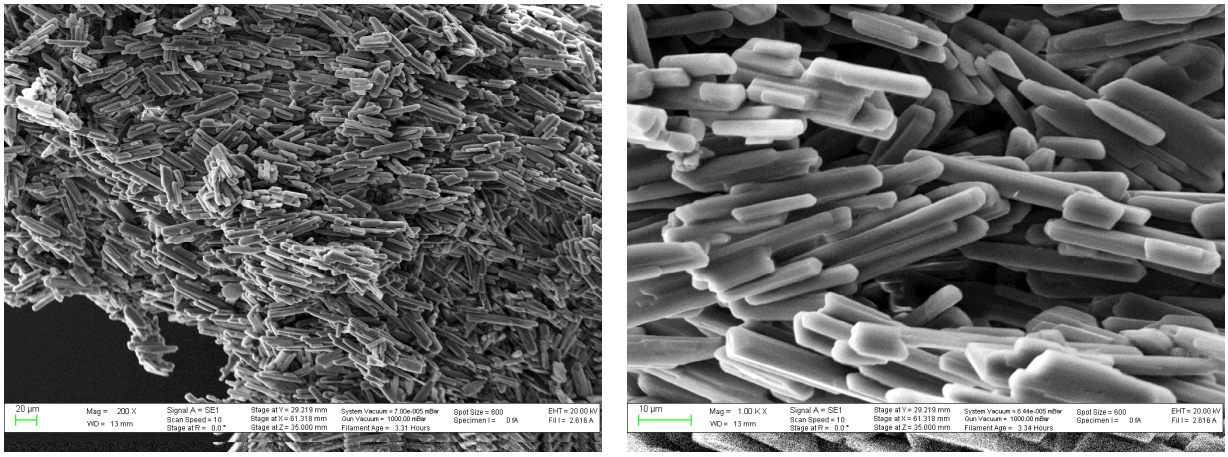

Figure 4: SEM images of the PG seed sample

3.3 Discussion - SEM

Both the EC and the BC samples exhibit extremely regular, rod morphology. The scale bar on the SEM images is 20µm, indicating that the rods are approximately 30 to 40µm in length. The sample EC shows more sign of wear than the sample BC, with rounded, possibly abraded, tips of the crystals.

The rod morphology is a consequence of growth-dominated crystallization at lower supersaturation. This morphology is usually generated under homogeneous conditions where the nuclei are subject to a constant environment of relatively low supersaturation. In this case, the very small size of the rods suggests that the supersaturation was moderate and not extremely low.

3.1 EDX

Table 1: EDX results

BC4					
Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Oxygen	K-series	53.51	62.84	79.00	6.72
Calcium	K-series	17.29	20.30	10.19	0.54
Sulfur	K-series	13.49	15.84	9.94	0.51
Sodium	K-series	0.81	0.95	0.83	0.09
Silicon	K-series	0.05	0.06	0.04	0.00
	Sum:	85.15	100.00	100.00	

EC4					
Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Oxygen	K-series	53.01	64.05	80.13	6.67
Calcium	K-series	17.33	20.94	10.46	0.54
Sulfur	K-series	12.26	14.81	9.25	0.47
Sodium	K-series	0.16	0.19	0.16	0.04
Silicon	K-series	0.01	0.01	0.01	0.00
	Sum:	82.76	100.00	100.00	

3.1 Discussion – EDX

The EDX results are given in Table 1. These indicate that there is very little difference between the elemental compositions of the samples. In particular, the silicon content of both samples is negligible.

4. References

Lewis, A. E., M. M. Seckler, H. Kramer and G. M. van Rosmalen (2015). Industrial Crystallization: Fundamentals and Applications, Cambridge University Press. http://dx.doi.org/10.1017/cbo9781107280427

Thursday, 9 February 2017

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Research Report
Part 4
Gypsum Crystallization – Additional Analysis

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TABLE OF CONTENTS

1. Synopsis 1
2. Seed samples 1
2.1 Scanning Electron Microscopy 1
- Feed tank seed samples 1
- Seed sample phase 2 2

2.2 Discussion 2
3. References 3

TABLE OF FIGURES

Figure 1: SEM images of the feed tank seed sample 1
Figure 2: SEM images of the seed sample phase 2 2
Figure 3: Illustration of the formation of macrosteps as a consequence of fast growth rates 3

1. Synopsis

The aims of this project are to provide an analysis of some additional gypsum crystals produced in the membrane testing process.

2. Seed samples

2.1 Scanning Electron Microscopy

All seed samples were analysed using Scanning Electron Microscopy with the preparation protocol being the same as outlined in the previous report.

- **Feed tank seed samples**

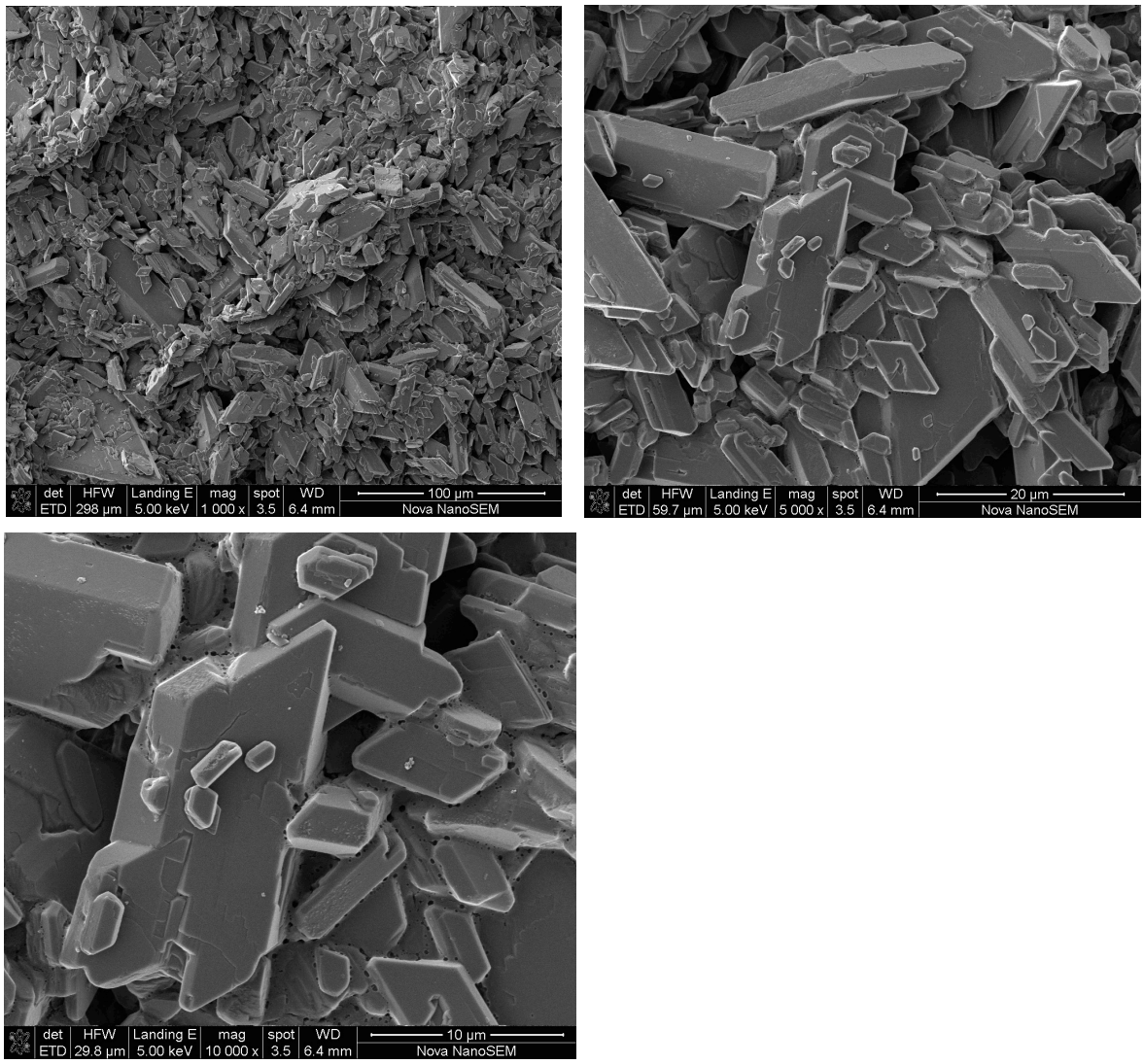


Figure 1: SEM images of the feed tank seed sample

- **Seed sample phase 2**

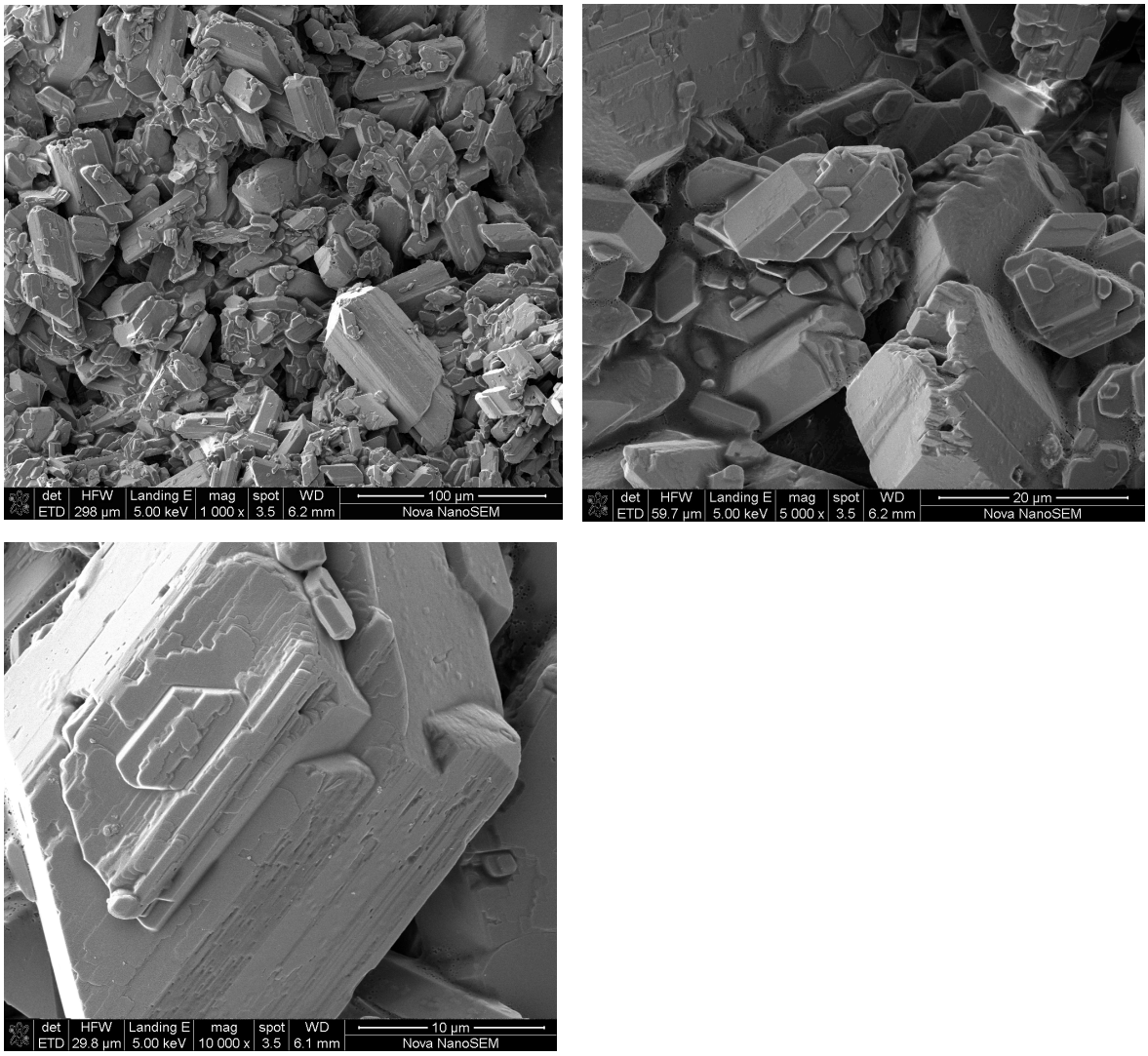


Figure 2: SEM images of the seed sample phase 2

2.2 Discussion

The feed tank seed samples exhibit a relatively wide size range and are of an intermediate morphology (between platelet and rod-like). The primary particles appear to be platelets (indication of a nucleation-dominated crystallization process), but their wide range of sizes, from approximately 1µm (see the third image at the highest magnification in Figure 1) to larger than 20µm, indicates that inhomogeneous growth has occurred in the process. The smallest platelets have expreienced little growth, whereas the larger particles have experienced much more growth and are beginning to exhibit some rod-like characteristics.

The seed sample phase 2 exhibits much larger crystals than the feed tank seed samples, as illustrated in the third image at the highest magnification in Figure 2. They also show much more evidence of irregular growth and a higher degree of attrition than the previous sample. There is evidence of macrosteps (very obvious in the third image at the highest magnification in Figure 2), which is symptomatic of higher supersaturation levels and faster growth rates. See Figure 3.

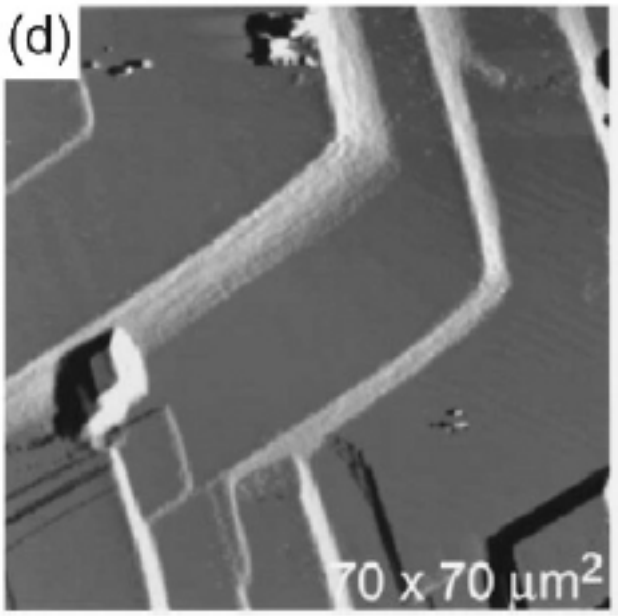
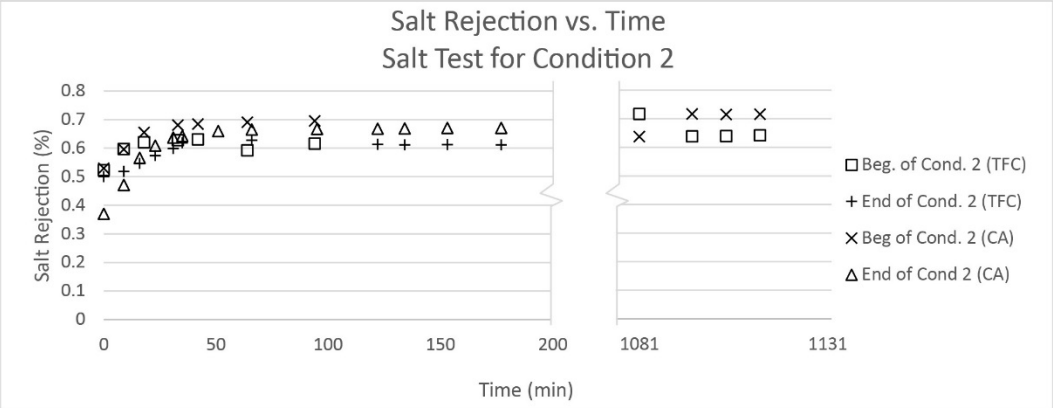


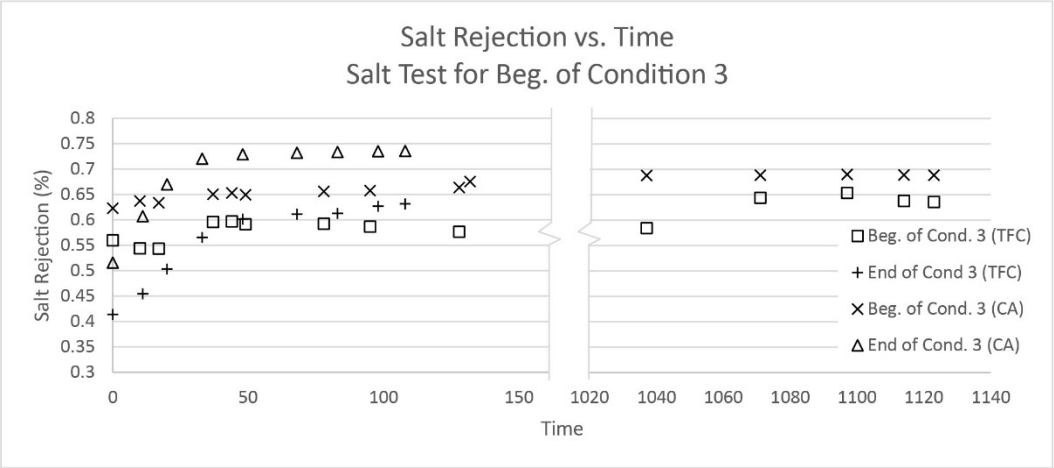
Figure 3: Illustration of the formation of macrosteps as a consequence of fast growth rates (Sangwal, 2007)

3. References

Sangwal, K. (2007). Additives and Crystallization Processes: From Fundamentals to Applications, Wiley.

Appendix D - Additional Graphs


Salt Rejection vs. Time
Salt Test for Condition 2
Salt Rejection (%)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50
100
150
200
1081
1131
Time (min)
Beg. of Cond. 2 (TFC)
End of Cond. 2 (TFC)
Beg of Cond. 2 (CA)
End of Cond 2 (CA)


Salt Rejection vs. Time
Salt Test for Beg. of Condition 3
Salt Rejection (%)
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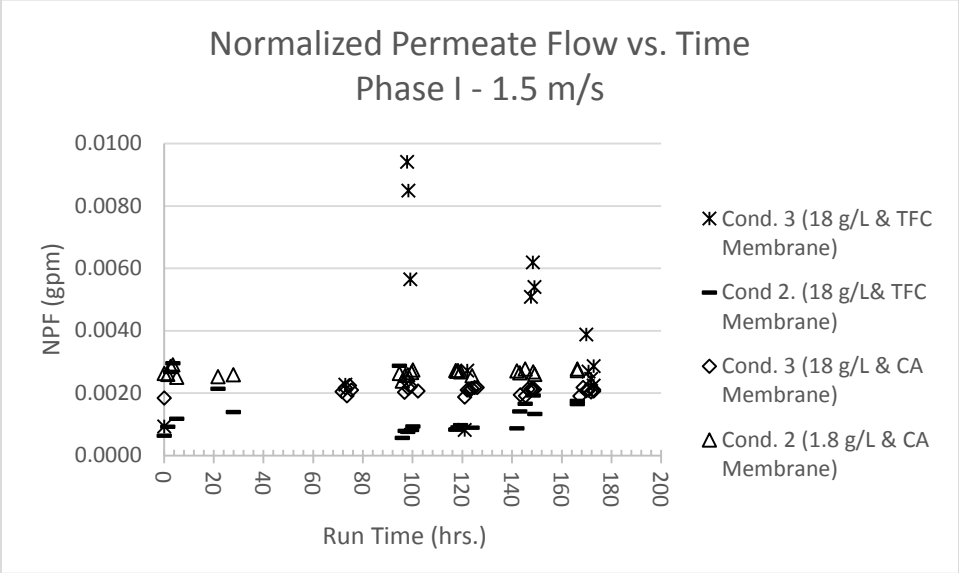
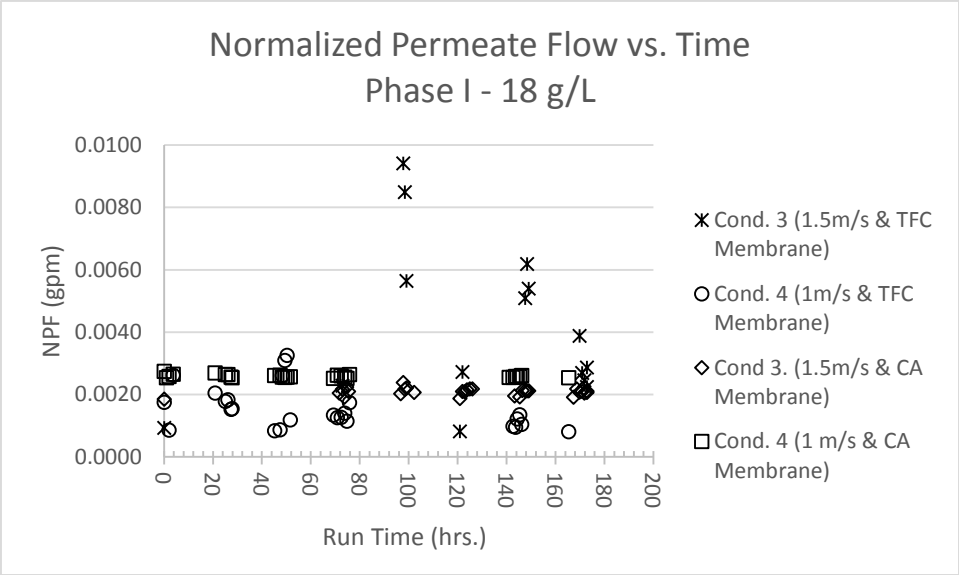
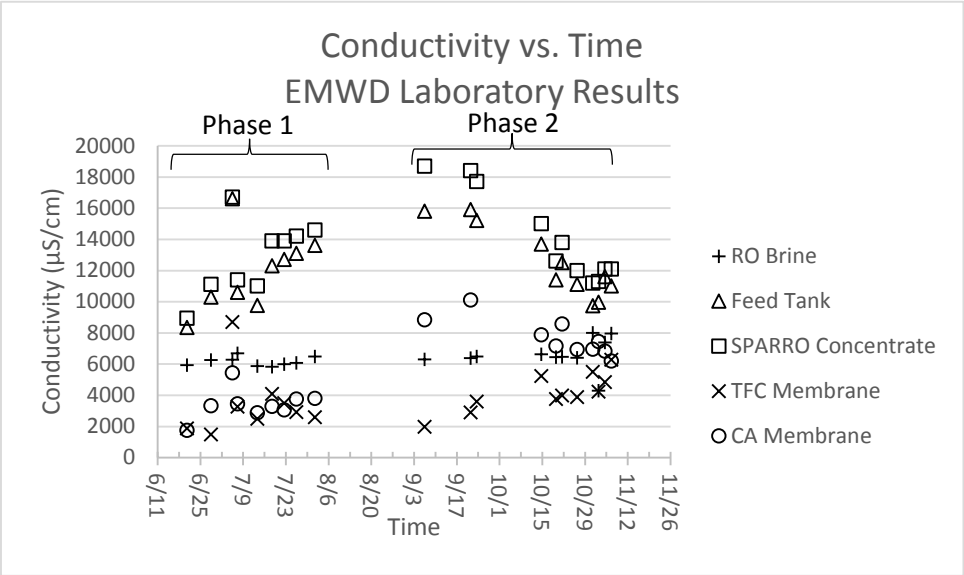
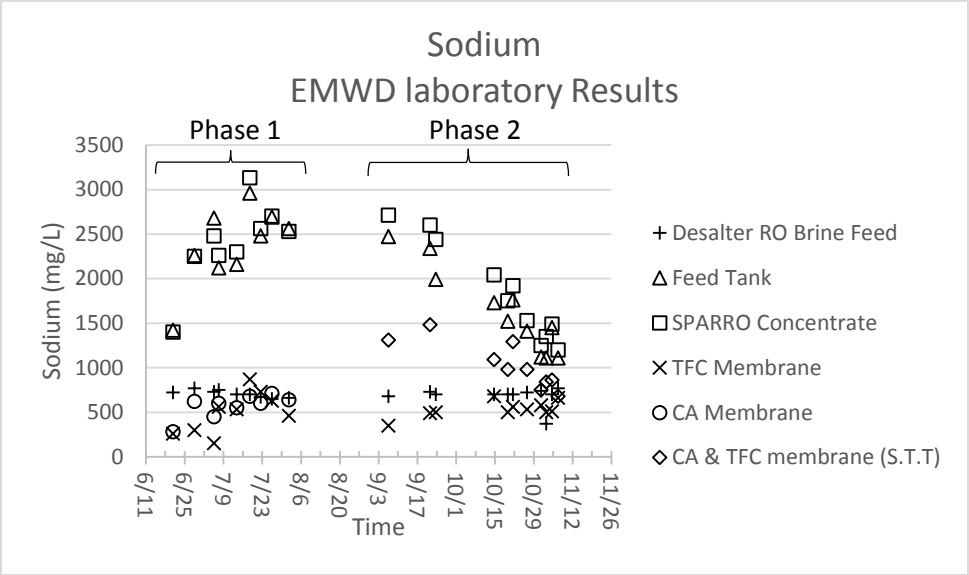
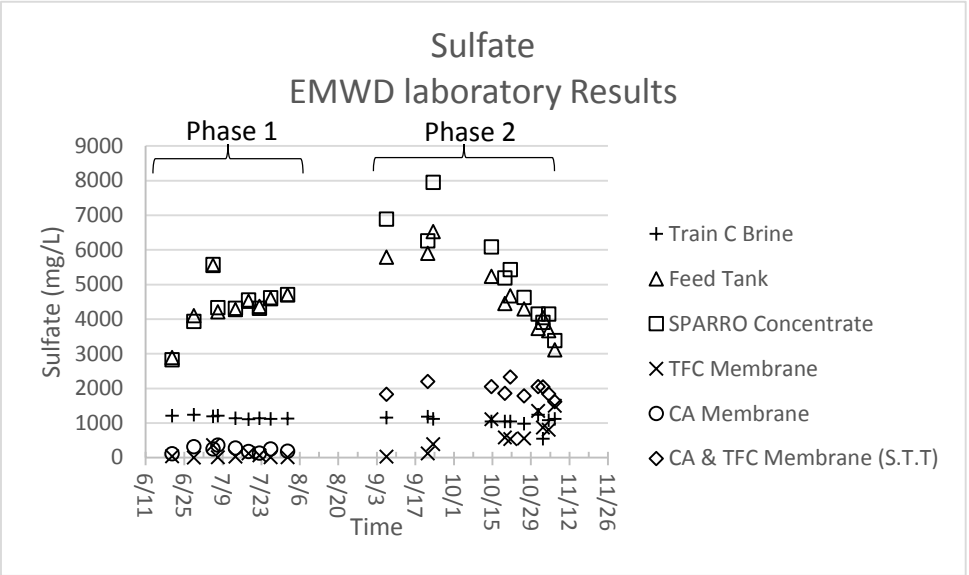
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
50
100
150
1020
1040
1060
1080
1100
1120
1140
Time
Beg. of Cond. 3 (TFC)
End of Cond 3 (TFC)
Beg. of Cond. 3 (CA)
End of Cond. 3 (CA)


Normalized Permeate Flow vs. Time
Phase I - 1.5 m/s
NPF (gpm)
0.0100
0.0080
0.0060
0.0040
0.0020
0.0000
0
20
40
60
80
100
120
140
160
180
200
Run Time (hrs.)
Cond. 3 (18 g/L & TFC Membrane)
Cond 2. (18 g/L& TFC Membrane)
Cond. 3 (18 g/L & CA Membrane)
Cond. 2 (1.8 g/L & CA Membrane)


Normalized Permeate Flow vs. Time
Phase I - 18 g/L
NPF (gpm)
0.0100
0.0080
0.0060
0.0040
0.0020
0.0000
0
20
40
60
80
100
120
140
160
180
200
Run Time (hrs.)
Cond. 3 (1.5m/s & TFC Membrane)
Cond. 4 (1m/s & TFC Membrane)
Cond 3. (1.5m/s & CA Membrane)
Cond. 4 (1 m/s & CA Membrane)


Conductivity vs. Time
EMWD Laboratory Results
Phase 1
Phase 2
Conductivity (µS/cm)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
6/11
6/25
7/9
7/23
8/6
8/20
9/3
9/17
10/1
10/15
10/29
11/12
11/26
Time
RO Brine
Feed Tank
SPARRO Concentrate
TFC Membrane
CA Membrane


Sodium
EMWD laboratory Results
Phase 1
Phase 2
Sodium (mg/L)
3500
3000
2500
2000
1500
1000
500
0
6/11
6/25
7/9
7/23
8/6
8/20
9/3
9/17
10/1
10/15
10/29
11/12
11/26
Time
Desalter RO Brine Feed
Feed Tank
SPARRO Concentrate
TFC Membrane
CA Membrane
CA & TFC membrane (S.T.T)


Sulfate
EMWD laboratory Results
Phase 1
Phase 2
Sulfate (mg/L)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
6/11
6/25
7/9
7/23
8/6
8/20
9/3
9/17
10/1
10/15
10/29
11/12
11/26
Time
Train C Brine
Feed Tank
SPARRO Concentrate
TFC Membrane
CA Membrane
CA & TFC Membrane (S.T.T)

Appendix E - OMYA – Gypsum Purity Analysis

RAM Laboratory
10521A Millington Court
Cincinnati, Ohio 45242
U.S.A.

