CASE STUDY: THE IMPACT OF FERROUS ION OXIDATION ON SILICA SCALING IN RO SYSTEMS

Mohannad Malki, Technical Director, American Water Chemicals, Inc, 1802 Corporate Center Lane,
Plant City, FL 33563, USA
momalki@membranechemicals.com, Ph: 813-246-5448

Abstract

A 6 MGD reverse osmosis plant in South Texas that was using chlorine to oxidize arsenic for improved membrane rejection was experiencing severe membrane fouling. The ferrous ions in the well water were being oxidized by the chlorine, resulting in ferric hydroxide fouling of the cartridge filters and membranes throughout the system. The RO facility did not have an acid dosing system and the antiscalant in use was not designed for such high ferric concentrations.

Despite numerous cleanings, the productivity of the system would not recover even while differential pressures would return to normal. A membrane autopsy revealed that the ferric hydroxide was seeding silica polymerization on the membrane system, so that even while the ferric hydroxide was removed, the silica scaling was continuing to grow.

A cleaning study was performed to determine the best cleaning chemicals and methodology for recouping the membranes' performance. Lab simulations were then performed to determine the optimal product and dosage for inhibiting scale formation in the presence of high concentrations of ferric ions in the feedwater. Finally, the antiscalant was used on-line at full scale. The normalized data showed excellent control of the scaling and significantly extended times between cleaning. Loss in membrane performance that occurred while the specialty antiscalant was online was found to be due to biological and suspended solids fouling.

I. INTRODUCTION

A 6 MGD plant in South Texas, TX that was commissioned in mid-2004 had been operating relatively smoothly until the EPA's new Arsenic Rule came into effect. The maximum contaminant level (MCL) for Arsenic was reduced from 50 ppb to 10 ppb, and municipal potable water plants around the country scrambled to comply by the January 2006 deadline.

The city's contract engineer performed multiple studies and eventually determined that chlorination was the simplest and most effective method to improve arsenic rejection by the RO membranes. The plant, which drew brackish water from the Gulf Coast Aquifer, saw a great improvement in arsenic rejection but also started experiencing more frequent membrane fouling.

The plant feedwater contained 0.6 ppm iron that existed in the soluble ferrous state. The chlorine was oxidizing the iron into the ferric state, making it highly insoluble. The plant had been designed without an acid dosing system, so antiscalant dosing was the only method available for iron control.

The precipitation of ferric salts caused an immediate increase in the cleaning frequency from membrane annual cleanings, to regular cleaning every 4 – 5 months. Increases in normalized differential pressure (ΔP) and decrease in normalized permeate flow (NPF) would be observed immediately after cleaning.

Due to heavy production demands, cleaning was only performed by the plant when the trains would shut down due to low concentrate flow alarms. Moderately high pH cleanings followed by low pH cleanings were effective at reversing the increasing pressure differentials (ΔP) across both stages. However, after multiple years of operation, a review of the normalized data found that cleaning was being performed as frequently as every 1 -2 months, and that the normalized permeate flow (NPF) was irreversibly trending downwards over time.