Tel: +1-513-387-4429

www.omya-na.com

CUSTOMER SERVICE REPORT

COMPOSITIONAL ANALYSIS OF REMINERALIZATION WASTE
Project No.: 2016-00417
LIMS Project ID: 251746
Date: December 13, 2016
Customer: Carollo
Requested By: Lee Clap
Distribution: L. Clap, J. Strebel

Laura Perry
laura.perry@omya.com
Phone Direct: +1 513-387-4489

Objective

Determine gypsum and calcite content of waste material from remineralization.

Background Information

A slurry containing waste from Carollo's remineralization process was dried in an oven at 80°C before being prepared for analytical testing. The mineralogy and composition of the sample was documented using X-ray diffraction (XRD; Reitveld refinement), X-ray fluorescence (XRF), and thermogravimetric (TGA) analysis.

Gypsum content determined through XRD analysis was cross-checked with XRF data by calculating a theoretical weight percent of gypsum according to XRF results; these calculations are detailed in Appendix I for reference.

Summary of Results

XRD analysis determined that the remineralization waste material consists of ~ 93% gypsum, ~ 4% calcite, and ~ 2% dolomite (fig. 1). Phases of dehydrated gypsum (i.e. bassanite and anhydrite) made up < 1% of the bulk mineralogy. Calculations based on XRF data indicate that should theoretically contain approximately 93% gypsum, which is consistent with XRD analysis. TGA also supports the presence of gypsum as the primary phase in the material (fig. 2).

The material was experimentally determined to contain 5.13% of acid insoluble minerals. XRD analysis of the acid insoluble residue from this material (fig. 1) suggests that the gypsum converted to bassanite (and anhydrite, to a lesser degree). This was most likely a result of heating and/or solution reactions involved in the acid dissolution procedure and does not reflect the original composition of the remineralization waste material.

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Table 1. XRF results.

	weight %
LOI	24.68
CaO	32.75
MgO	0
Al_2O_3	0
Fe_2O_3	0.0044
SiO_2	0.091
K_2O	0.0024
SO_3	42.496
P_2O_5	0.0106
SrO	0.0716
MnO	0.0067
BaO	0.0035
Na_2O	0
TiO_2	0.025
Ca as $CaCO_3$	58.54

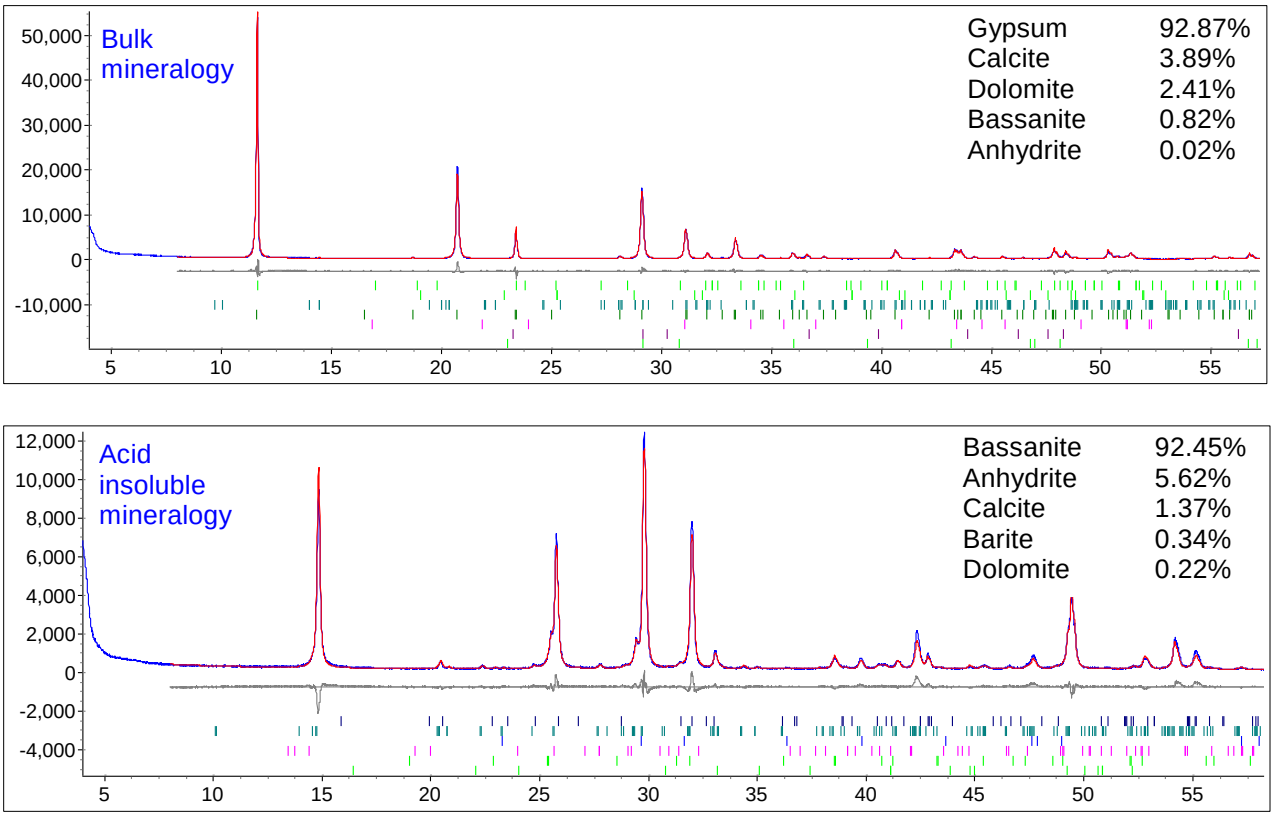

Figure 1. (Top) X-ray diffraction pattern analysis of bulk mineralogy. GOF = 2.44. (Bottom) X-ray diffraction pattern analysis of acid insoluble mineralogy. GOF = 2.11. Bassanite (also known as calcium sulfate hemihydrate) forms as gypsum dehydrates during heating and is typically considered to be metastable in natural environments.

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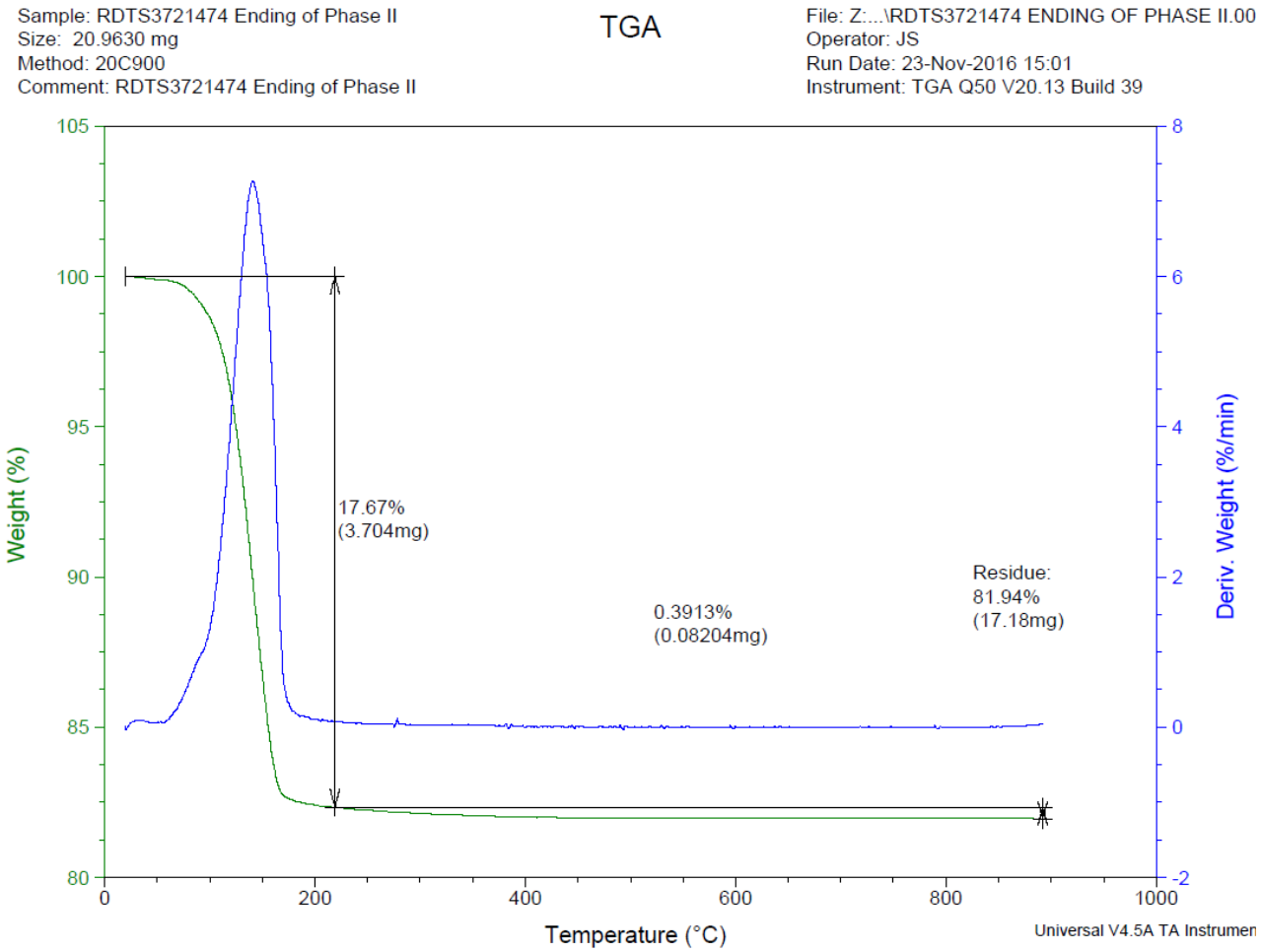

Figure 2. TGA curve shows an initial weight loss of 17.67% representing the dehydration of gypsum.

Appendix I

Gypsum ($CaSO_4 \cdot 2H_2O$) content is approximated using the sum of %Ca and $\%SO_4$ provided by XRF data. Note that these calculations assume that all calcium is present exclusively within gypsum and does not account for calcium carbonate, therefore gypsum content may be slightly overestimated.

Given %CaO and $\%SO_3$,

$$\%Ca = \frac{\text{molar mass of } Ca}{\text{molar mass of } CaO} \times \%CaO$$

$$= \frac{40.08 \frac{g}{mol} Ca}{56.08 \frac{g}{mol} CaO} \times 32.75\%\ CaO = 23.41\%\ Ca$$

$$\%SO_4 = \frac{\text{molar mass of } SO_4}{\text{molar mass of } SO_3} \times \%SO_3$$

$$= \frac{96.07 \frac{g}{mol} SO_4}{80.07 \frac{g}{mol} SO_3} \times 42.50\%\ SO_3 = 50.99\%\ SO_4$$

Then,

$$\%\ CaSO_4 = 23.41 + 50.99 = 74.39\%$$

Finally, this is normalized to account for H_2O in gypsum's chemical formula by dividing $\%CaSO_4$ by 0.80 (gypsum is approx. 80% $CaSO_4$, 20% H_2O by weight). Therefore the theoretical ***gypsum content is equal to 92.99% by weight*** according to XRF.

Reviewer: Jeff Strebel

Date: December 13, 2016

Project	251746
Sample Group	SG35577

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Appendix F - American Water Chemical – Membrane Autopsy on Pressure Vessel PV-1 TFC Membranes

Membrane Autopsy Report

Date:

02-06-2017

Tests Performed For:

Carollo Engineers Inc.

Manufacturer: PCI
Model: AFC80
Position: Top
AWC LSA#: 02-17001

Tests Performed By:

Joshua Utter
Vana Abbas

Table of Contents

Introduction 4
Membrane Information 4
Shipping and Handling Condition 5
Inspection of Membrane 6
  Fouled Membrane 6
  Virgin Membrane 7
Inspection of Permeate Side 8
  Fouled Membrane 8
  Virgin Membrane 8
Loss on Ignition Test with Foulant 9
    Results 9
Cell Test 11
    Results 11
Pressurized Dye Test 14
    Results 14
  Post Cleaning Membrane Coupons 15
  Virgin Membrane 16
Chemical Solubility Testing of Foulant 17
    Results 17
  Foulant 18
  LOI Residue 19
Humic and Fulvic Acids Testing 20
    Results 20
Electron Microscopy and X-Ray Spectroscopy Analysis 21
Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) with Superimposed Elemental Imaging (SEI™) 21
    Results 21
  Membrane Surface Analysis 47
    Virgin Membrane 47

Fouled Membrane (after attempted cleaning with pH restrictions) 49
FTIR analysis 54
Results: Dehydrated Foulant 55
Results: LOI residue 56
BART Test 57
Results 57
Optical Microscopy 60
Live Wet Mounts 60
Results 60
Results and Discussion 62
Release of Liability 64

Introduction

This report describes the membrane autopsy procedures performed for **Carollo Engineers Inc.** The observed findings are presented herein.

Membrane Information

Element Position	Manufacturer	Model Number	Serial Number
Top First in Series	**PCI**	**AFC80**	**N/A**

Table 1: Membrane Information.

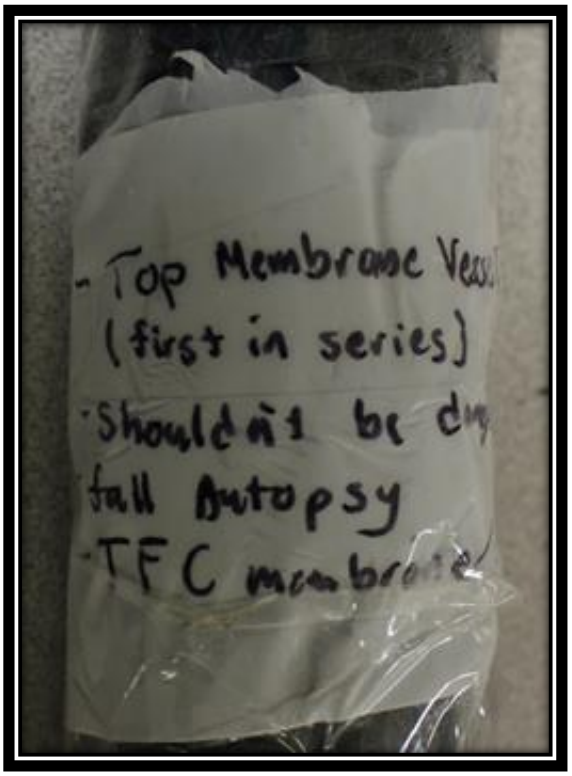


Figure 1: Membrane Information.

Shipping and Handling Condition

The membrane tubes arrived at AWC's facility packaged in a cylindrical container. Upon the removal of the membrane tubes from the container, they were placed inside a black plastic bag and sealed.

Figure 2: The membrane tubes arrived in a sealed cylindrical container.

Figure 3: The membrane tubes were placed inside a black plastic bag and sealed.

Inspection of Membrane

Brown foulant was found on the feed side of the fouled membrane. Sporadic brown spots were found on the feed side of the fouled membrane and the virgin membrane.

Fouled Membrane

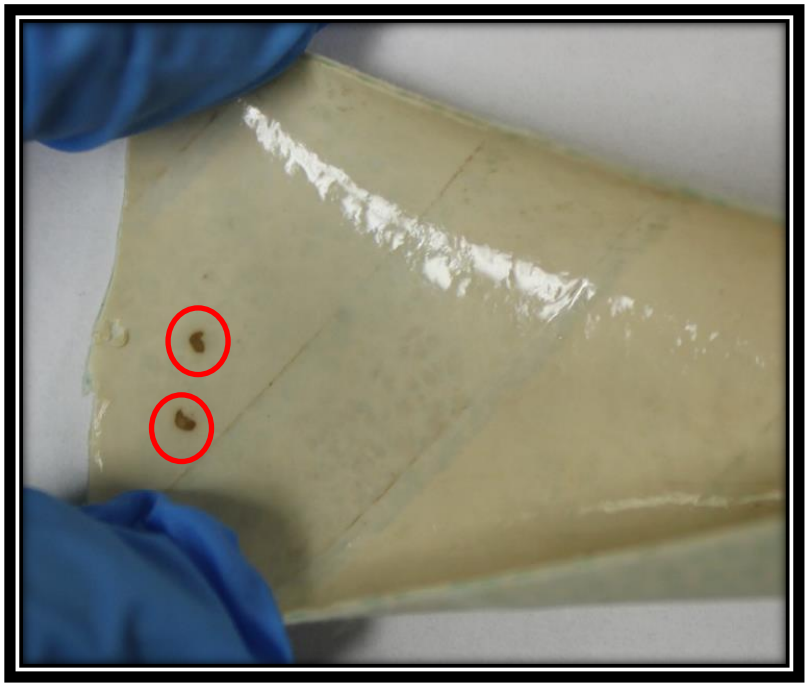


Figure 4: Brown foulant was found on the feed side of the membrane tubes. Sporadic brown spots were also found on the membrane.

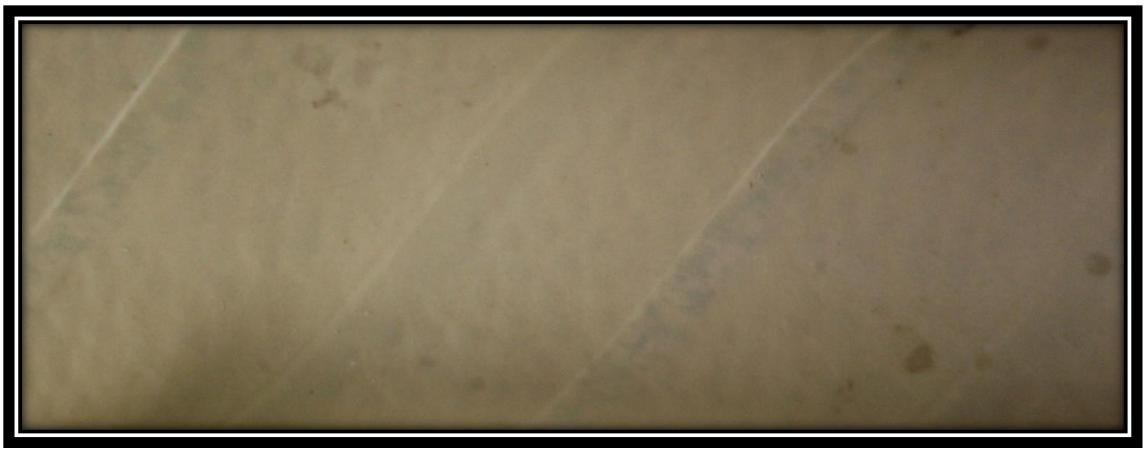


Figure 5: Brown foulant found on the feed side of the membrane.

Virgin Membrane

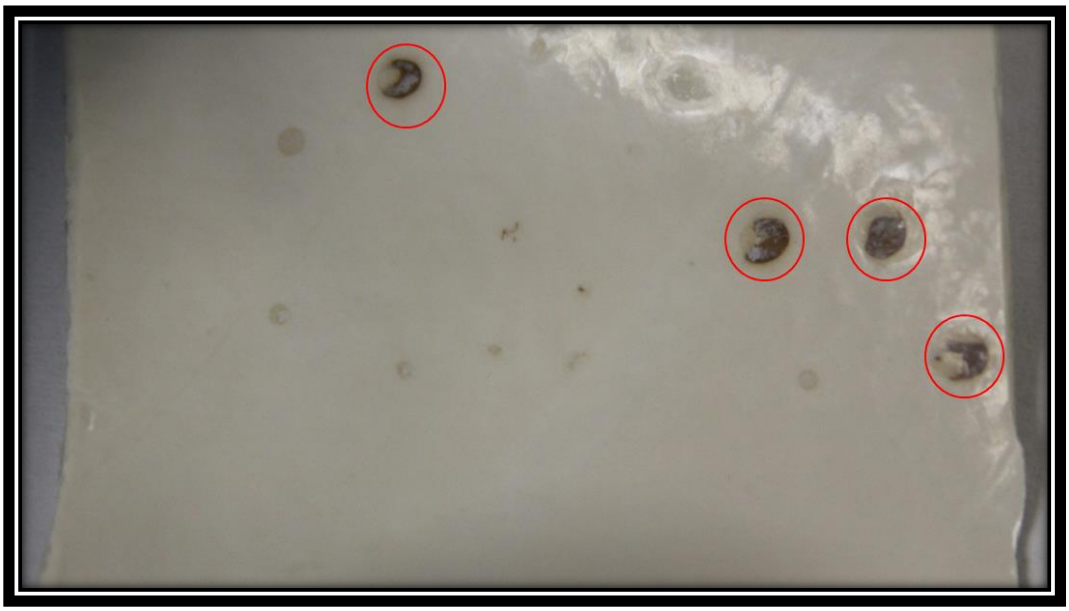


Figure 6: Sporadic brown spots found on the virgin membrane.

Inspection of Permeate Side

Inspection of the permeate side of the fouled membrane identified brown, green and yellow bands at the seams of the fouled membrane. These yellow bands were not found on the seams of the virgin membrane.

Fouled Membrane

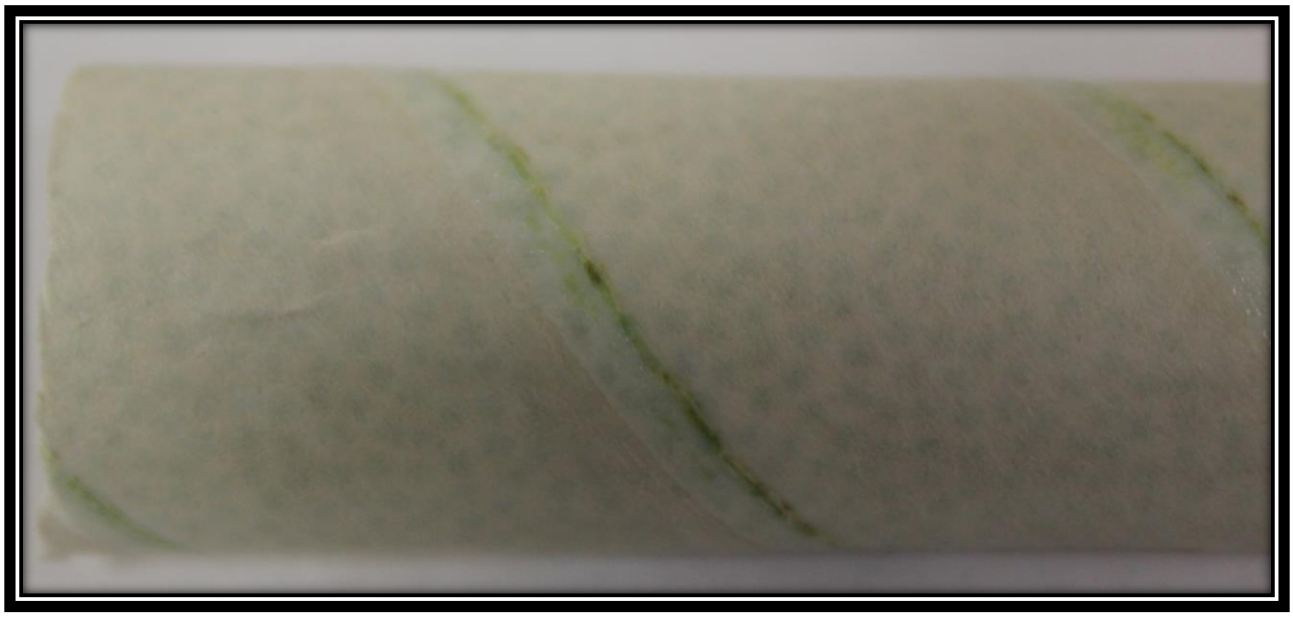


Figure 7: Brown, green and yellow deposits along the seams of the wrapped membrane.

Virgin Membrane

Figure 8: Permeate side of the virgin membrane.

Loss on Ignition Test with Foulant

A Loss on Ignition (LOI) test is performed to determine the organic/inorganic content of the foulant. The collected foulant samples are first heated at 105 °C overnight to remove moisture and volatile compounds. The dehydrated samples are then fired at 450 °C for 8 hours to combust any organic materials. The percentages of moisture, organics and inorganics are then calculated based on the loss of mass.

Results

The foulant consisted of ~27.1% organic matter and ~72.9% inorganic matter.

	Foulant from membrane	**Calculated Without Moisture**
Moisture and Volatiles	99.93%	--
Organic Content	0.02%	27.06%
Inorganic Content	0.05%	72.94%

Table 2: LOI results for foulant from the membrane surface.

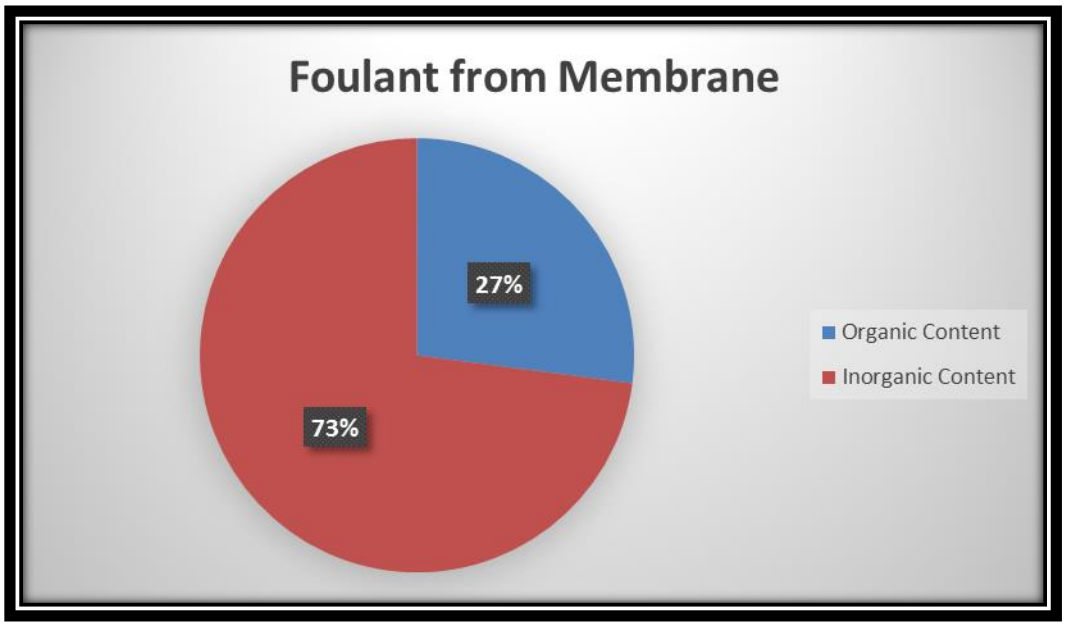


Figure 9: LOI results chart from table 2.

Figure 10: LOI residue.

Cell Test

Cell testing is performed in order to determine the performance of the membrane. Samples of the membrane are collected from the element and soaked in deionized water for 24 hours to help remove fouling. They are then tested using the performance test conditions set by the manufacturer. Salt rejection and flux measurements are compared with the manufacturer's specifications and the initial full element performance tests. Cell tests were performed before and after cleaning.

Test Conditions:

Feed Pressure	**580 PSI**
Feed Concentration	**5000 ppm, NaCl**
Concentrate Flow	**0.8 GPM**
Feed Temperature	**25ºC**

Results

The tubular membranes were cut lengthwise and spread open for testing in a flat-sheet cell test unit. Due to the possibility of mechanical damage caused by the flattening of the membrane, a virgin membrane was mounted using the same method and used as a reference.

Initial cell testing results found the salt rejection to be ~14.4% lower than the virgin membrane and the flux to be ~2.1% higher.

AWC C-239 was selected for cleaning because of sulfate scaling identified by SEM/EDS analysis. However, the optimal performance of this product occurs at pH 12 – 13, whereas the membrane could not tolerate pH>10.5.

After high pH cleaning with AWC C-239 for 6 hours, the membrane salt rejection decreased by ~16.4% and the flux increased by ~43.4% when compared with the initial cell test results.

Low pH cleaning with AWC C-234 for 2 hours increased the membrane salt rejection by ~5.7% and the flux decreased by ~13.7%.

After cleaning, the membrane salt rejection decreased by ~11.6% when compared to the initial cell test results and the flux increased by ~23.8%.

Overall, the membrane after cleaning had a salt rejection that was 24.3% lower than the virgin membrane and a flux that was ~26.4% higher.

	Manufacturer's Specifications at 15ºC	Virgin Membrane (tested on-site) normalized to 15ºC
% Salt Rejection	85% (max)	90.28%
Flux, gfd	20.58 (min)	24.99

Cell Test Results: Virgin Membrane normalized to 15ºC					
	Cell 1	Cell 2	Cell 3	Cell 4	Average
% Salt Rejection	92.04%	91.48%	89.43%	89.93%	90.28%
Flux, gfd	30.52	26.29	25.06	23.62	24.99

Table 3: Flux (GFD) and salt rejection (%) results of individual areas of the virgin membrane.

Cell Test Results: Initial Test- Post Soak in DI Water for 24 hours normalized to 15ºC					
	Cell 1	Cell 2	Cell 3	Cell 4	Average
% Salt Rejection	77.82%	75.24%	80.50%	75.67%	77.31%
Flux, gfd	27.67	25.52	22.00	26.87	25.51

Table 4: Flux (GFD) and salt rejection (%) results of individual areas of the membrane- Post Soak in DI Water for 24 hours.

Cell Test Results: Post high pH cleaning- 2% C-239 at pH 10.2 for 6 hours at 24°C normalized to 15ºC					
	Cell 1	Cell 2	Cell 3	Cell 4	Average
% Salt Rejection	64.66%	60.35%	71.57%	62.05%	64.66%
Flux, gfd	39.74	38.05	29.18	39.41	36.59

Table 5: Flux (GFD) and salt rejection (%) results of individual areas of the membrane- post high pH cleaning with 2% C-239 at pH 10.2 for 6 hours at 24°C.

Cell Test Results: Post low pH cleaning- 2% C-234 at pH 1.8 for 2 hours at 23°C normalized to 15ºC					
	Cell 1	Cell 2	Cell 3	Cell 4	Average
% Salt Rejection	68.79%	65.19%	73.69%	65.75%	68.36%
Flux, gfd	34.55	35.92	25.77	30.11	31.59

Table 6: Flux (GFD) and salt rejection (%) results of individual areas of the membrane- Post low pH cleaning with 2% C-234 at pH 1.8 for 2 hours at 23°C.

Pressurized Dye Test

In this test, a dye solution is applied under pressure to the feed side of the membrane sheet, after cell testing and cleaning of the membrane coupons. This allows for exposure of any damage beneath the foulant, and can be correlated to the cell test salt rejection and flux results. The membrane coupons are tested in the same cells in which cleaning had been performed, eliminating the risk of surface damage due to mishandling. If the membrane is damaged mechanically or chemically, the dye color will penetrate to the permeate side of the membrane.

Results

Dye penetration was observed on the permeate side of the cleaned membrane coupons. The pattern suggested surface abrasion. Heavy dye penetration was observed at locations that corresponded to brown spots on the feed side of the membrane.

No significant dye penetration was observed on the virgin membrane.

Post Cleaning Membrane Coupons

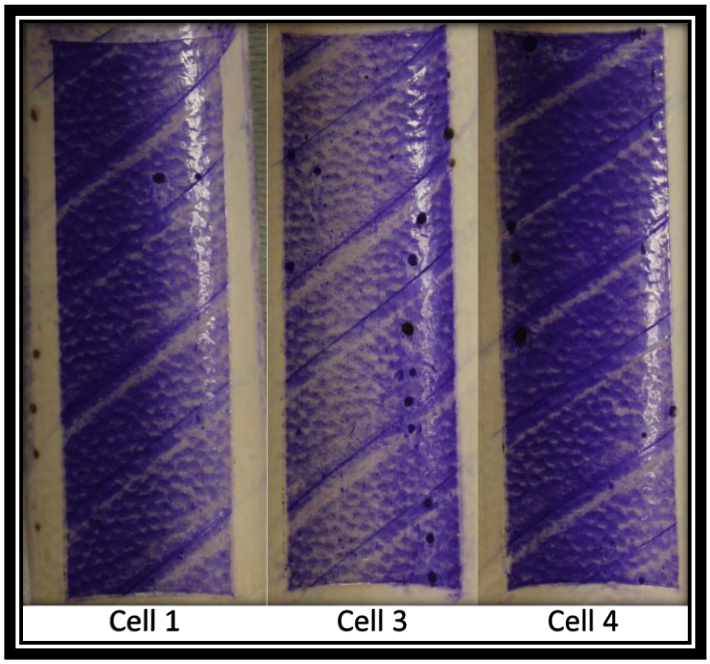


Figure 11: Pressurized Dye Test- Feed Side of the fouled membrane.

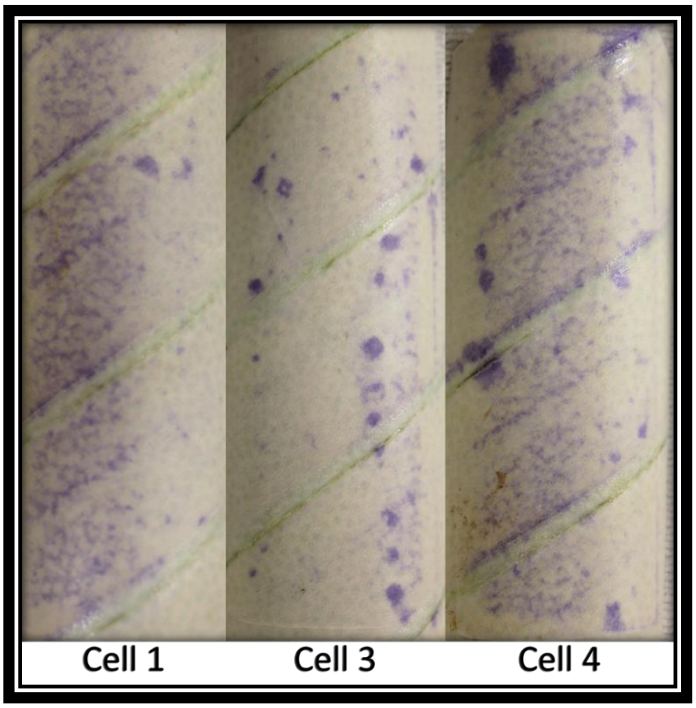


Figure 12: Dye penetration was observed on the permeate side of all the coupons tested. Heavier dye penetration was observed on the brown spots found on the feed side of the membrane.

Virgin Membrane

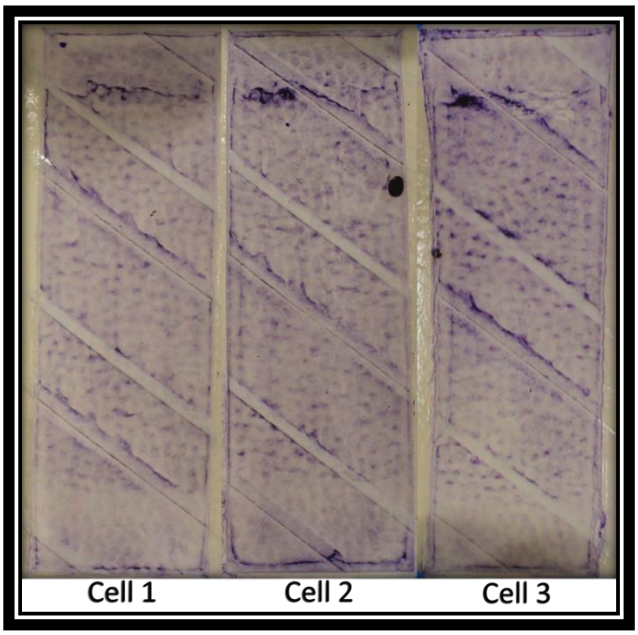


Figure 13: Pressurized Dye Test- Feed Side of the virgin membrane.

Figure 14: Permeate side of the virgin membrane.

Chemical Solubility Testing of Foulant

Samples collected from the membrane surface are tested for solubility in concentrated acid and caustic solutions. The LOI residue, which is the inorganic portion of the foulant once the organics had been volatilized, is also tested for solubility in 37% hydrochloric acid and 50% sodium hydroxide solutions.

Effervescence in the presence of acid usually indicates the presence of carbonate salts such as calcium carbonate. The solubility of the foulant in 50% NaOH will be indicated by the disintegration of the foulant and/or a change in the color of the solution. Foulants soluble in caustic solutions are typically of an organic nature; however, sulfate scales are also soluble in concentrated NaOH.

Results

The foulant and the LOI residue were both insoluble in the 50% NaOH and the 37% HCl solution.

No effervescence was observed upon the addition of acid to both the foulant and the LOI residue.

Foulant

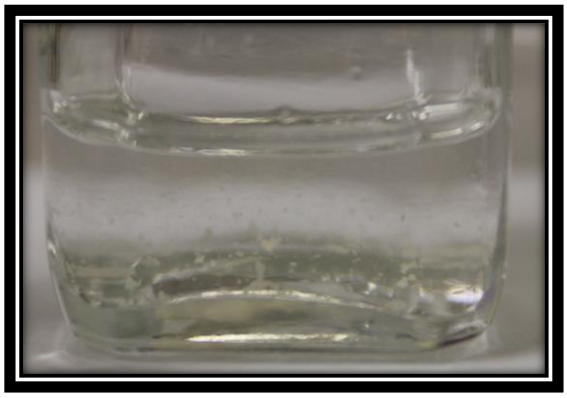


Figure 15: The foulant was insoluble in the 50% NaOH solution.

Figure 16: The foulant was insoluble in the 37% HCl solution.

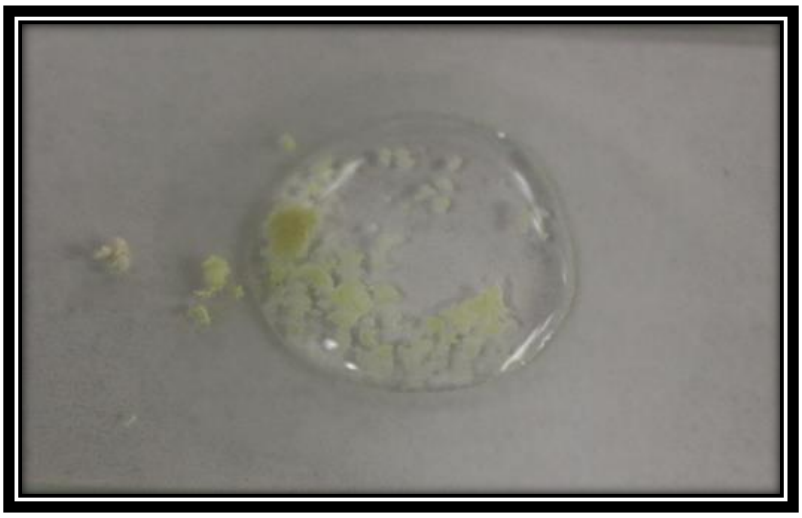


Figure 17: No effervescence was observed upon the addition of acid to the foulant.

LOI Residue

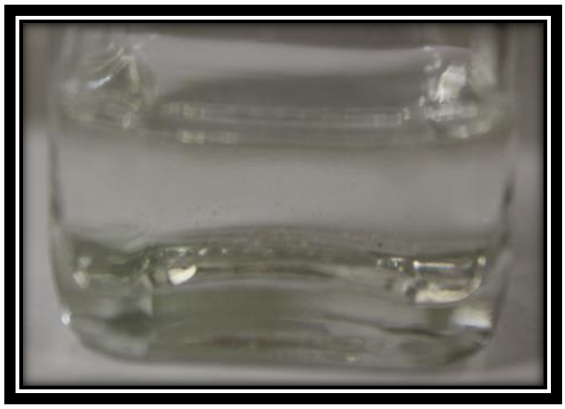


Figure 18: The LOI residue was insoluble in the 50% NaOH solution.

Figure 19: The LOI residue was insoluble in the 37% HCl solution.

Figure 20: No effervescence was observed upon the addition of acid to the LOI residue.

Humic and Fulvic Acids Testing

This test is performed to determine the presence of humic and fulvic acids in the membrane foulant. Humic and fulvic acids are produced from the biodegradation of plant matter and, when present in the water, can foul the membrane.

The membrane foulant is added to a high pH solution in order dissolve any organic material present. The solution is then filtered to remove any insoluble matter. The pH of the filtrate is then lowered to precipitate dissolved humic acids. The acidified solution is filtered and the color of the filtrate will qualitatively determine the presence of fulvic acids.

Results

The membrane foulant tested positive for humic acids and negative for fulvic acids using this qualitative method.

Figure 21: The foulant was positive for humic acids.

Figure 22 Figure 23: Negative for fulvic acids.

Electron Microscopy and X-Ray Spectroscopy Analysis

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) with Superimposed Elemental Imaging (SEI™)

Scanning Electron Microscopy (SEM) analysis is used to determine the topography and morphology of a sample. The SEM shows very detailed 3-dimensional images at much higher magnification than an optical microscope.

Energy Dispersive X-ray Spectroscopy (EDS) analysis is generally performed together with electron microscopy to identify and quantify the elemental composition of a sample surface. The sample material is bombarded with electrons from an SEM which produce X-rays. The produced X-rays are then measured by an X-ray dispersive spectrometer. Every chemical element has its own characteristic wavelength by which it can be identified. EDS spectra, together with composition (Weight percent and Atomic percent) are attached in the section.

Results

The foulant on the membrane surface consisted mainly of barium sulfate.

Sporadic deposits of calcium sulfate, amorphous silica, limestone, dolomite, silts and clays were also identified.

Sodium sulfate was found throughout, however, this is a highly soluble salt; it most likely formed upon dehydration caused by placing the sample in high vacuum for SEM analysis.

Surface damage was observed on all the fouled membrane samples tested, and the extent of damage was gauged based on a comparison to a virgin membrane sample.

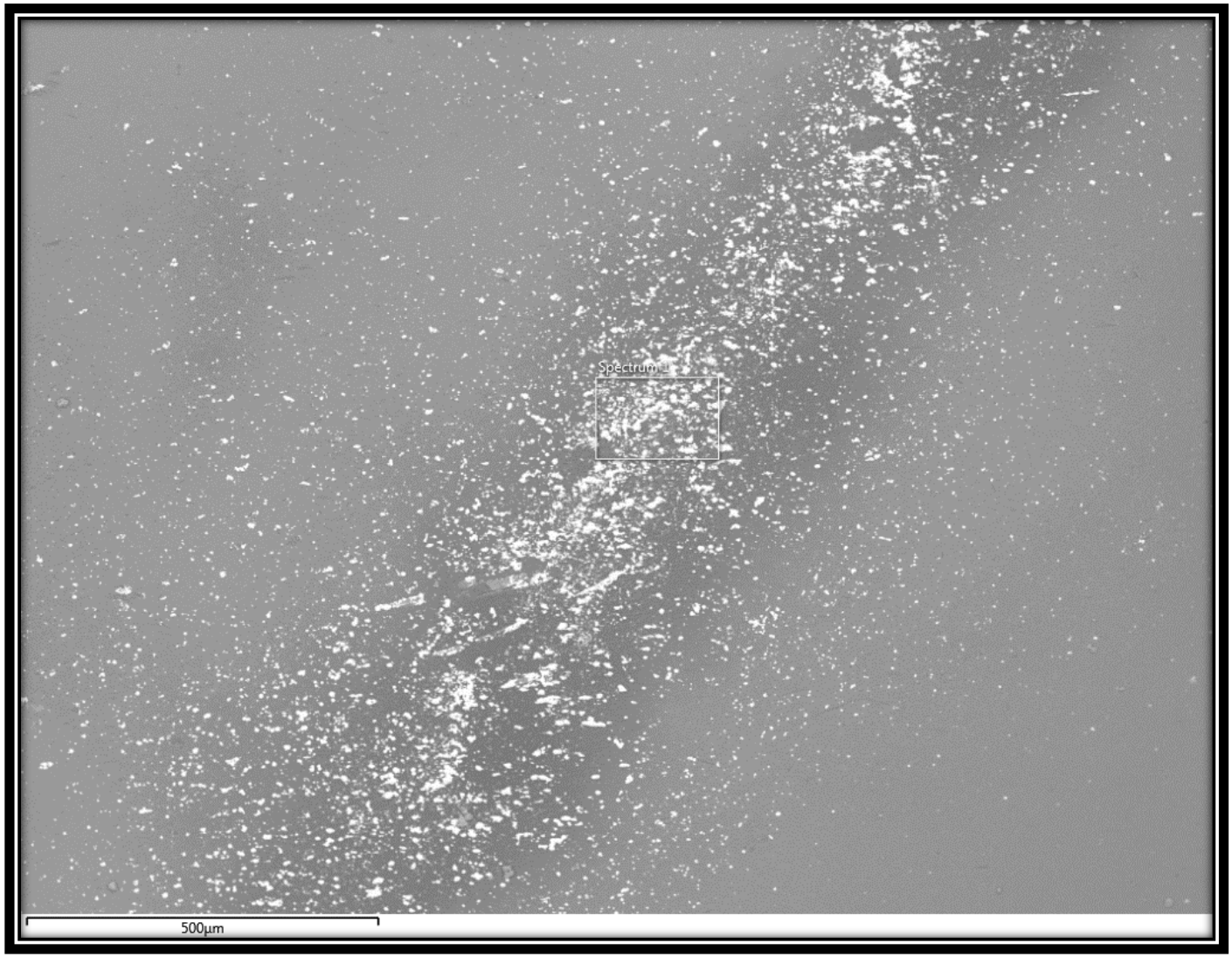


Figure 24: Electron micrograph of the membrane surface at 75X magnification (Spectrum 1).

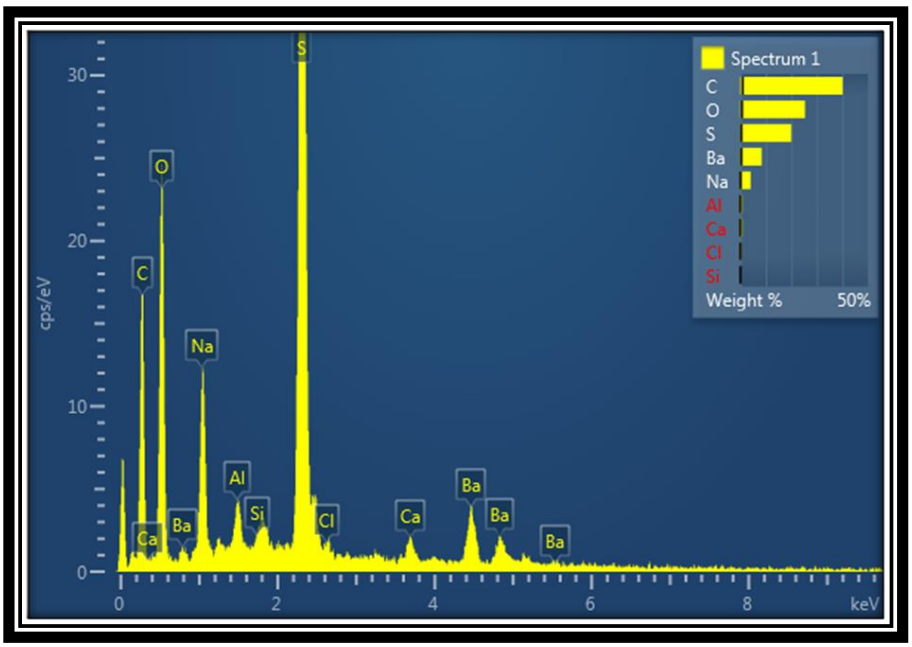


Figure 25: EDS and composition bar graph analysis of the membrane deposit from Spectrum 1.

Spectrum 1	Atomic %
C	57.14
O	27.05
Na	3.04
Al	0.52
Si	0.02
S	10.65
Cl	0.20
Ca	0.35
Ba	1.04
Total	100.00

Spectrum 1	Atomic %
Carbon and Oxygen Ignored	
Na	18.51
Al	3.58
Si	0.13
S	67.56
Cl	1.48
Ca	2.26
Ba	6.47
Total	100.00

Table 7: Composition table from the EDS spectrum of localized deposit from Spectrum 1.

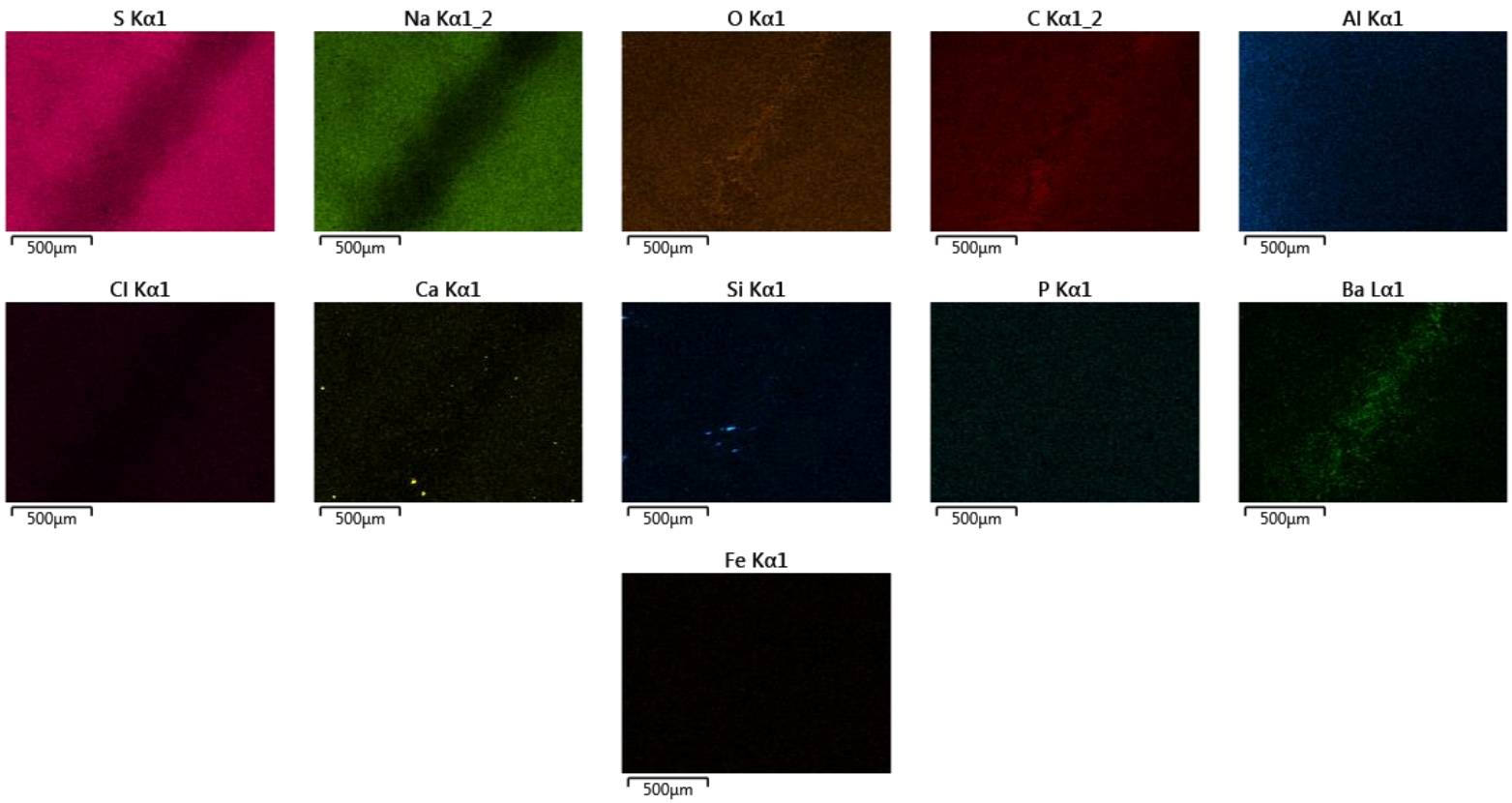


Figure 26: Prismatic Elemental Delineation (PED®) of membrane surface at 75X magnification. Deposits found: Barium sulfate, calcium sulfate, silts and/or clays.

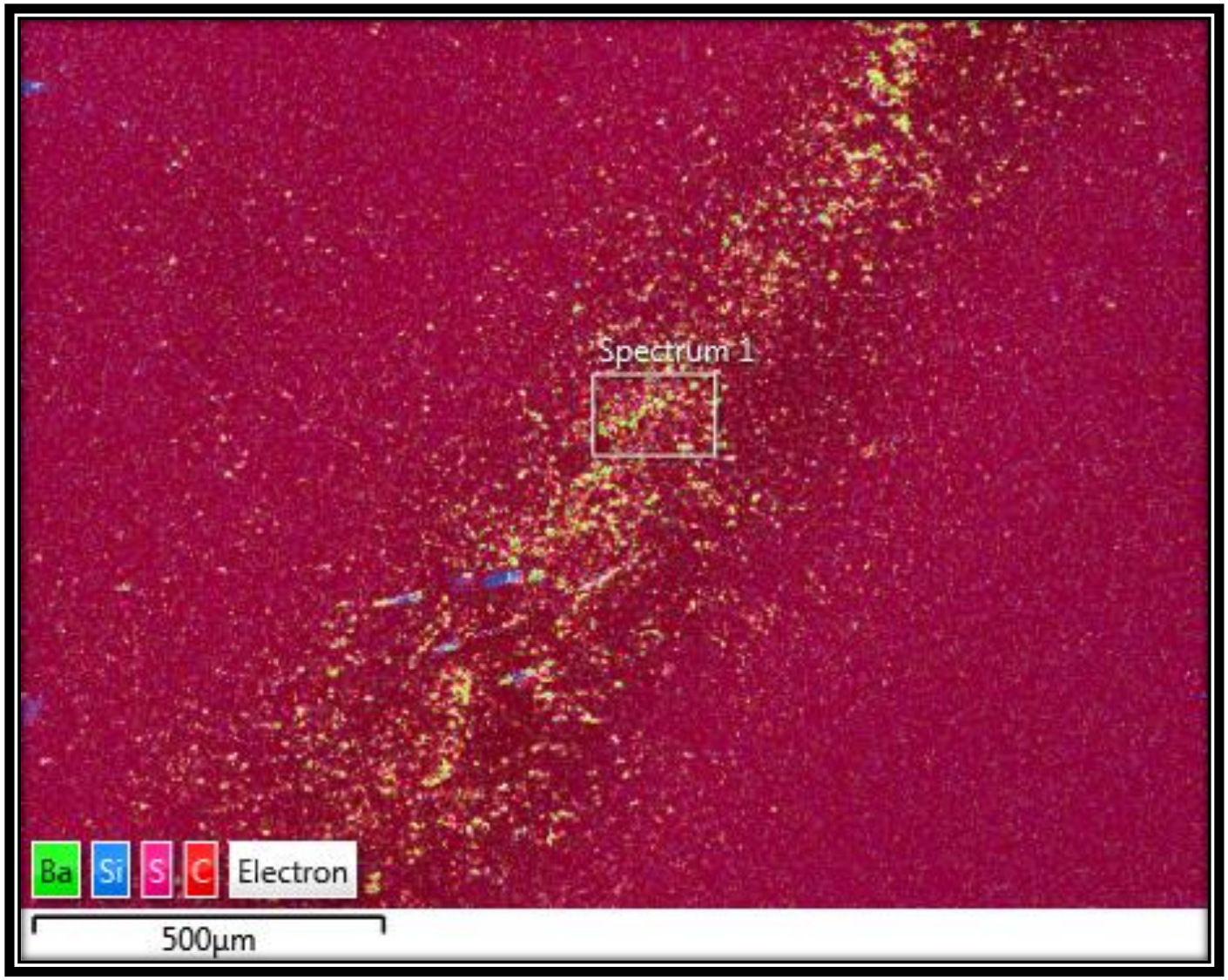
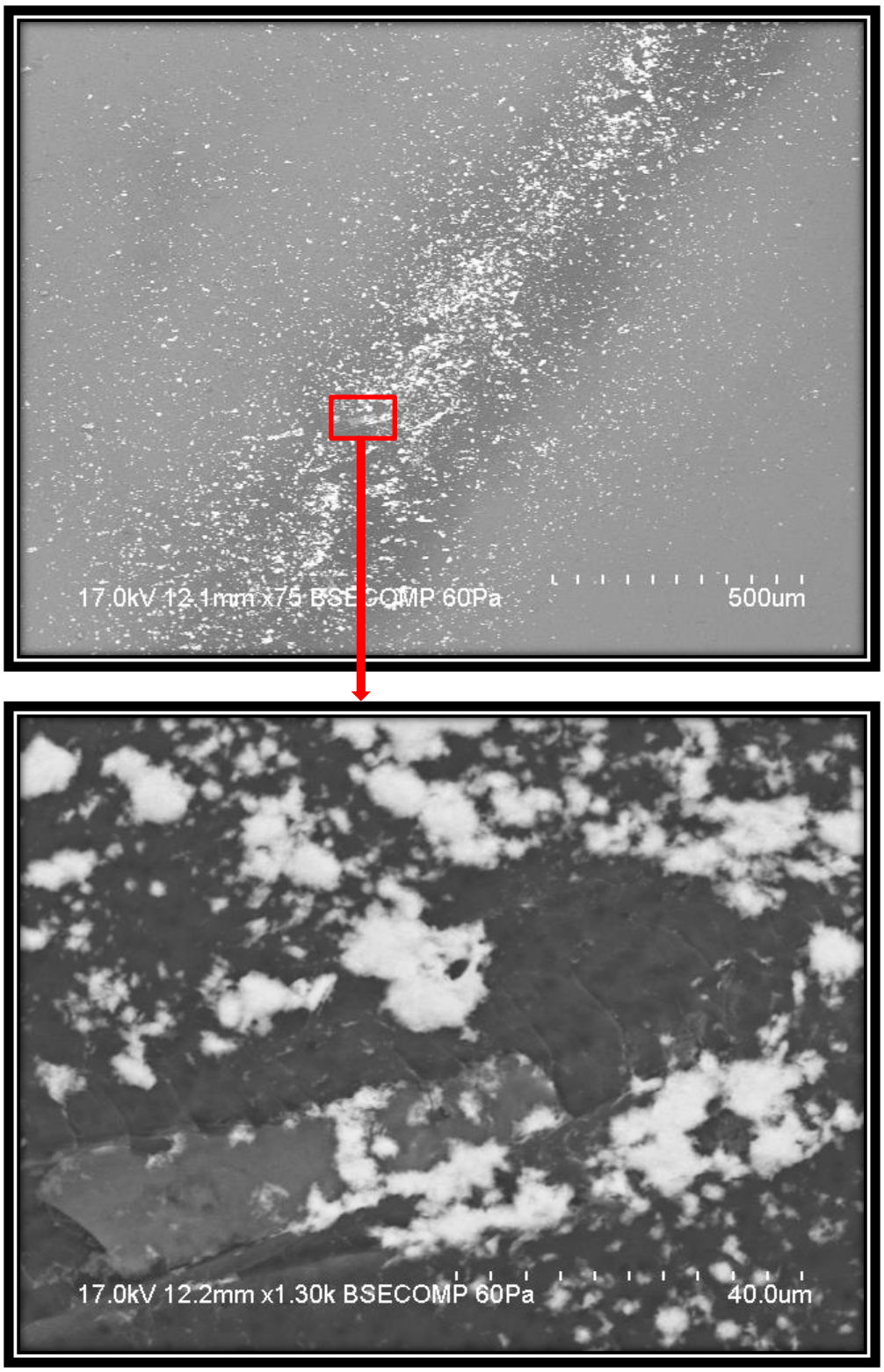


Figure 27: Superimposed Elemental Imaging (SEI®) of barium sulfate, silts and/or clays.


17.0kV 12.1mm x75 BSECOMP 60Pa
500um
17.0kV 12.2mm x1.30k BSECOMP 60Pa
40.0um

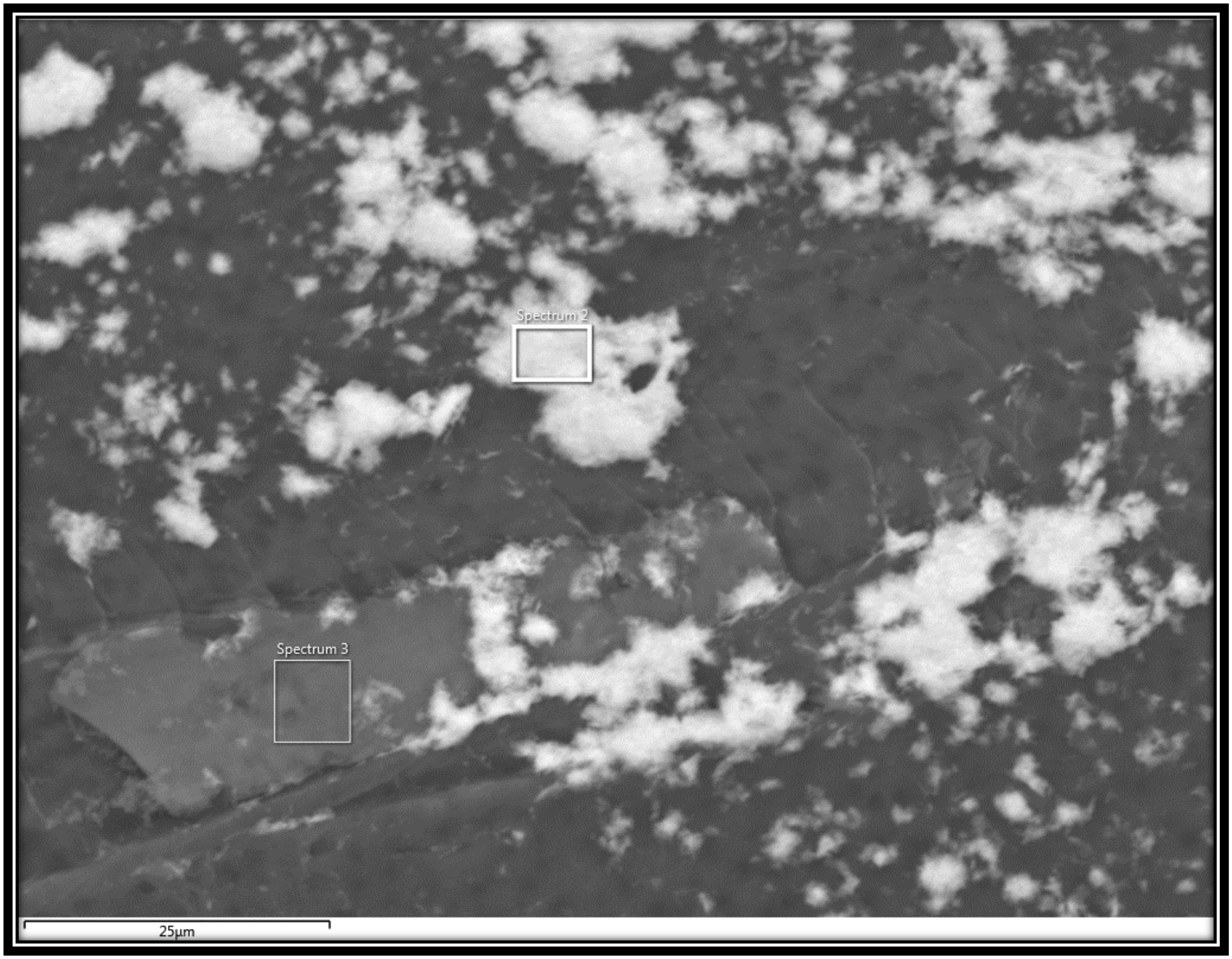


Figure 28: Electron micrograph of the membrane surface at 1300X magnification (Spectrum 2 & Spectrum 3).

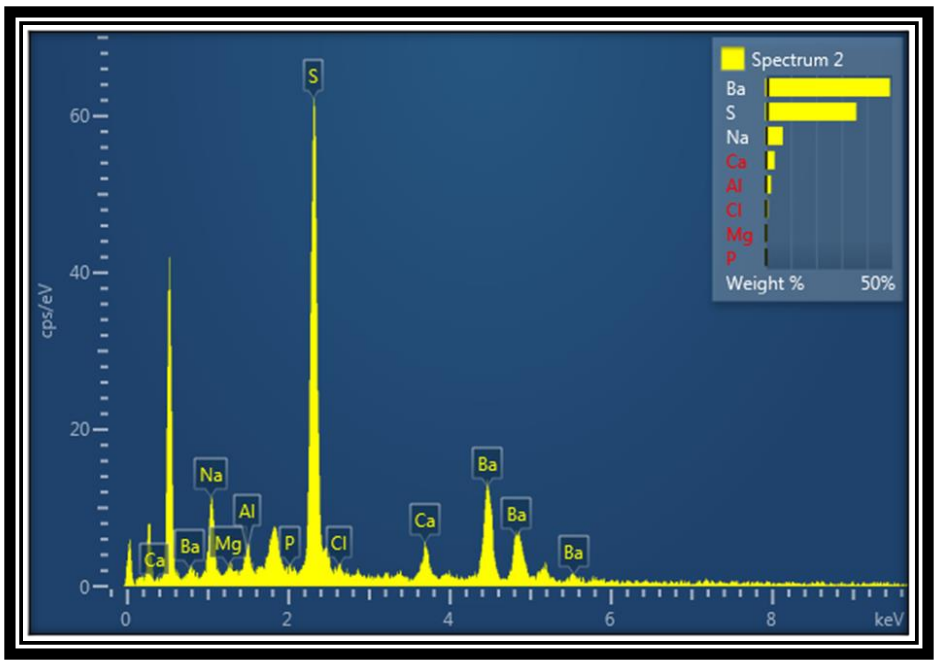


Figure 29: EDS and composition bar graph analysis of the membrane deposit from Spectrum 2.

Spectrum 2	Atomic %
C	32.44
O	40.65
Na	3.93
Mg	0.38
Al	1.03
P	0.22
S	14.74
Cl	0.36
Ca	1.23
Ba	5.01
Total	100.00

Spectrum 2	Atomic %
Carbon and Oxygen Ignored	
Na	14.81
Mg	1.57
Al	4.16
P	0.85
S	55.09
Cl	1.44
Ca	4.47
Ba	17.62
Total	100.00

Table 8: Composition table from the EDS spectrum of localized deposit from Spectrum 2.

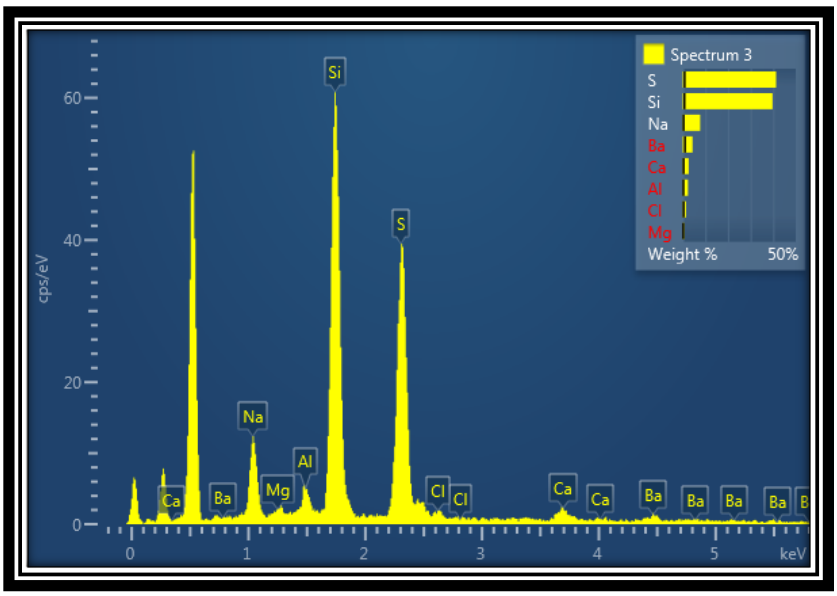


Figure 30: EDS and composition bar graph analysis of the membrane deposit from Spectrum 3.

Spectrum 3	Atomic %
C	31.26
O	45.98
Na	3.00
Mg	0.21
Al	0.64
Si	10.21
S	7.86
Cl	0.21
Ca	0.40
Ba	0.21
Total	100.00

Spectrum 3	Atomic %
Carbon and Oxygen Ignored	
Na	10.17
Mg	0.82
Al	2.61
Si	43.05
S	39.23
Cl	1.20
Ca	1.96
Ba	0.97
Total	100.00

Table 9: Composition table from the EDS spectrum of localized deposit from Spectrum 3.

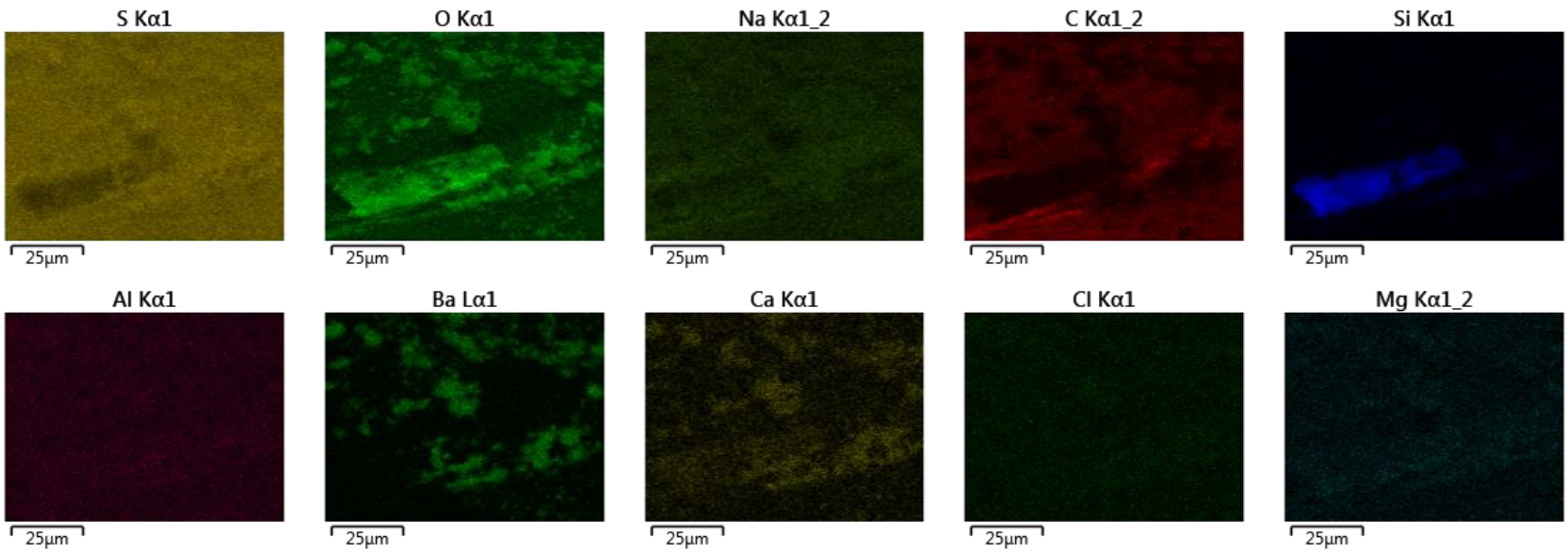


Figure 31: Prismatic Elemental Delineation (PED®) of membrane surface at 1300X magnification. Deposits found: Barium sulfate, calcium sulfate, amorphous silica.

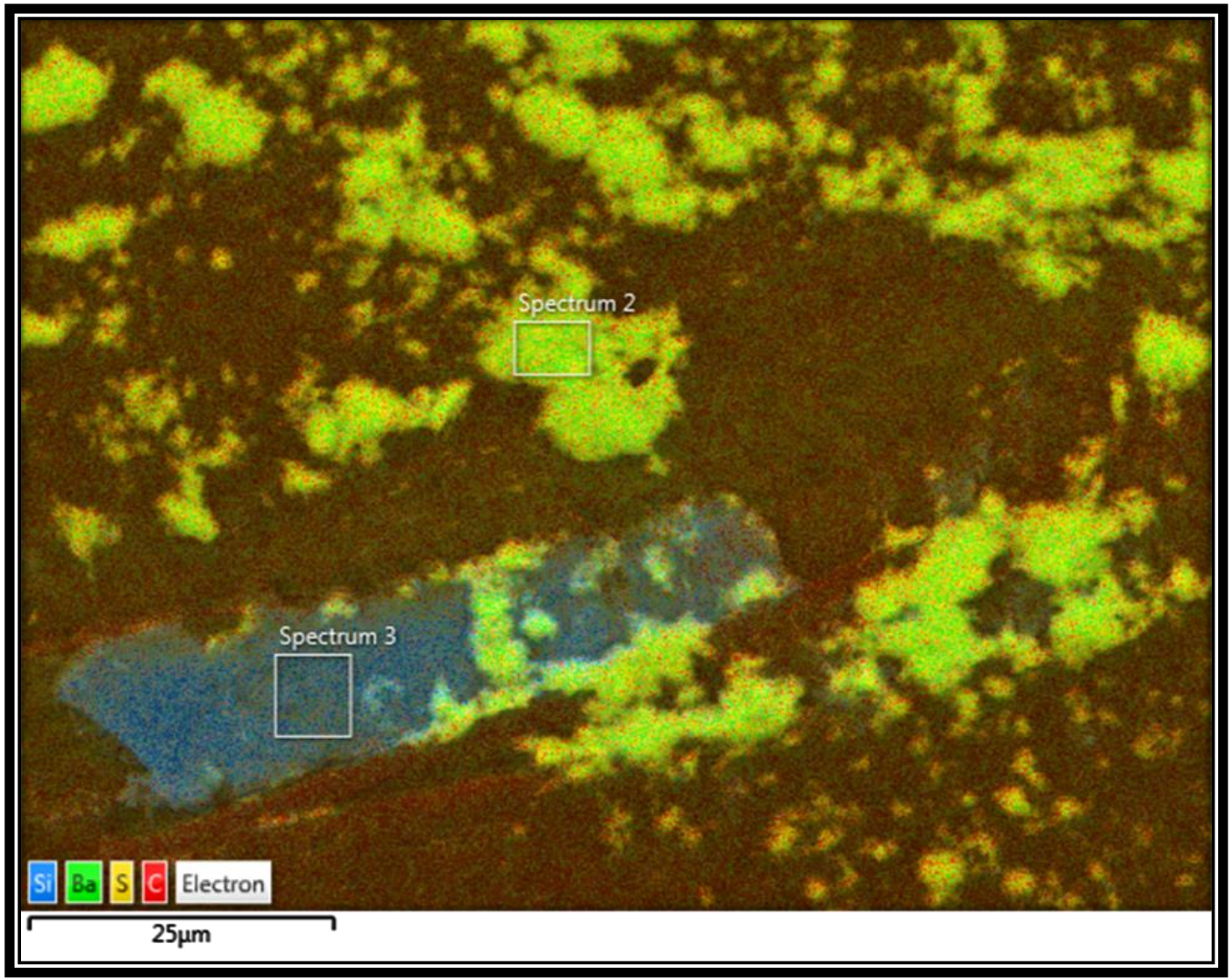


Figure 32: Superimposed Elemental Imaging (SEI®) of barium sulfate, calcium sulfate, amorphous silica.

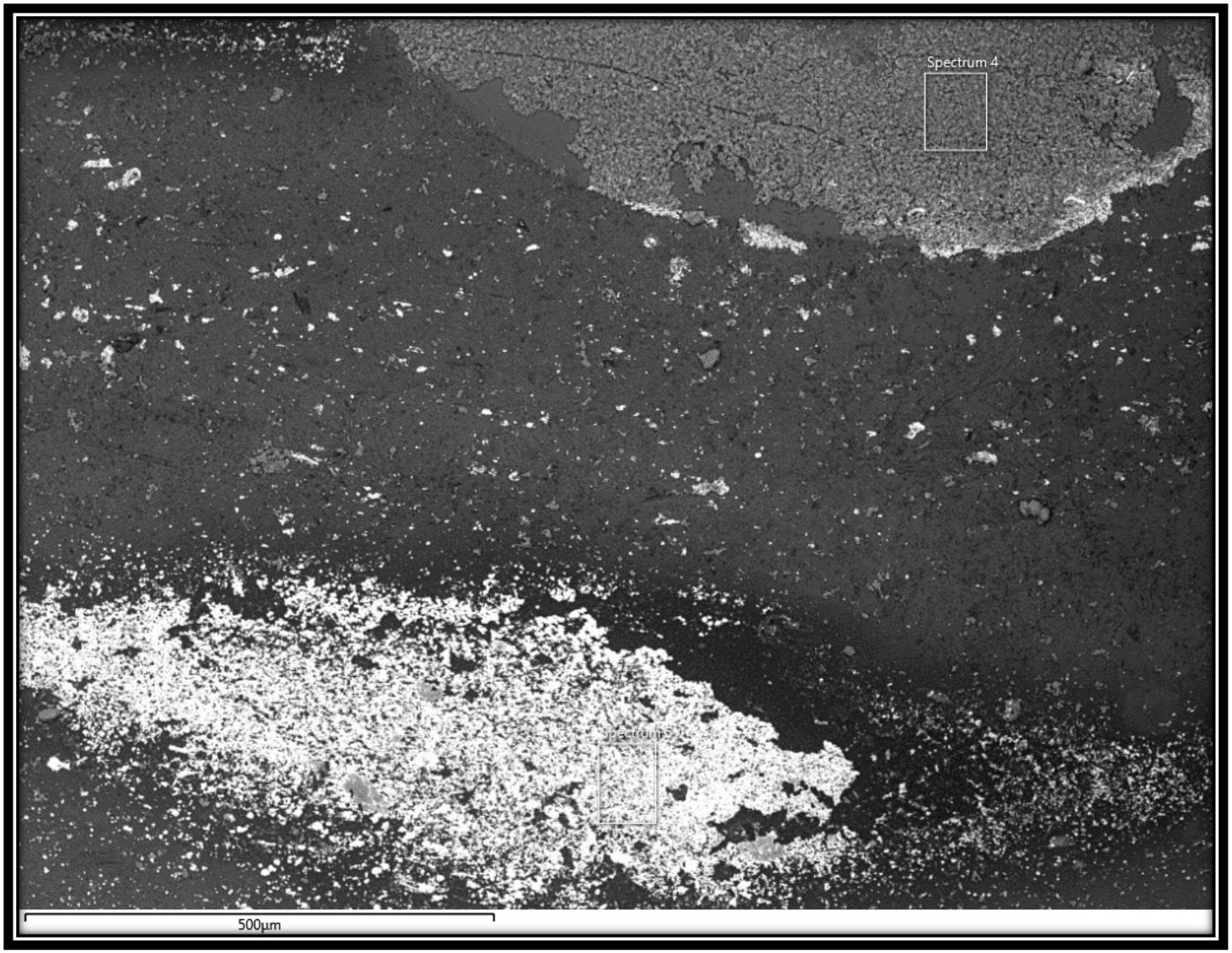


Figure 33: Electron micrograph of the membrane surface at 100X magnification (Spectrum 4 & Spectrum 5).

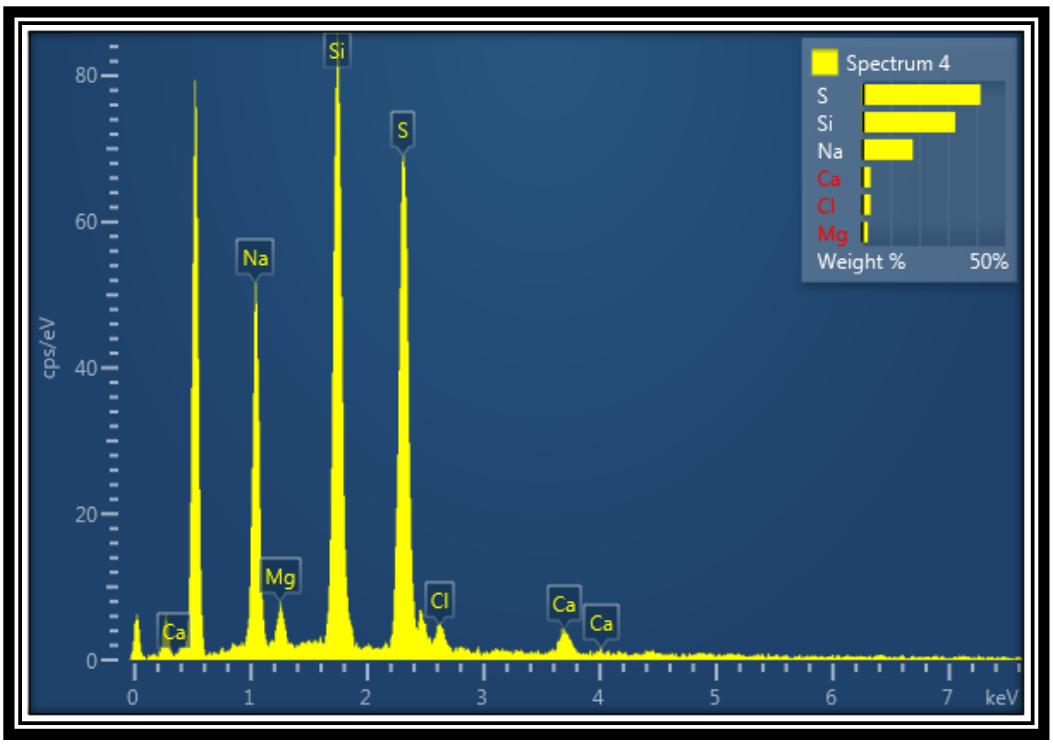


Figure 34: EDS and composition bar graph analysis of the membrane deposit from Spectrum 4.

Spectrum 4	Atomic %
C	20.46
O	47.25
Na	9.18
Mg	0.85
Si	10.64
S	10.39
Cl	0.62
Ca	0.61
Total	100.00

Spectrum 4	Atomic %
Carbon and Oxygen Ignored	
Na	22.28
Mg	2.53
Si	33.39
S	37.14
Cl	2.46
Ca	2.20
Total	100.00

Table 10: Composition table from the EDS spectrum of localized deposit from Spectrum 4.

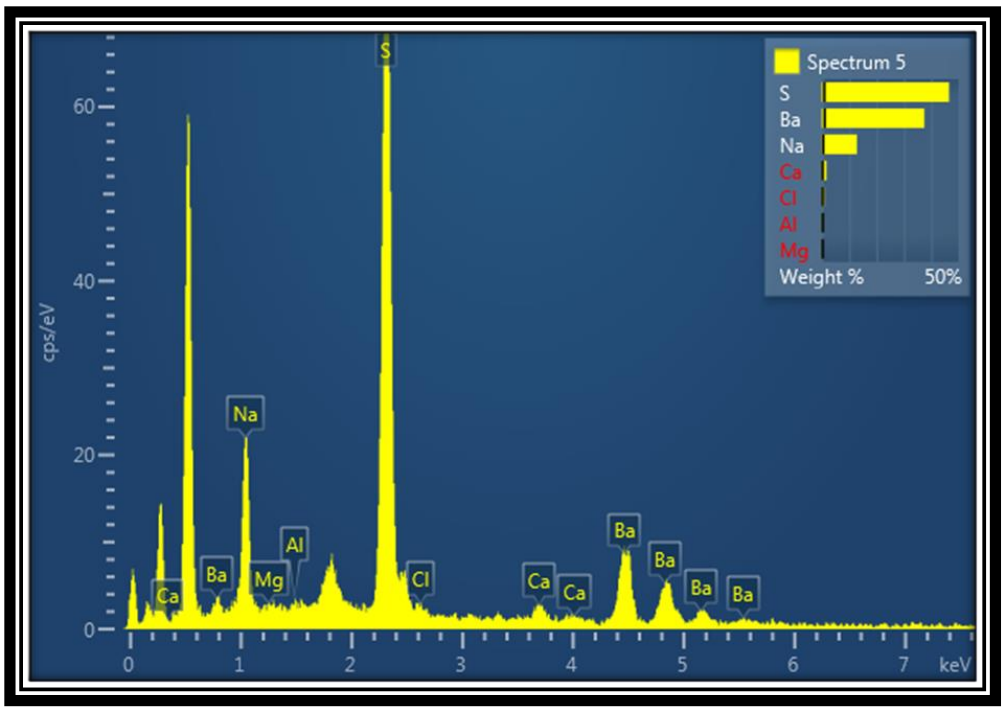


Figure 35: EDS and composition bar graph analysis of the membrane deposit from Spectrum 5.

Spectrum 5	Atomic %
C	39.73
O	40.05
Na	4.84
Mg	0.05
Al	0.09
S	12.26
Cl	0.21
Ca	0.35
Ba	2.42
Total	100.00

Spectrum 5	Atomic %
Carbon and Oxygen Ignored	
Na	23.52
Mg	0.32
Al	0.51
S	61.25
Cl	1.16
Ca	1.73
Ba	11.50
Total	100.00

Table 11: Composition table from the EDS spectrum of localized deposit from Spectrum 5.

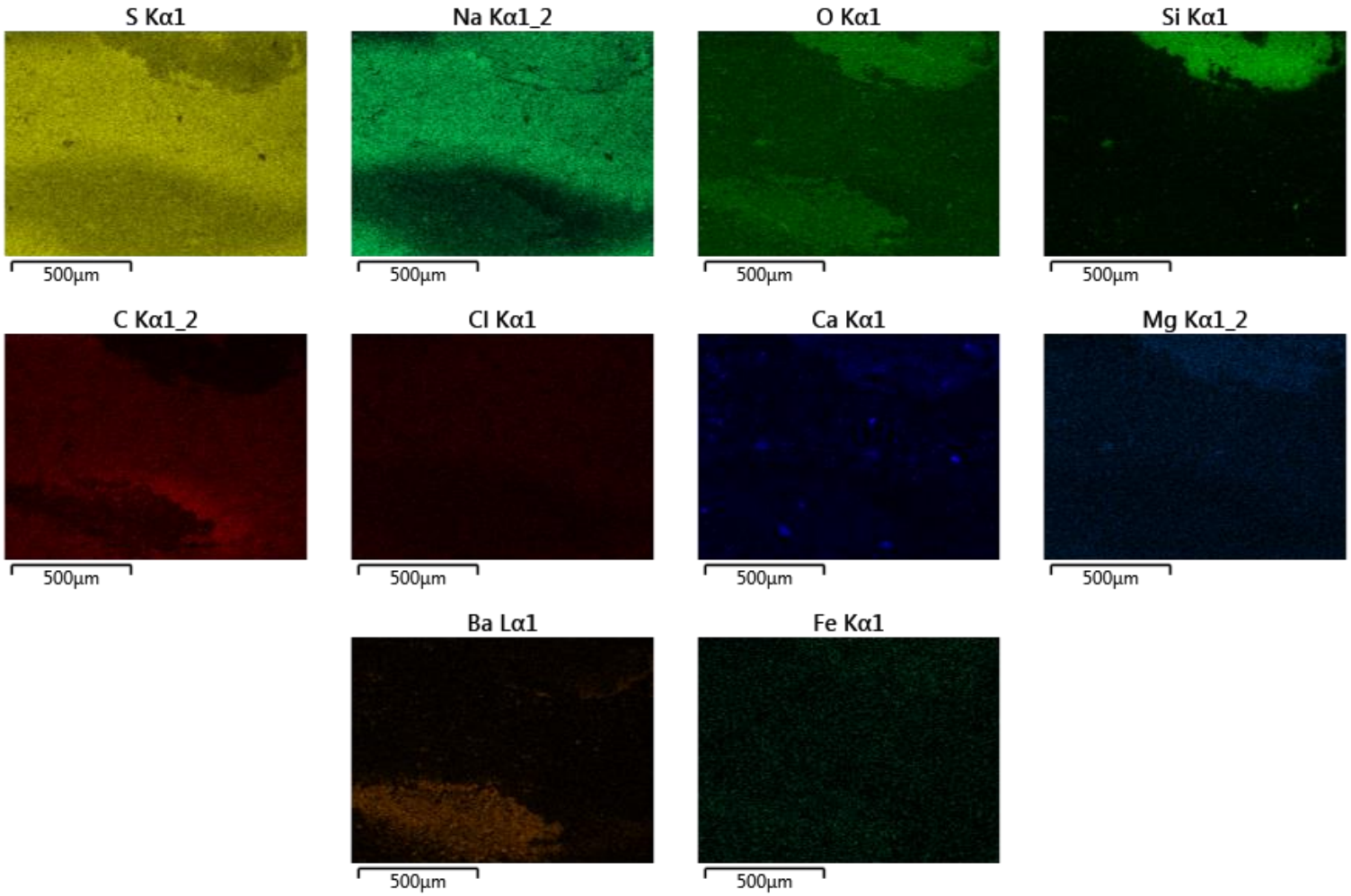


Figure 36: Prismatic Elemental Delineation (PED®) of membrane surface at 100X magnification. Deposits found: Barium sulfate, sodium sulfate, calcium sulfate, amorphous silica, silts and/or clays.

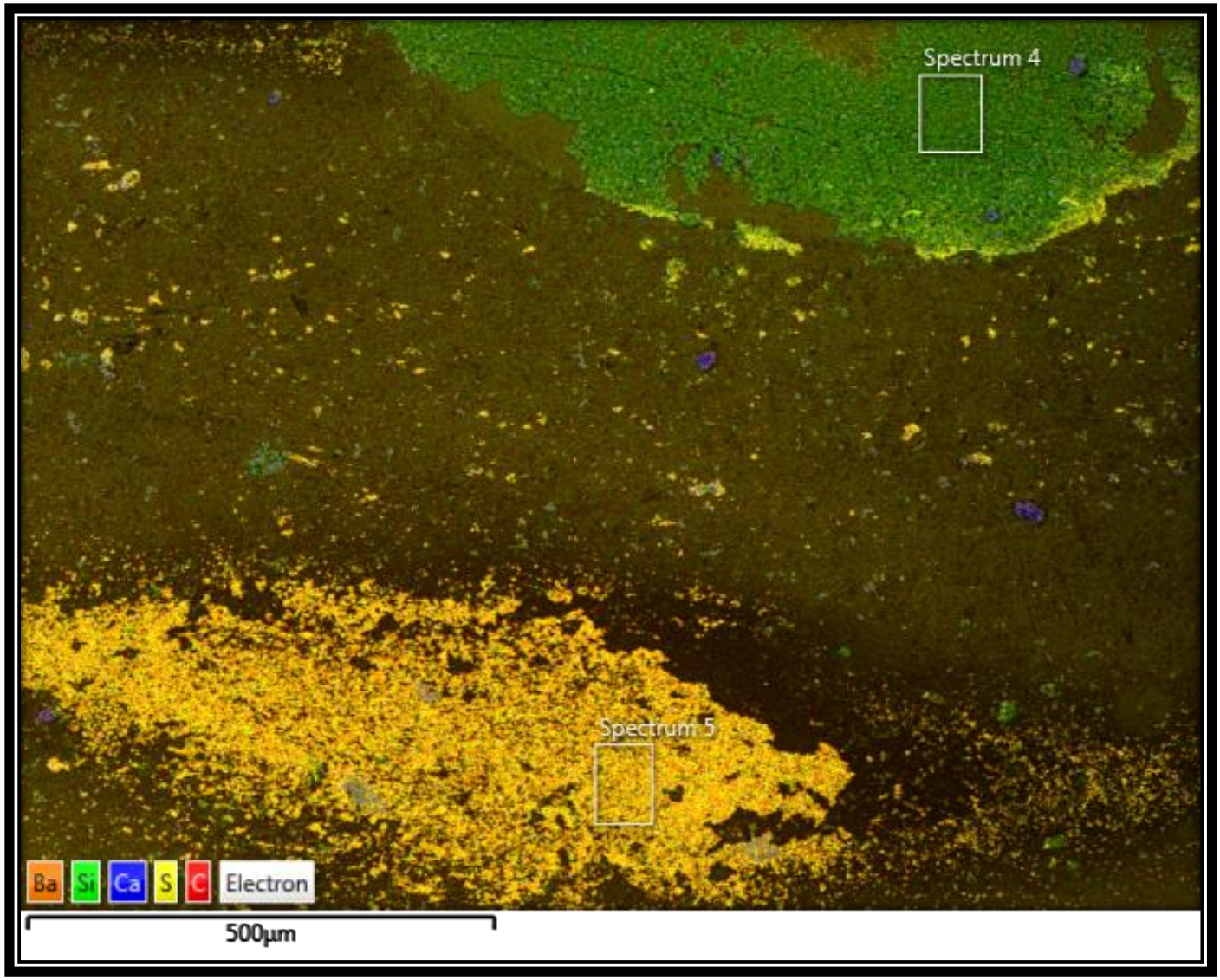
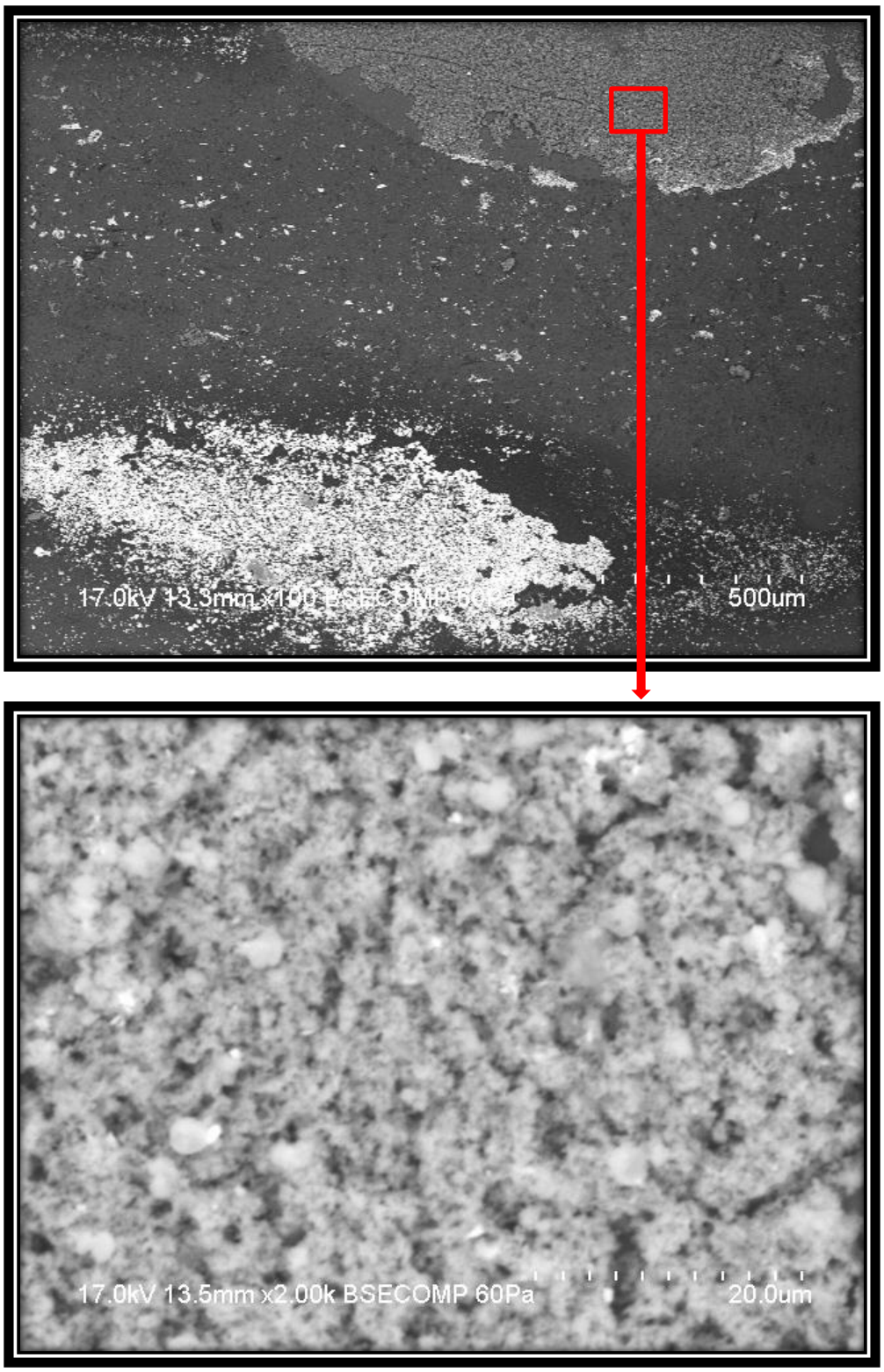


Figure 37: Superimposed Elemental Imaging (SEI®) of barium sulfate, sodium sulfate, calcium sulfate, amorphous silica, silts and/or clays.


500um
17.0kV 13.5mm x2.00k BSECOMP 60Pa
20.0um

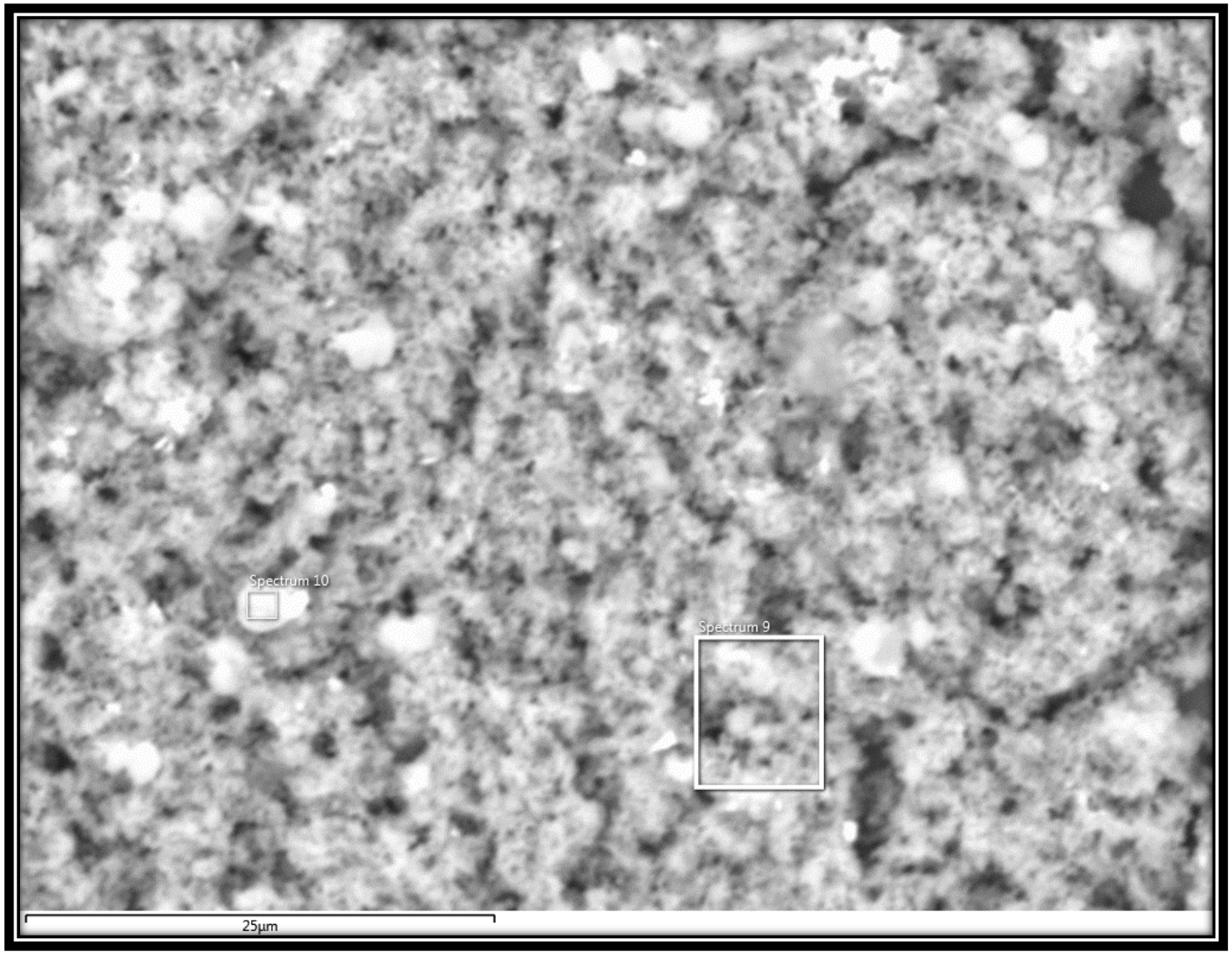


Figure 38: Electron micrograph of the membrane surface at 2000X magnification (Spectrum 9 & Spectrum 10).

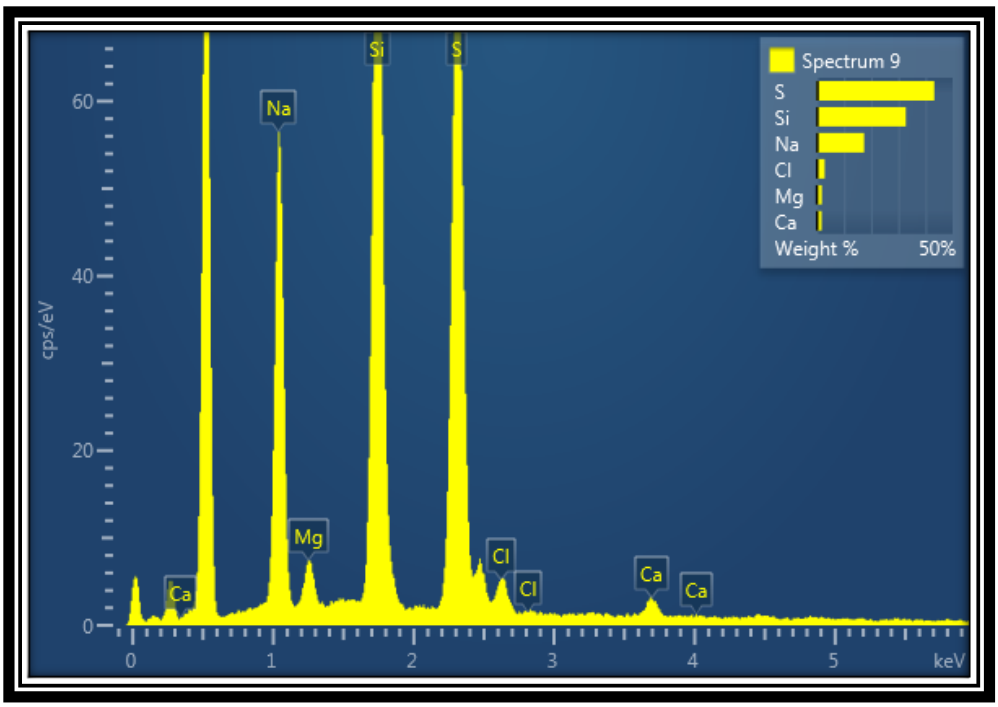


Figure 39: EDS and composition bar graph analysis of the membrane deposit from Spectrum 9.

Spectrum 9	Atomic %
C	16.91
O	49.40
Na	9.39
Mg	0.79
Si	11.18
S	11.34
Cl	0.62
Ca	0.37
Total	100.00

Spectrum 9	Atomic %
Carbon and Oxygen Ignored	
Na	21.77
Mg	2.22
Si	33.53
S	38.81
Cl	2.38
Ca	1.29
Total	100.00

Table 12: Composition table from the EDS spectrum of localized deposit from Spectrum 9.

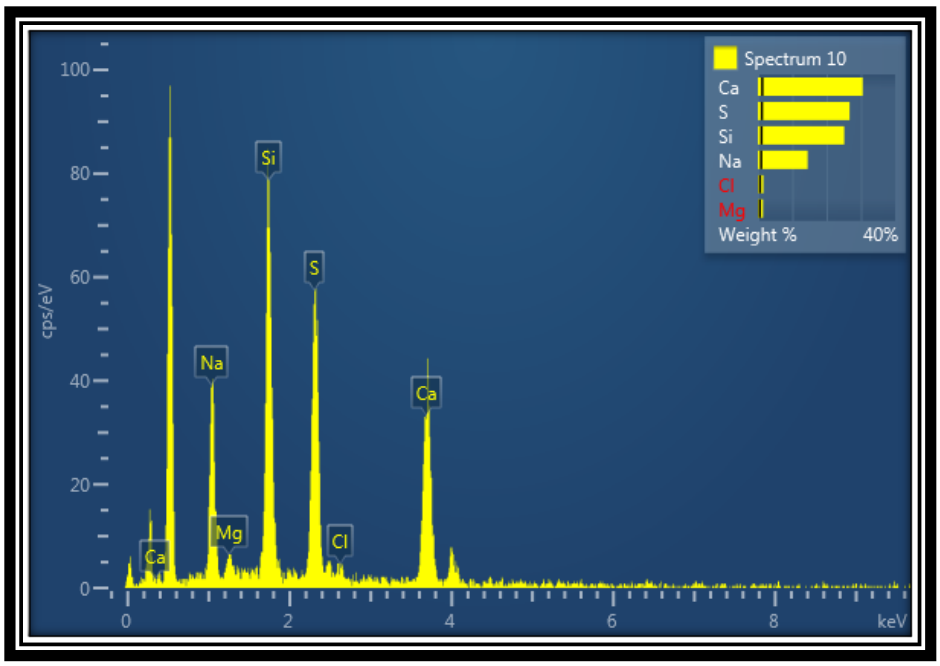


Figure 40: EDS and composition bar graph analysis of the membrane deposit from Spectrum 10.

Spectrum 10	Atomic %
C	22.50
O	51.61
Na	6.11
Mg	0.50
Si	7.21
S	6.10
Cl	0.31
Ca	5.66
Total	100.00

Spectrum 10	Atomic %
Carbon and Oxygen Ignored	
Na	19.54
Mg	1.88
Si	27.75
S	25.83
Cl	1.41
Ca	23.60
Total	100.00

Table 13: Composition table from the EDS spectrum of localized deposit from Spectrum 10.

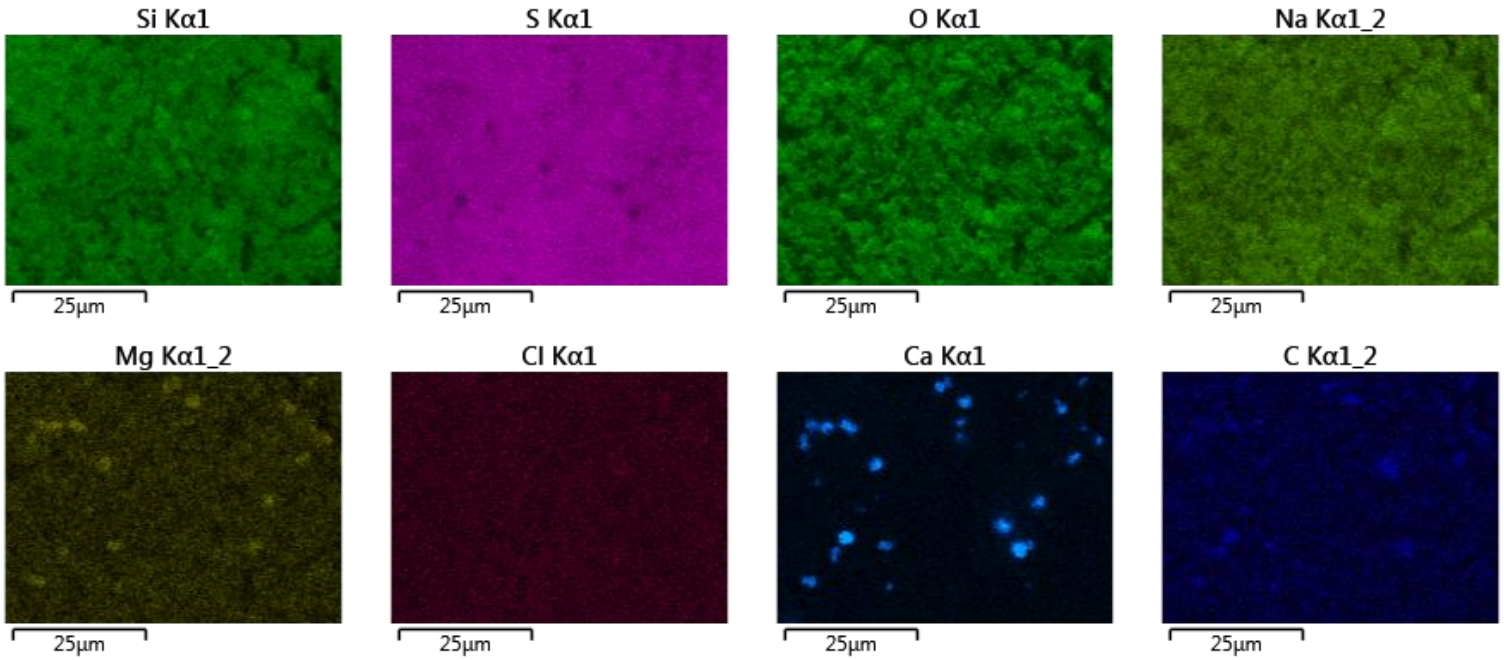


Figure 41: Prismatic Elemental Delineation (PED®) of membrane surface at 2000X magnification. Deposits found: Amorphous silica, sodium sulfate, dolomite and limestone.

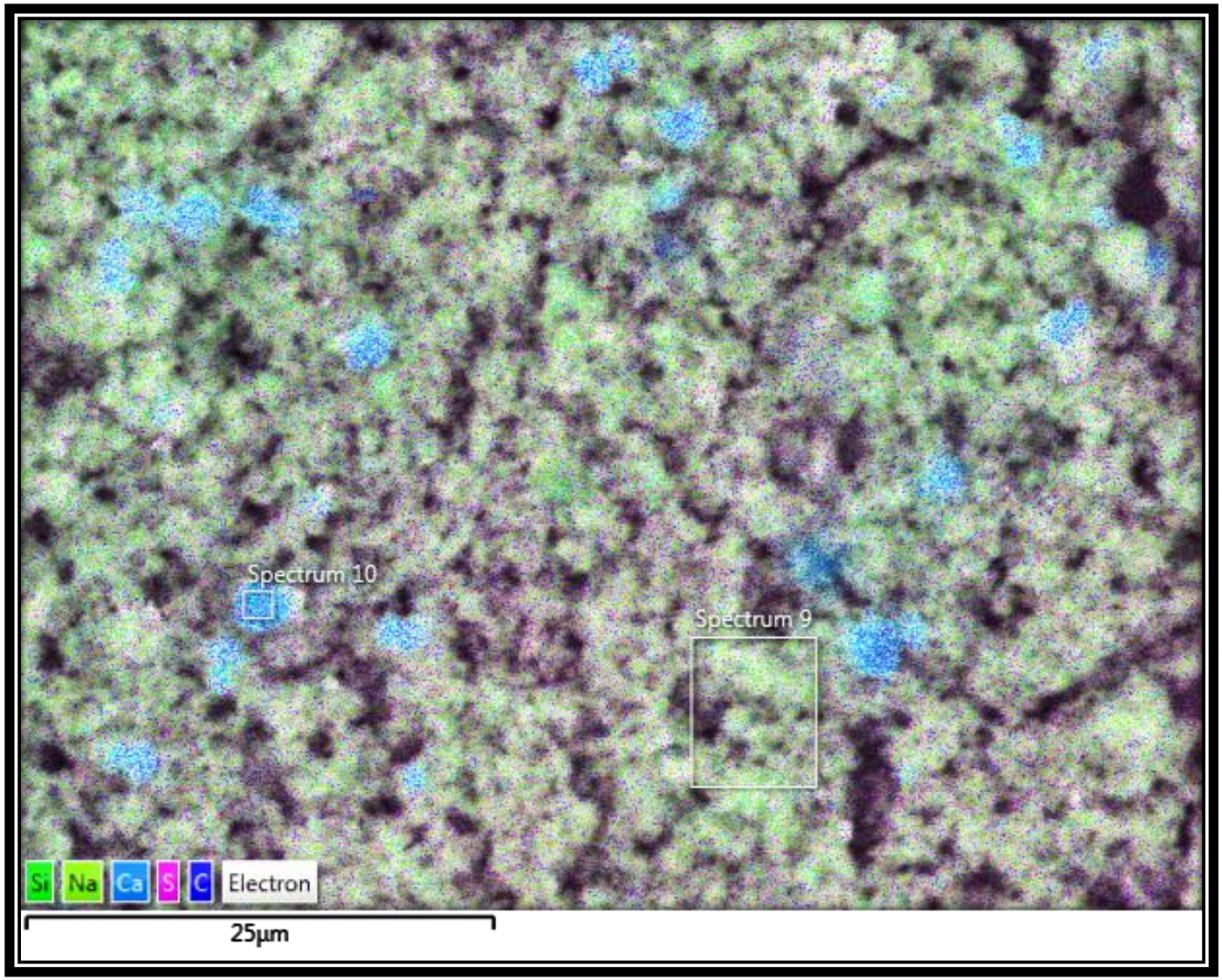


Figure 42: Superimposed Elemental Imaging (SEI®) of Amorphous silica, sodium sulfate, dolomite and limestone.

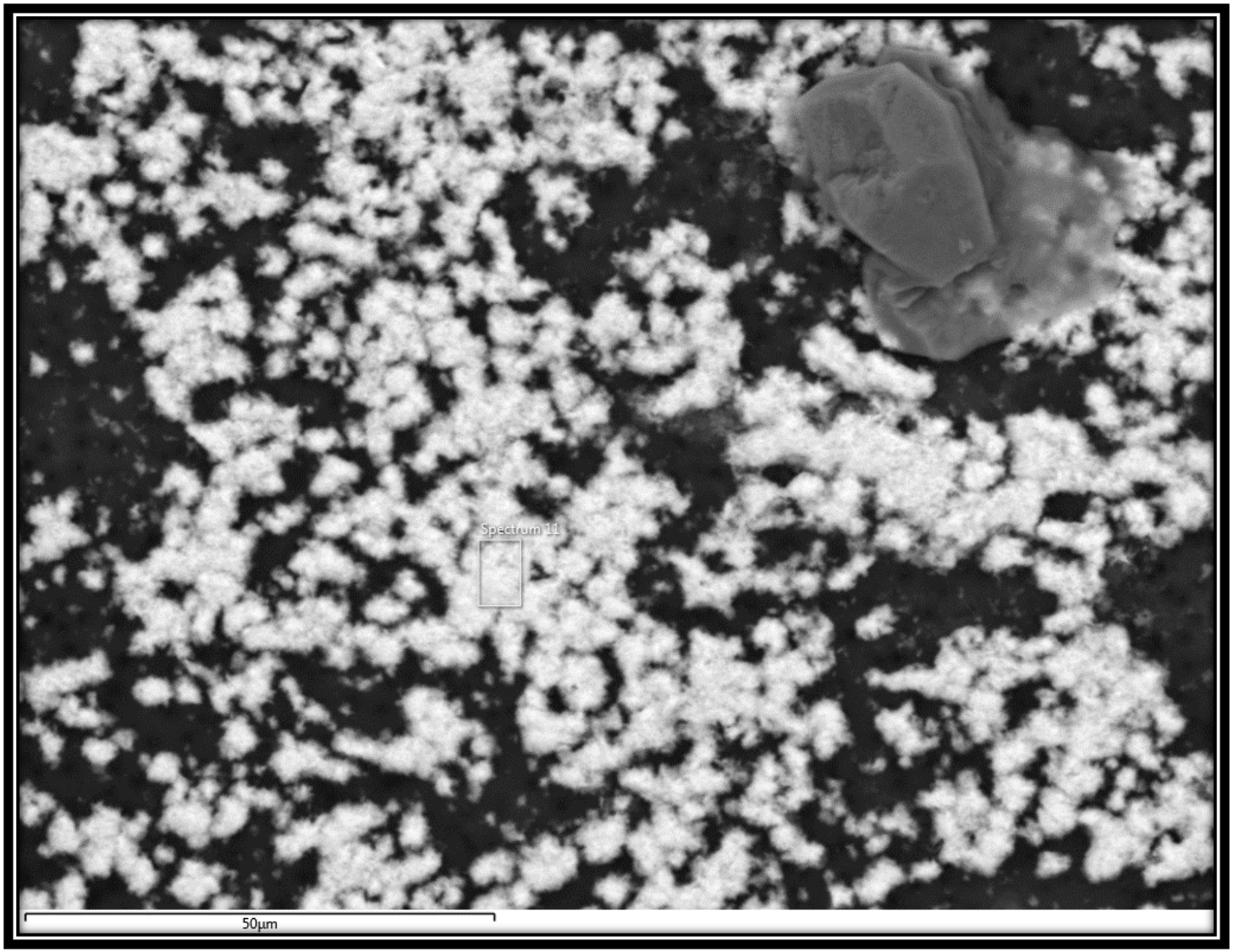


Figure 43: Electron micrograph of the membrane surface at 1000X magnification (Spectrum 11).

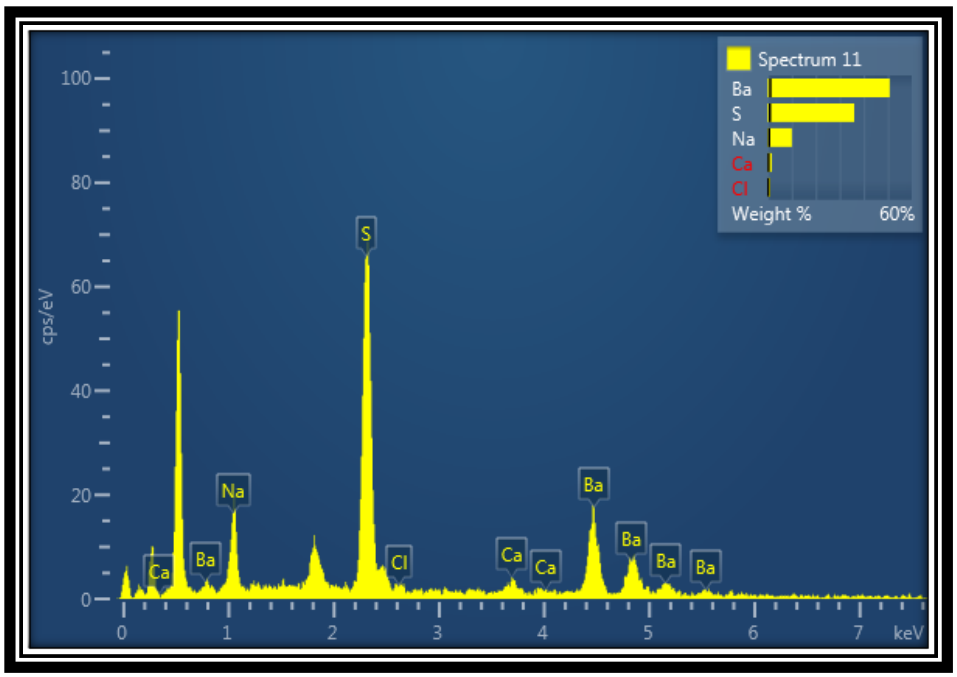


Figure 44: EDS and composition bar graph analysis of the membrane deposit from Spectrum 11.

Spectrum 11	Atomic %
C	32.44
O	42.59
Na	5.34
S	13.83
Cl	0.38
Ca	0.57
Ba	4.86
Total	100.00

Spectrum 11	Atomic %
Carbon and Oxygen Ignored	
Na	21.82
S	55.92
Cl	1.62
Ca	2.24
Ba	18.41
Total	100.00

Table 14: Composition table from the EDS spectrum of localized deposit from Spectrum 11.

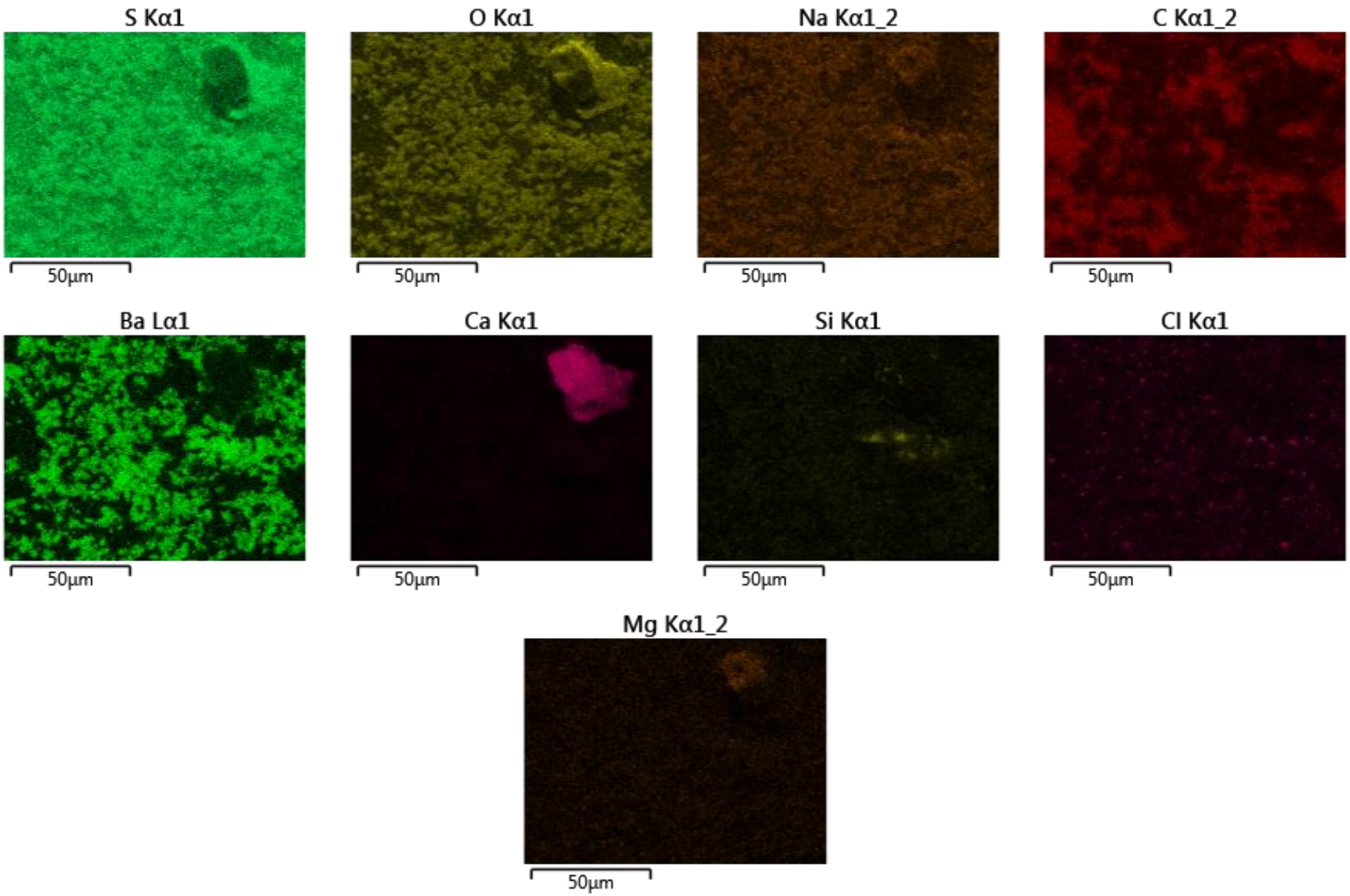


Figure 45: Prismatic Elemental Delineation (PED®) of membrane surface at 1000X magnification. Deposits found: Calcium sulfate, barium sulfate, silts and/or clays.

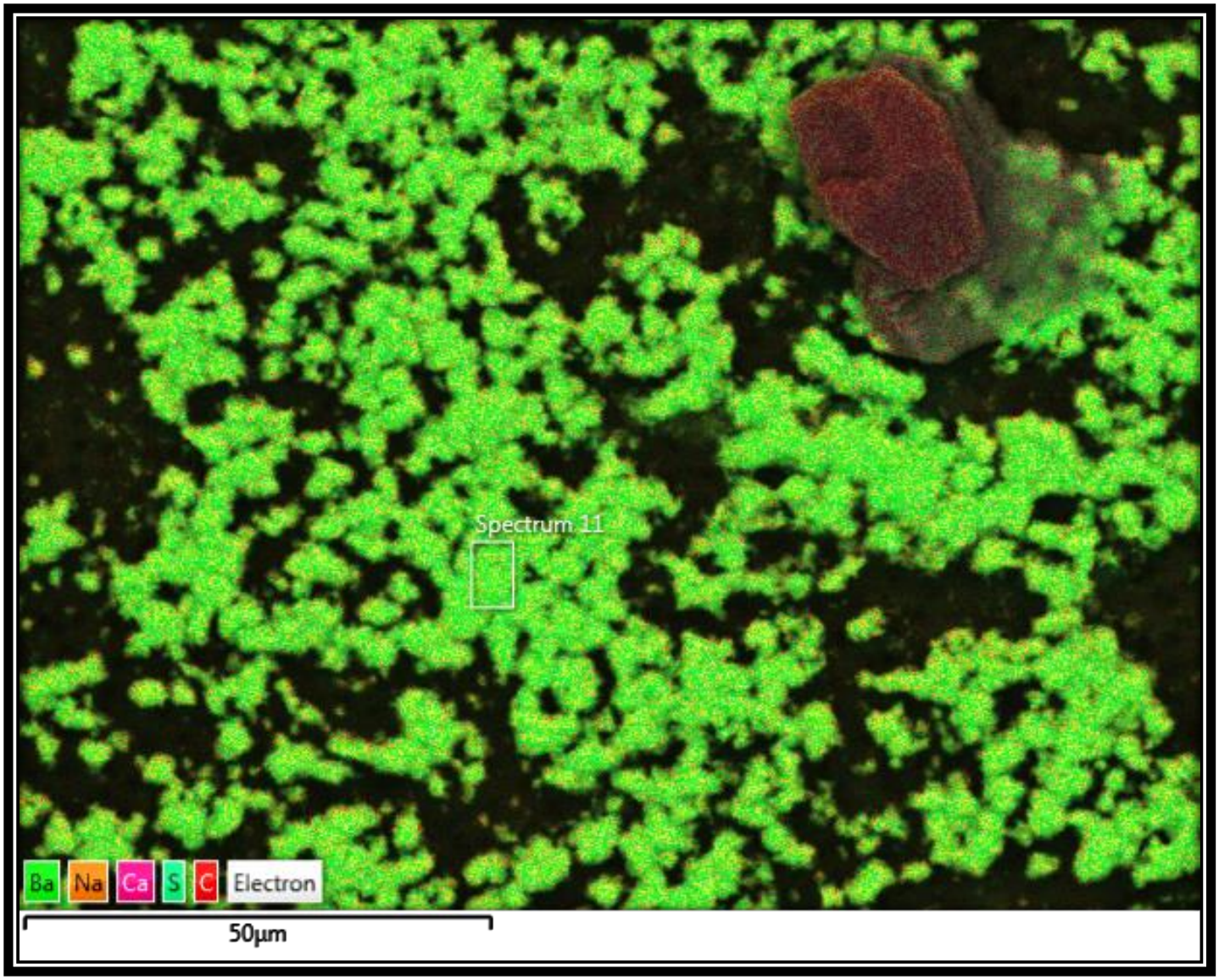


Figure 46: Superimposed Elemental Imaging (SEI®) of calcium sulfate, barium sulfate, silts and/or clays.

Membrane Surface Analysis

Virgin Membrane

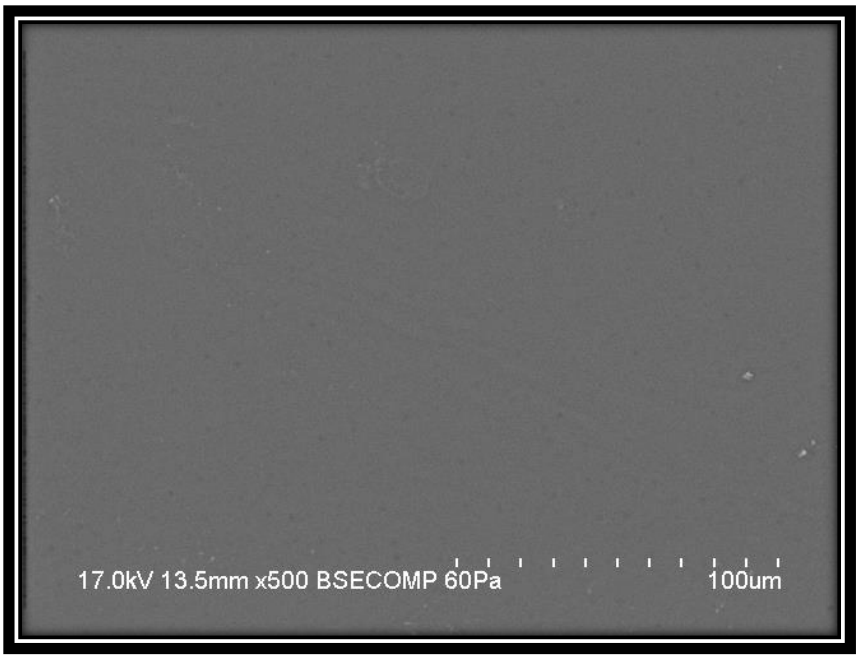


Figure 47: Electron micrograph of the membrane surface at 500X magnification.

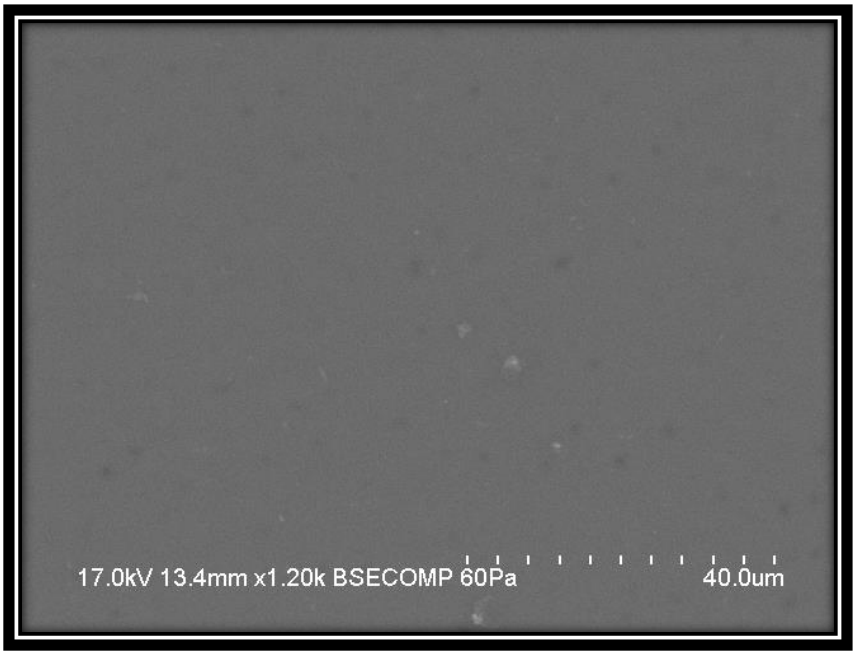


Figure 48: Electron micrograph of the membrane surface at 1200X magnification.

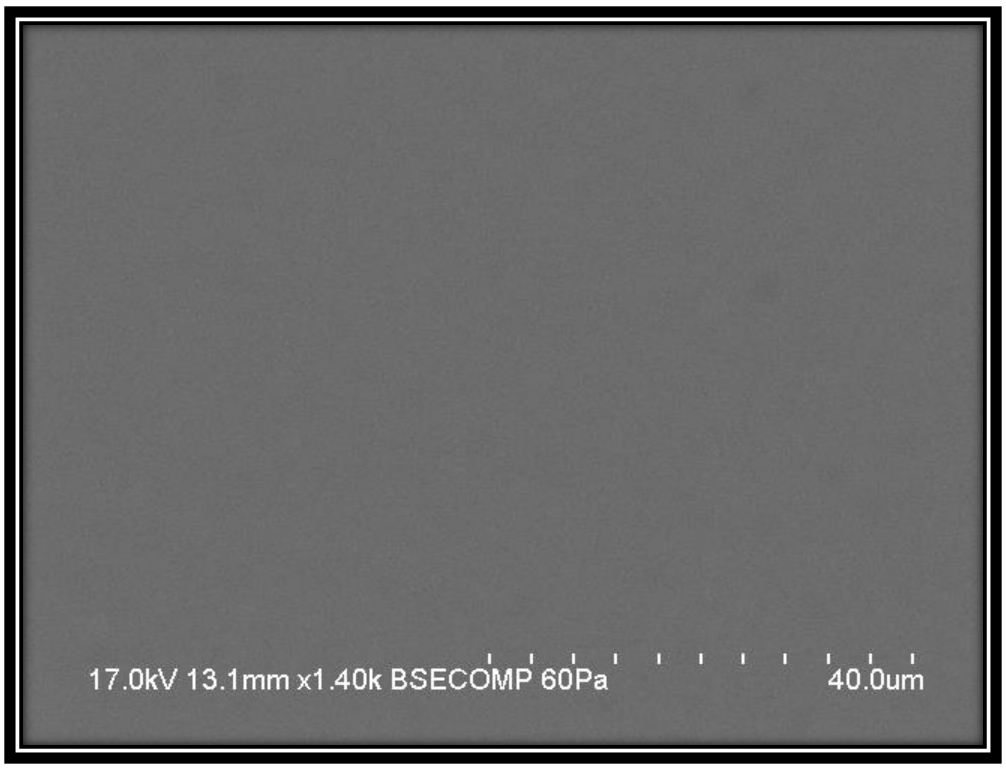


Figure 49: Electron micrograph of the membrane surface at 1400X magnification.

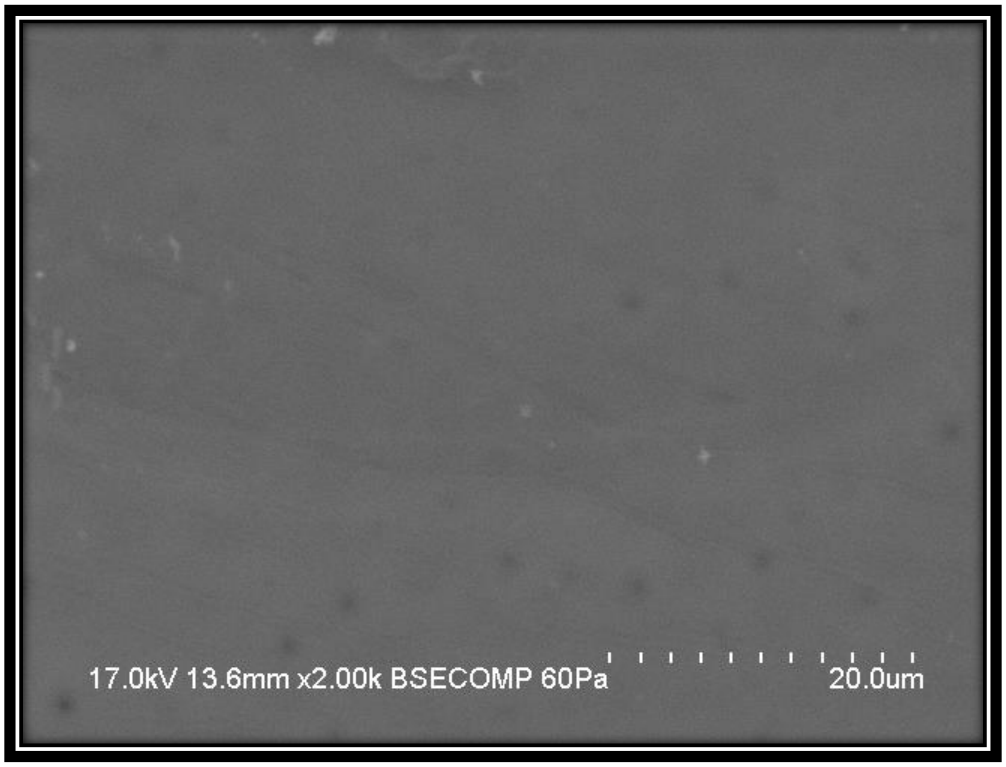


Figure 50: Electron micrograph of the membrane surface at 2000X magnification.

Fouled Membrane (after attempted cleaning with pH restrictions)

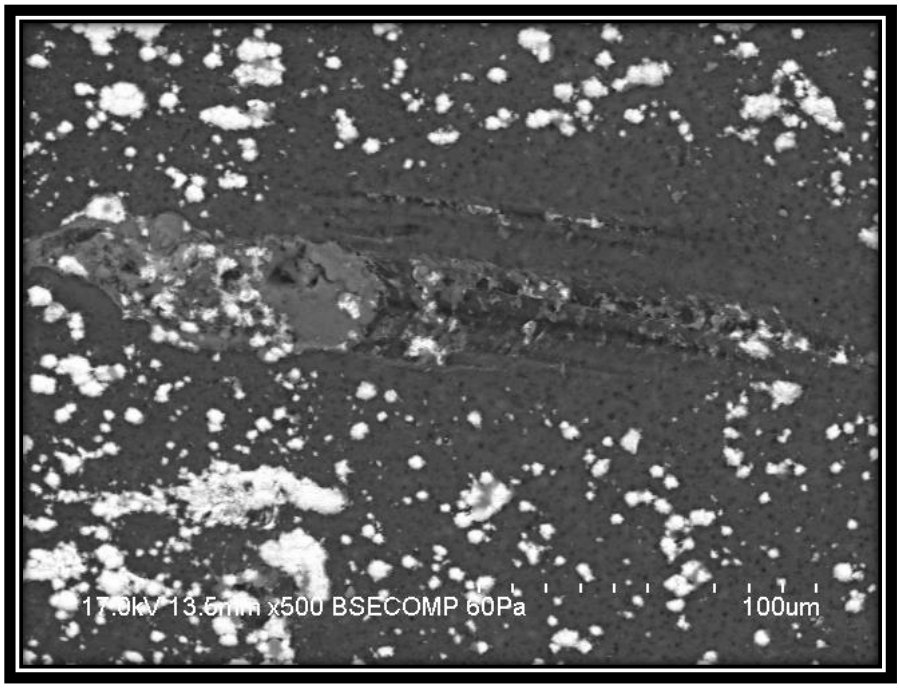


Figure 51: Electron micrograph of the membrane surface damage at 500X magnification.

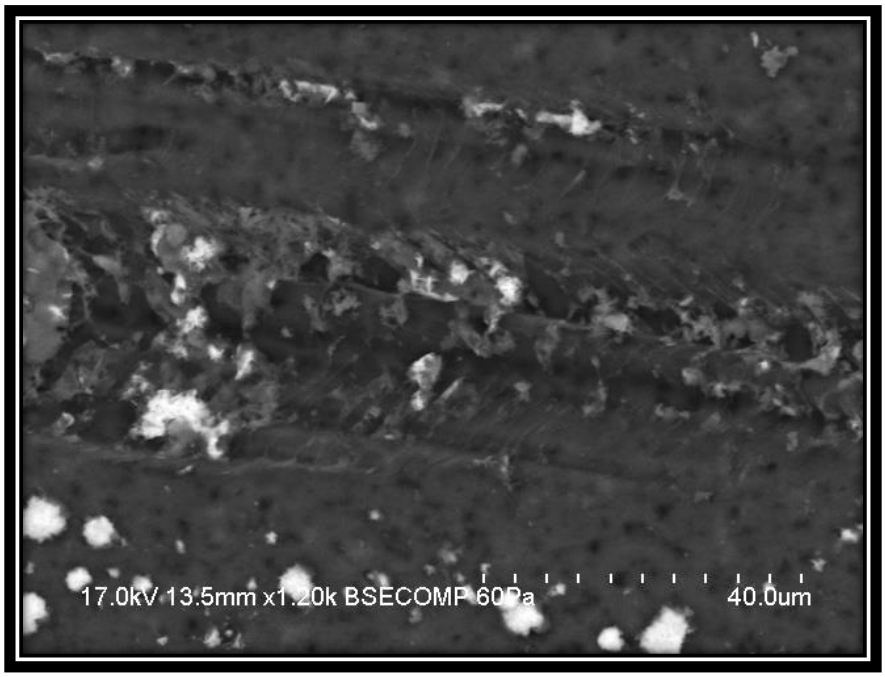


Figure 52: Electron micrograph of the membrane surface damage at 1200X magnification.

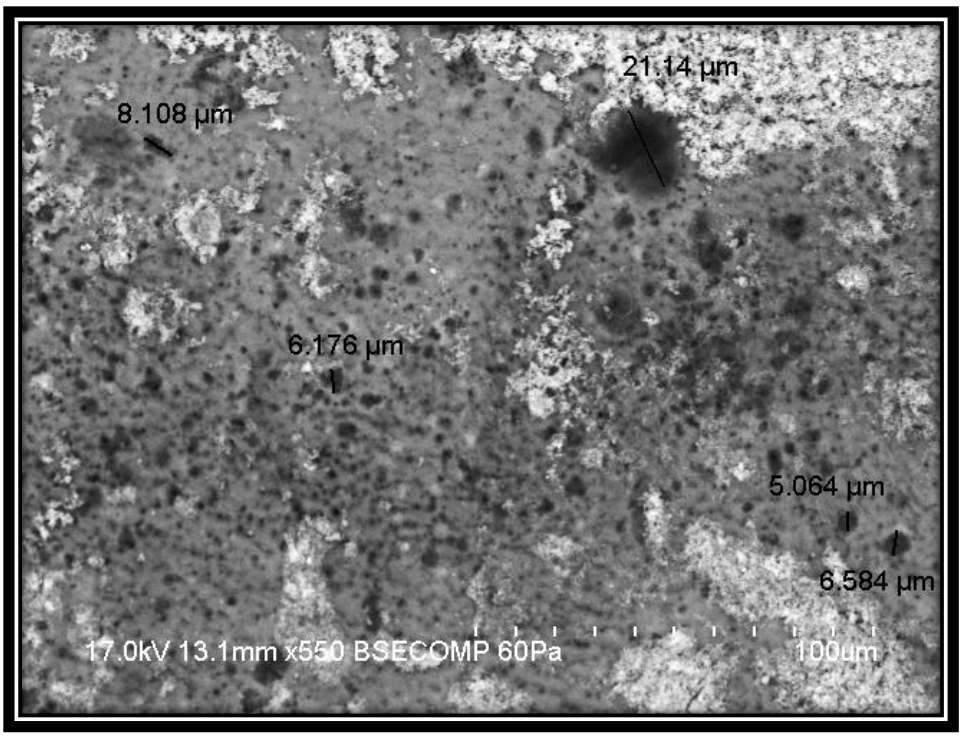


Figure 53: Electron micrograph of the membrane surface damage at 550X magnification. The size of the damage ranged from <5 µm to ~21 µm.

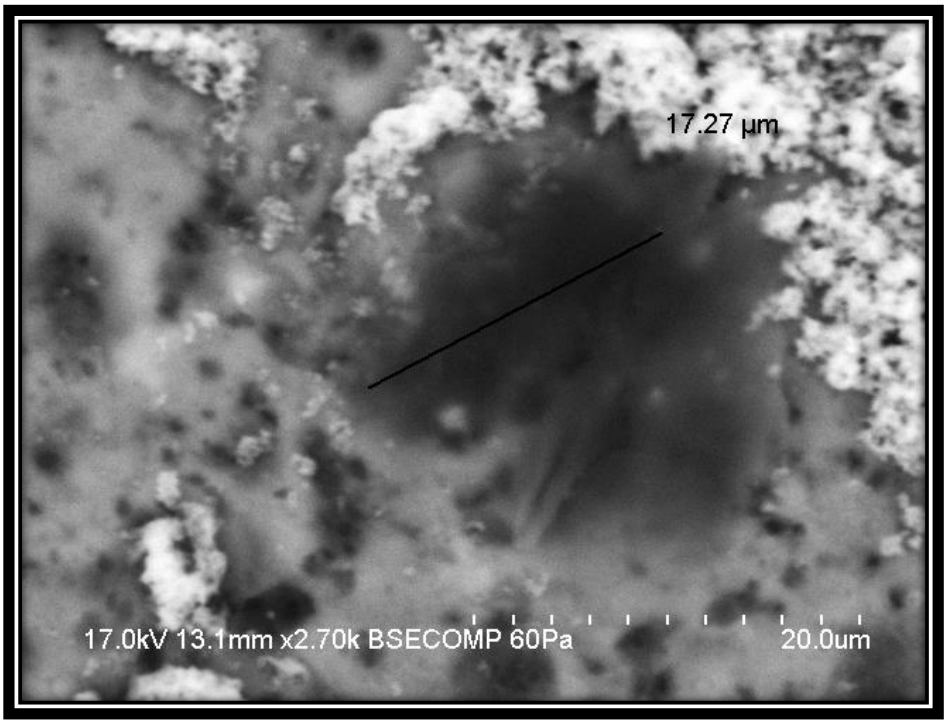


Figure 54: Electron micrograph of the membrane surface damage at 2700X magnification.

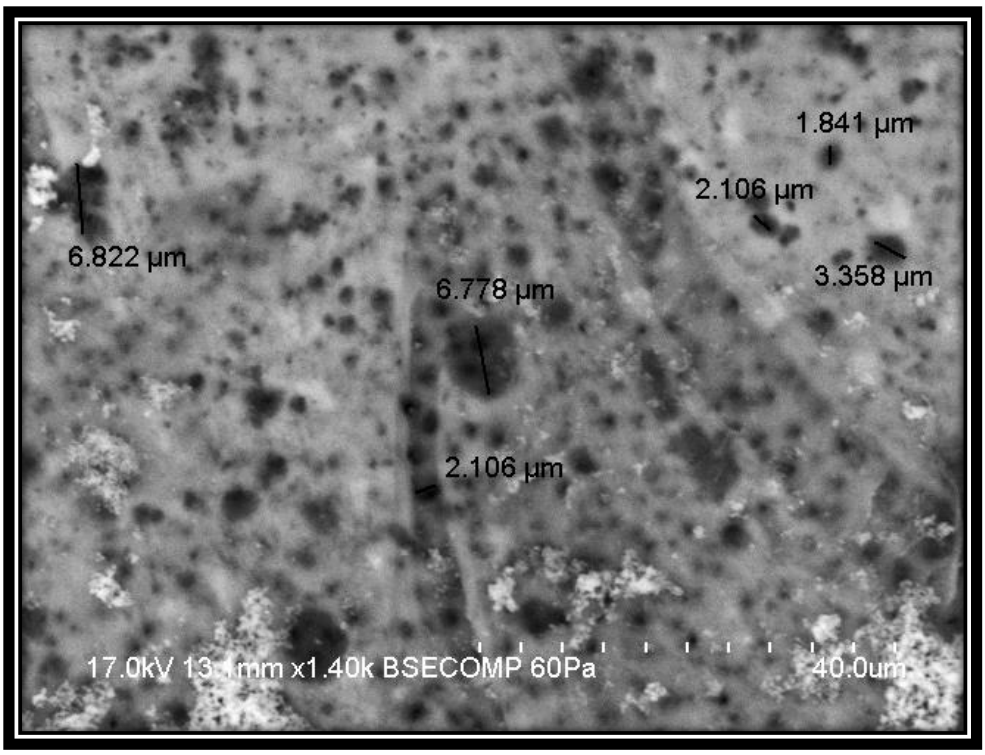


Figure 55: Electron micrograph of the membrane surface damage at 1400X magnification. The size of the damage ranged from <1 µm to ~6 µm.

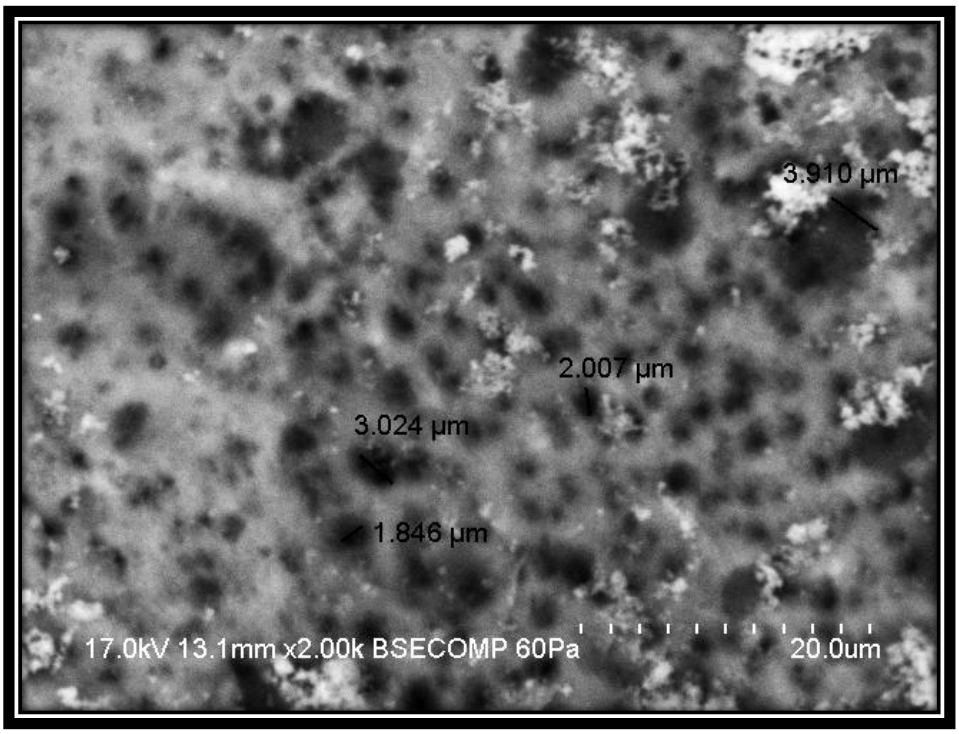


Figure 56: Electron micrograph of the membrane surface damage at 2000X magnification. The size of the damage ranged from <1 µm to ~4 µm.

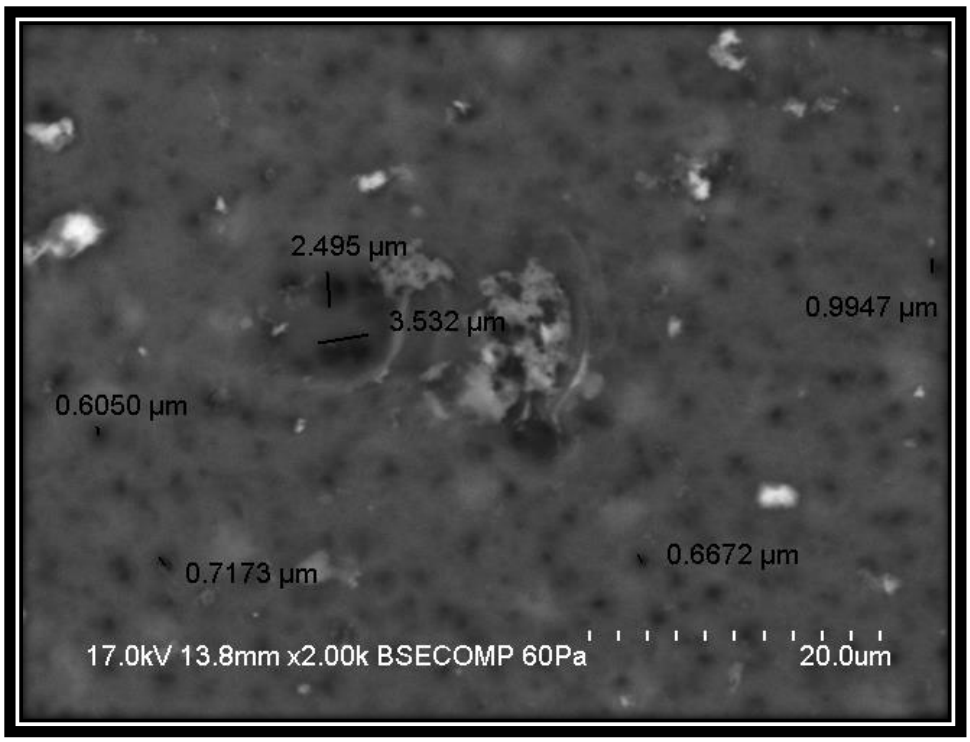


Figure 57: Electron micrograph of the membrane surface damage at 2000X magnification. The size of the damage ranged from <1 µm to ~3.5 µm.

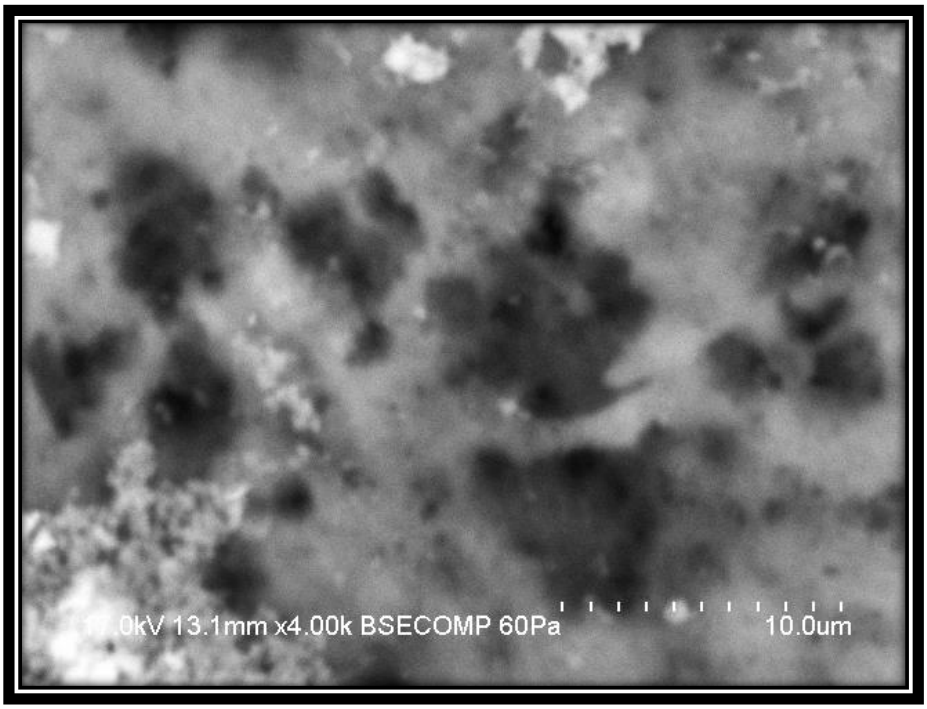


Figure 58: Electron micrograph of the membrane surface damage at 4000X magnification.

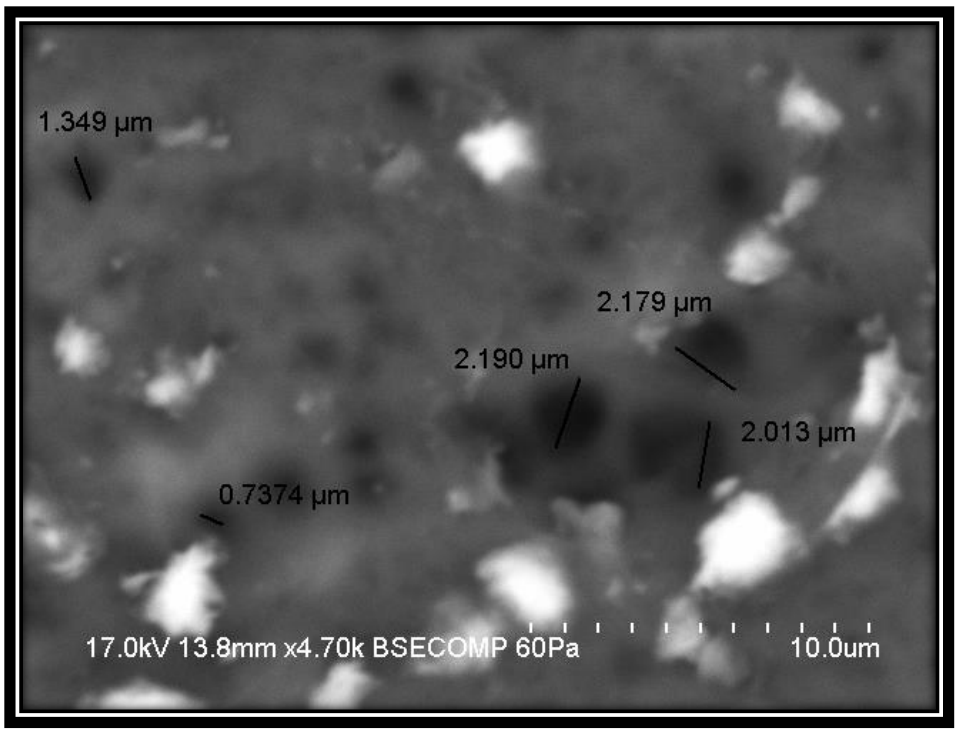


Figure 59: Electron micrograph of the membrane surface damage at 4700X magnification. The size of the damage ranged from <1 µm to ~2 µm.

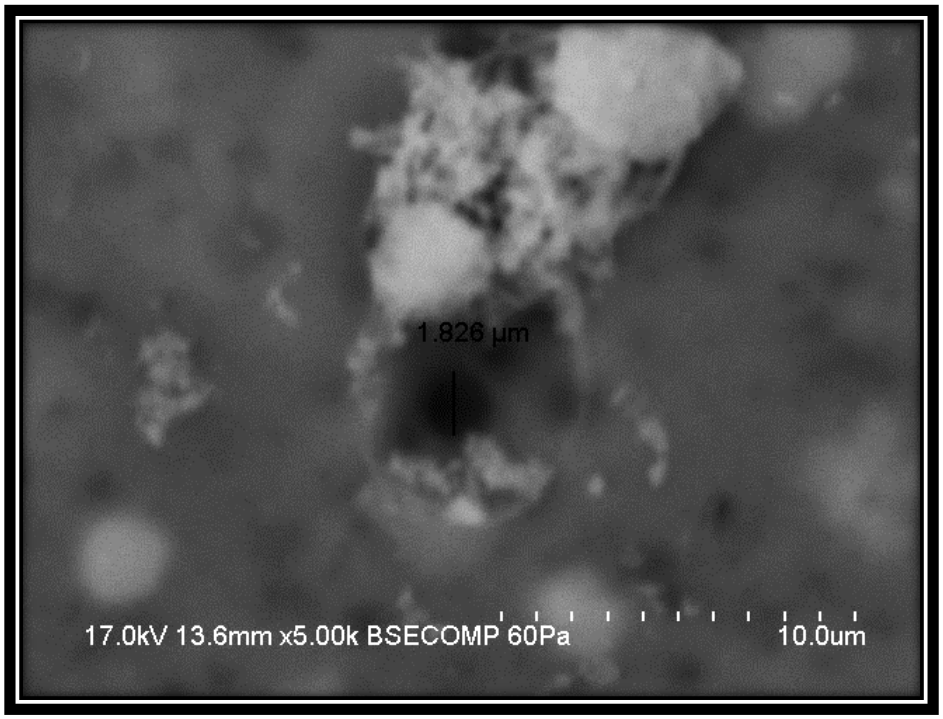


Figure 60: Electron micrograph of the membrane surface damage at 5000X magnification. The size of the damage was ~2 µm.

FTIR analysis

Fourier Transform Infrared spectrometer (FTIR) is a powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic to the chemical bond. The tested material can be identified by comparing its spectrum to the spectra of documented compounds in the database.

The following samples were analyzed with FTIR:

- The LOI residue of the foulant collected from the membrane surface (see Figure 61).
- The membrane foulant dehydrated at 105°C for 8 hours (see Figure 63).

Results: Dehydrated Foulant

The FTIR spectrum of the dehydrated foulant had peaks associated with silts/clays and sulfate salts. A library search found a ~63% correlation to calcium sulfate.

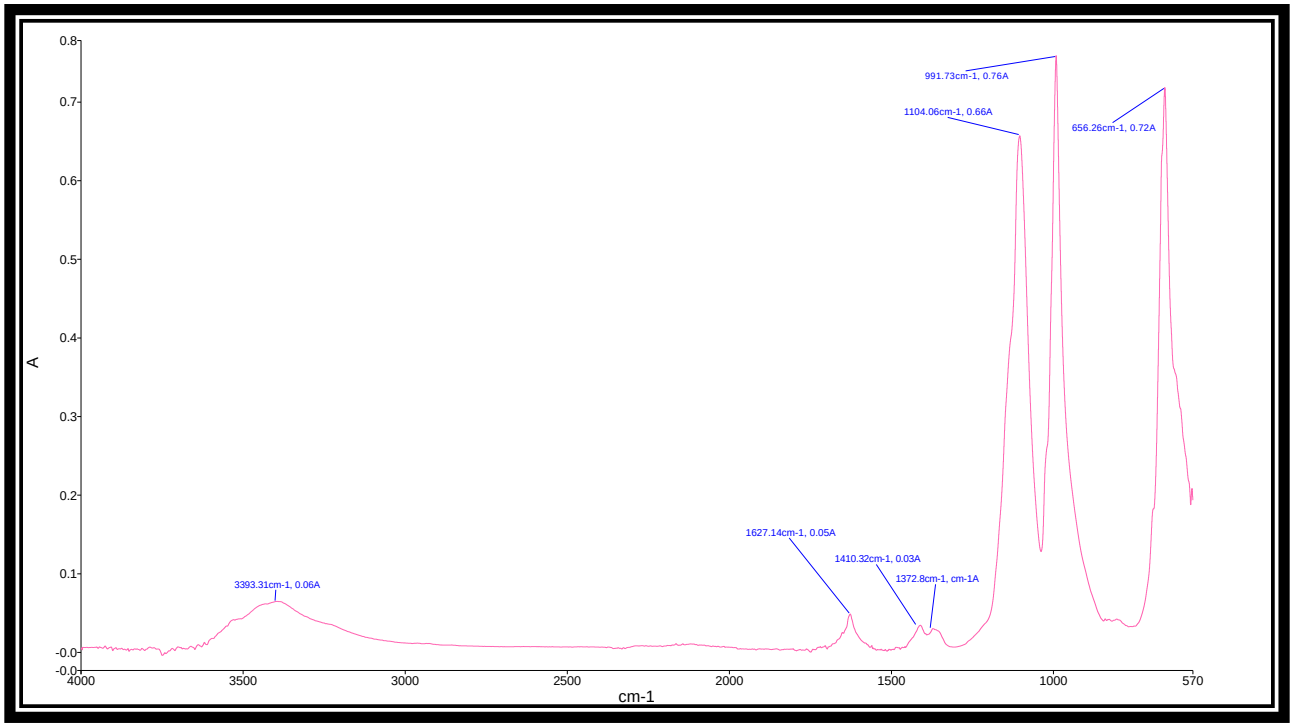


Figure 61: FTIR spectrum of the foulant.

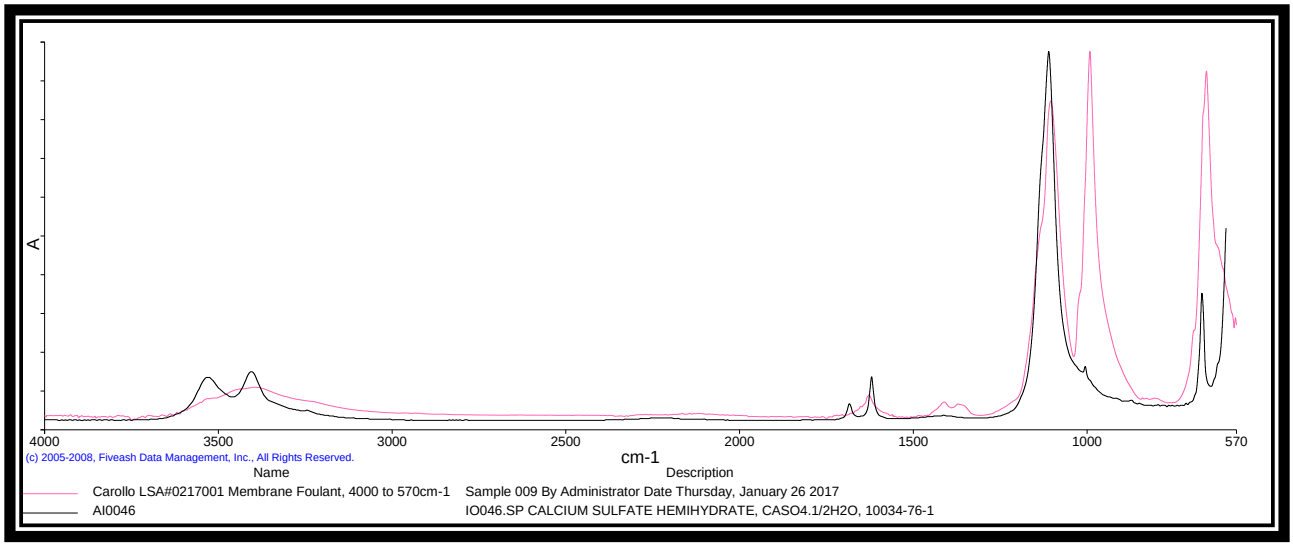


Figure 62: The spectrum of the foulant had a 62.6% correlation to calcium sulfate.

Results: LOI residue

The FTIR spectrum of the LOI residue had peaks associated with silts/clays and sulfate salts. A library search found a 64% correlation to barium sulfate.

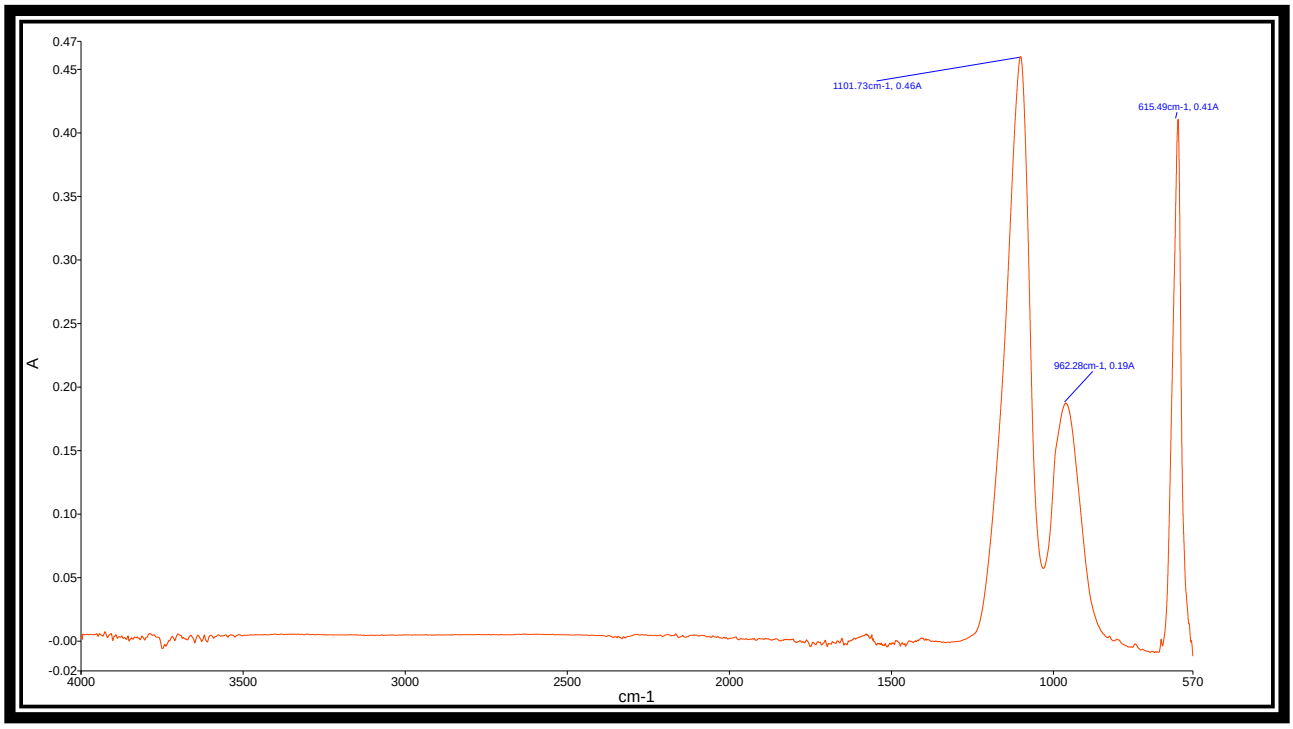


Figure 63: FTIR spectrum of the LOI residue.

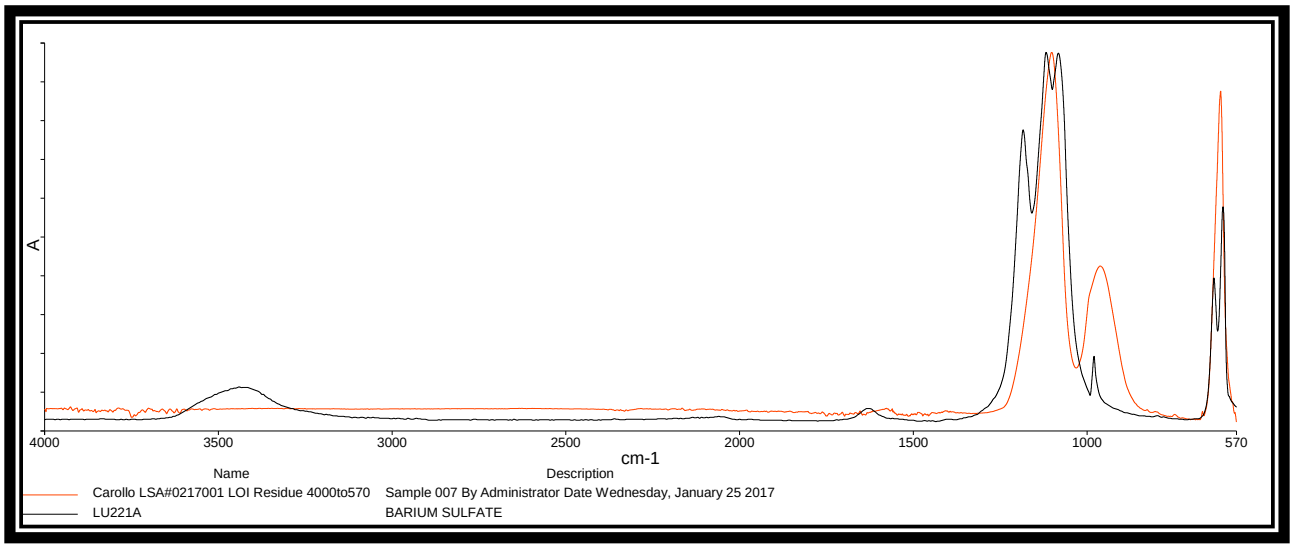


Figure 64: The FTIR spectrum of the LOI residue had a 63.5% correlation to barium sulfate.

BART Test

Iron related bacteria (IRB), slime forming bacteria, sulfate reducing bacteria (SRB), heterotrophic aerobic bacteria (HAB), and denitrifying bacteria tests were performed. When the BART tests are performed using biofilm rather than water samples, the population counts should only be used comparatively to determine the most dominant types of bacteria.

Results

The dominant types of bacteria detected were Heterotrophic aerobic bacteria. Slime forming, sulfate reducing, and iron related bacteria were also detected.

Test	Test duration (days)	Day of failure	Population Cfu/mL
Iron related bacteria	8	4	9,000
Slime forming bacteria	8	3	66,500
Sulfate reducing bacteria	8	6	1,200
Heterotrophic aerobic bacteria	4	1	7,000,000
Nitrifying bacteria	Positive/ Negative	Negative	N/A

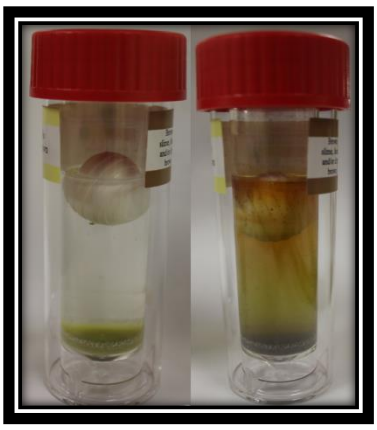


Figure 65: IRB - start (left), positive for iron related bacteria (right).

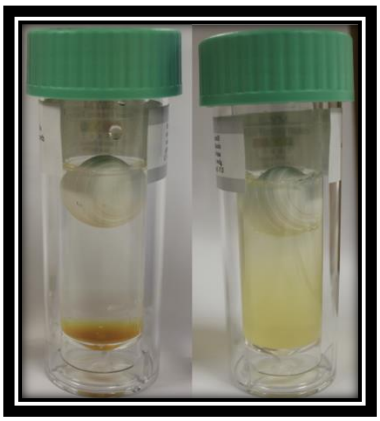


Figure 66: SLYM – start (left), positive for slime forming bacteria (right).

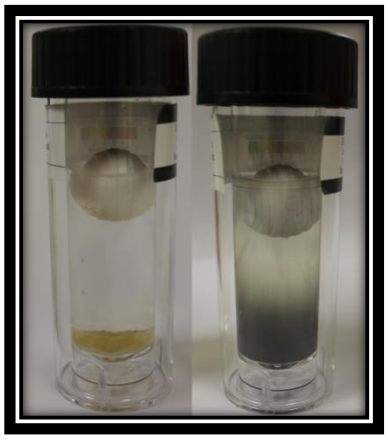


Figure 67: SRB – start (left), positive for sulfate reducing bacteria (right).

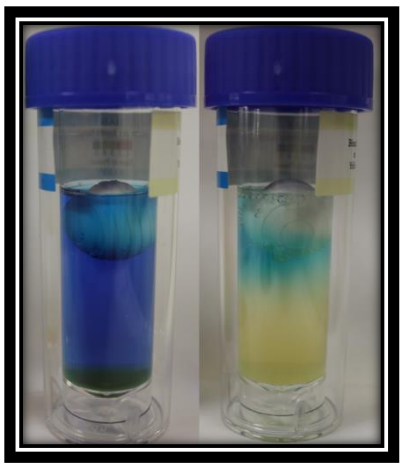


Figure 68: HAB – start (left), positive for heterotrophic aerobic bacteria (right).

Figure 69: N– start (left), negative for nitrifying bacteria (right).

Optical Microscopy

Live Wet Mounts

Wet mounts were made of xx material. Slides were observed at 100X and 400X using an inverted microscope equipped with phase contrast optics and epi-fluorescence.

Results

Microscopic observations revealed that the sample was dominated by flagellates (Figs. 70-72) and motile and non-motile bacterial rods (Fig. 73). Sparse amoeboid protozoans were also observed (Fig. 74).

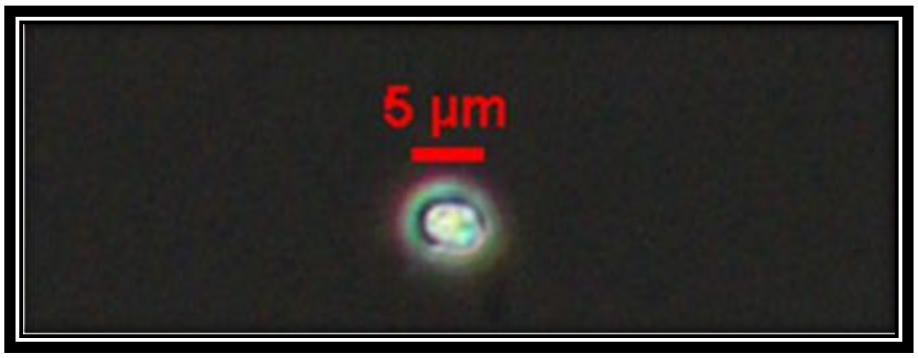


Figure 70: Flagellate sp. at 400X (scale bar = 5 µm).

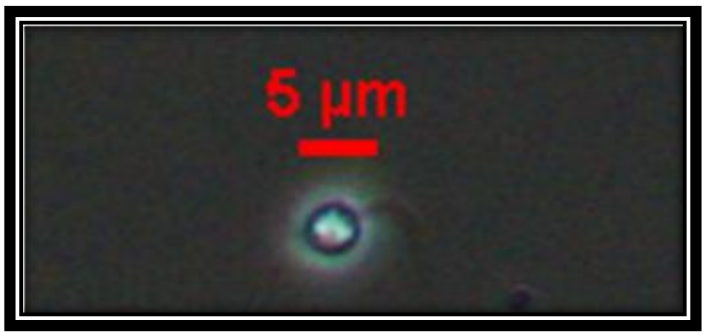


Figure 71: Flagellate sp. at 400X (scale bar = 5 µm).

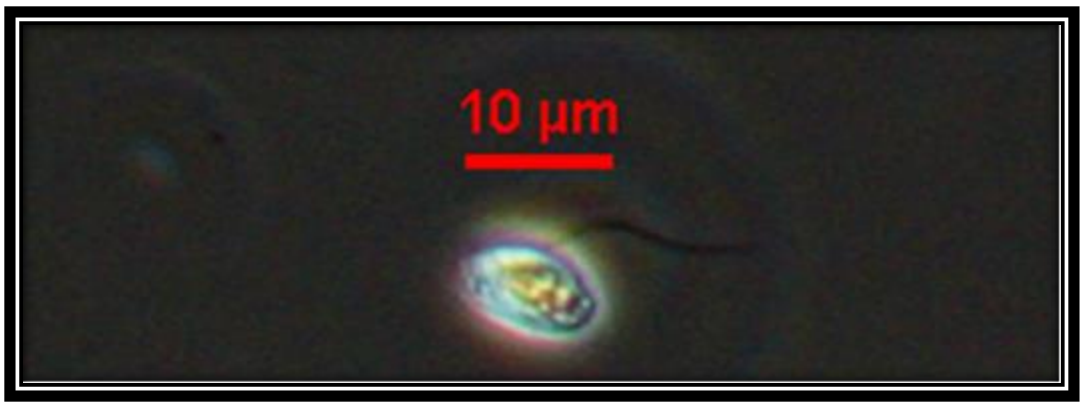


Figure 72: Flagellate sp. at 400X (scale bar = 10 µm).

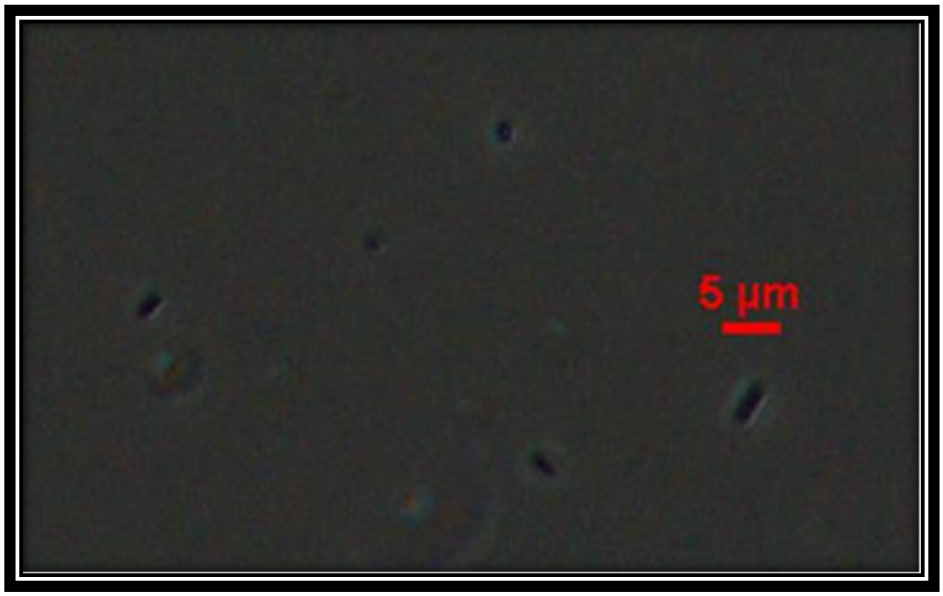


Figure 73: Bacterial rods at 400X (scale bar = 5 µm).

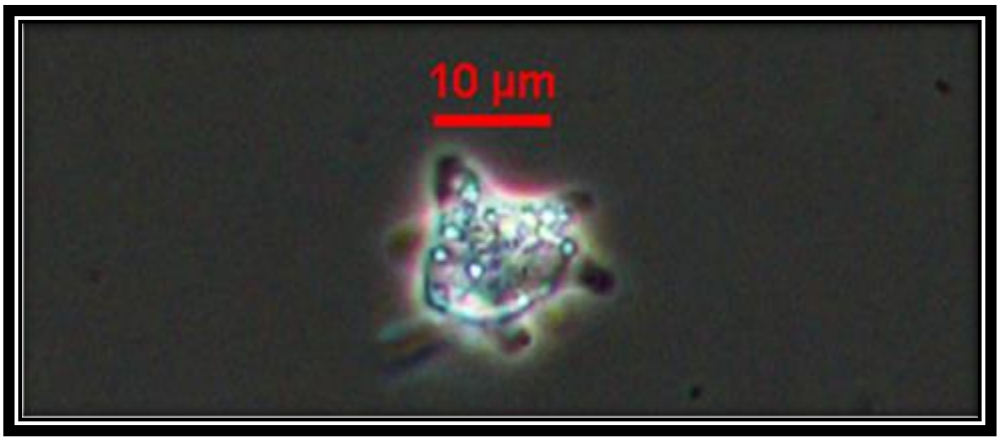


Figure 74: Amoeboid protozoan at 400X (scale bar = 10 µm).

Results and Discussion

A virgin membrane was obtained for comparison so as to better interpret the autopsy results.

Brown foulant was found on the feed side of the fouled membrane. The LOI test determined the foulant to consist of ~27.1% organic matter and ~72.9% inorganic matter.

The foulant was positive for humic acids.

Sporadic brown spots were found on the feed side of the fouled membrane.

Inspection of the permeate side of the fouled membrane identified brown, green and yellow bands at the seams of the fouled membrane. These bands were not observed on the seams of the virgin membrane.

Initial cell testing results found the salt rejection to be ~14.4% lower than the virgin membrane and the flux to be ~2.1% higher. After cleaning, the membrane salt rejection decreased by ~11.6% when compared to the initial cell test results and the flux increased by ~23.8%. Overall, the membrane after cleaning had a salt rejection that was 24.3% lower than the virgin membrane and a flux that was ~26.4% higher.

Dye penetration was observed on the permeate side of the cleaned membrane coupons. The pattern suggested surface abrasion. Heavy dye penetration was observed at locations that corresponded to brown spots on the feed side of the membrane. Since this test was performed in a flat sheet cell test unit by spreading open a tubular membrane, a virgin membrane was also dye tested for comparison. No significant dye penetration was observed, verifying that the damage was caused during operation rather than by sample preparation.

SEM/EDS/SEI/PED analysis of the membrane surface found the primary scale to be barium sulfate. Sporadic deposits of calcium sulfate, amorphous silica, limestone, dolomite, silts and clays were also identified. Sodium sulfate was found throughout, however, this is a highly soluble salt; it most likely formed upon dehydration caused by placing the sample in high vacuum for SEM analysis.

An attempt was made at cleaning the membrane, after which a surface analysis was performed by SEM. Surface damage was observed on all the fouled membrane samples tested, and the extent of damage was gauged based on a comparison to a virgin membrane sample.

FTIR spectrum of the dehydrated foulant had peaks associated with silts/clays. A library search found a ~63% correlation to calcium sulfate. The spectrum of the LOI residue had peaks associated with silts and/or clays. A library search found a 64% correlation to barium sulfate.

Optical microscopy revealed that the dominant biological organisms were flagellates and motile and non-motile bacterial rods. Sparse amoeboid protozoans were also observed. The dominant types of bacteria detected were Heterotrophic aerobic bacteria. Slime forming, sulfate reducing, and iron related bacteria were also detected.

In conclusion, the membrane was scaled primarily with barium sulfate, and fouled with biofilm and humic acids (NOM). Other foulants and scales were also present but to a much lesser extent. Cleaning could not be performed at optimal conditions due to the pH limitations of the membrane, and barium sulfate scaling was still present after cleaning. A comparison of membrane performance after cleaning to that of a virgin membrane found an excessively high flux and poor salt rejection, suggesting mechanical damage; this was verified by pressurized dye testing. SEM imaging found severe surface abrasion throughout.

A review of the reported operating conditions found that a very high dosage of sulfuric acid was being used for pH reduction to prevent calcium carbonate scale formation. The high concentration of sulfates appeared to have resulted in barium sulfate and calcium sulfate scaling; these scales were likely contributors to the membrane surface damage.

Release of Liability

The Membrane Autopsy Service (The Service) was performed in accordance with the standards of care, skill, and diligence normally provided by a professional in the performance of similar services. American Water Chemicals, Inc. makes no warranty of any kind with the respect to The Service and will not be liable for any damages resulting from the use or misuse of The Service. In no event shall American Water Chemicals, Inc. have any liability for The Service, including, but not limited to, special, indirect, incidental, consequential, or other direct damages whether such liability arises in contract, negligence, strict liability, or otherwise, and the Client hereby agrees to release and indemnify American Water Chemicals, Inc. against same.