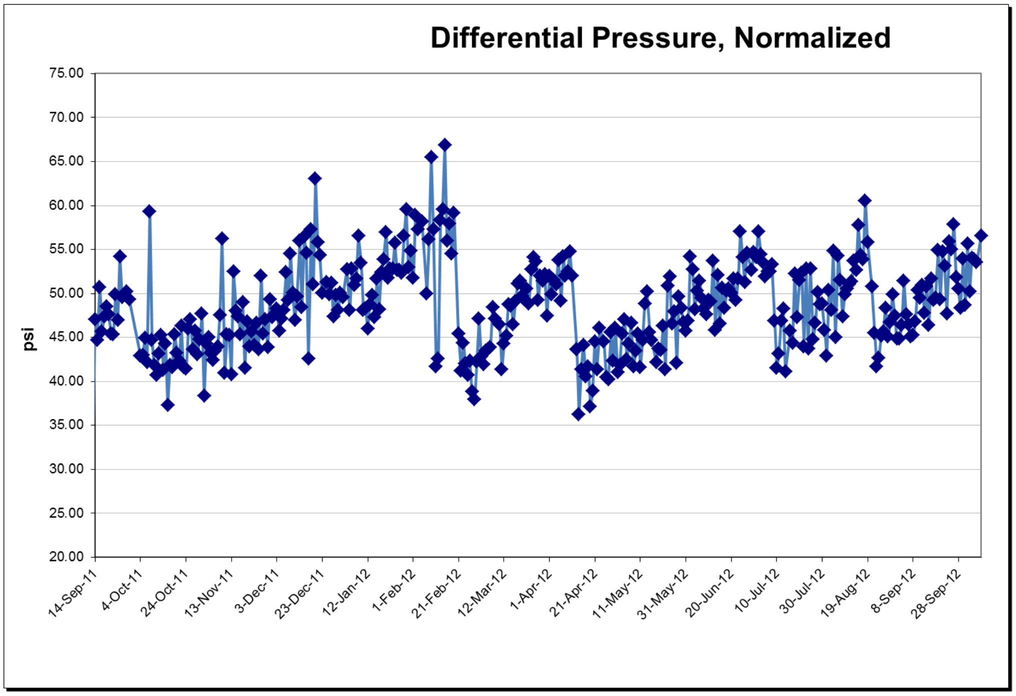


Figure 1: Normalized differential pressure (NΔP) for 6 MGD plant in South Texas over a 1 year period. Cleaning frequency had increased, with intervals to reduce NΔP decreasing from ~120 days to ~30 – ~60 days

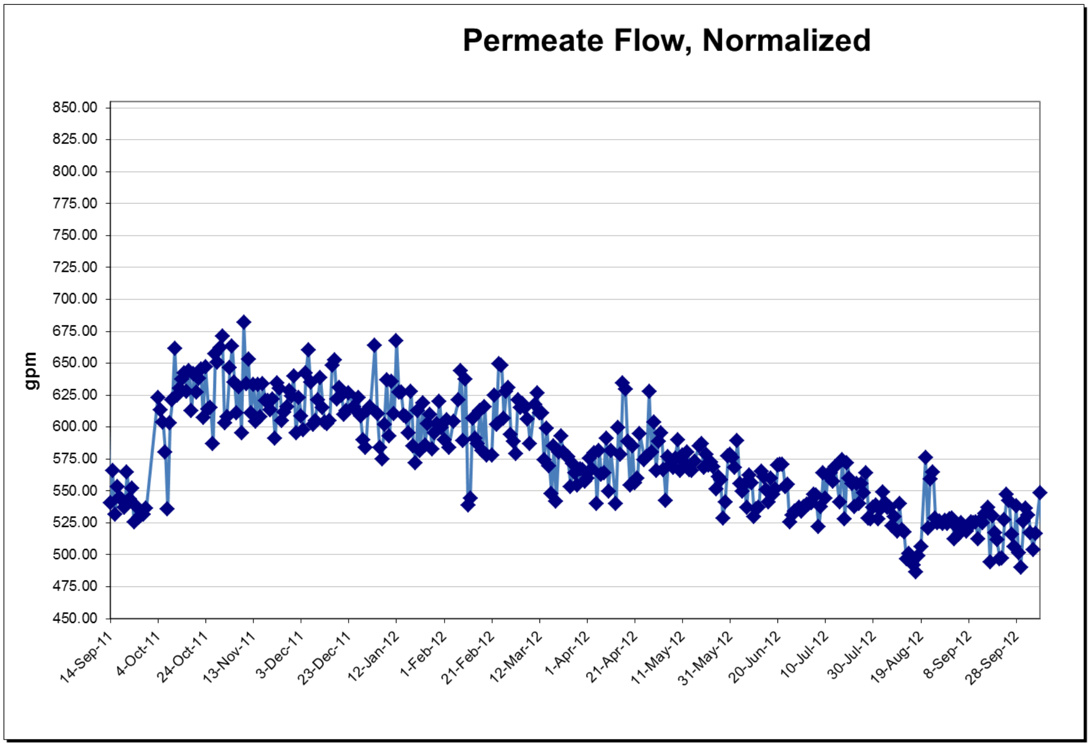


Figure 2: Normalized Permeate Flow (NPF) for 6 MGD Plant in South Texas over a 1 year period. It is evident that although increased NΔP was reversed with each cleaning, NPF was not recovered.

A membrane autopsy found heavy iron fouling, silica scaling, suspended solids and biological fouling on the tail elements of the second stage. Since the feed water concentrations were not considered overly high, an in-depth study was conducted to identify the cause of the silica scaling. This included a review of the water quality, lab simulations, cleaning studies, and finally, a full scale cleaning and full scale antiscalant trial at the plant.

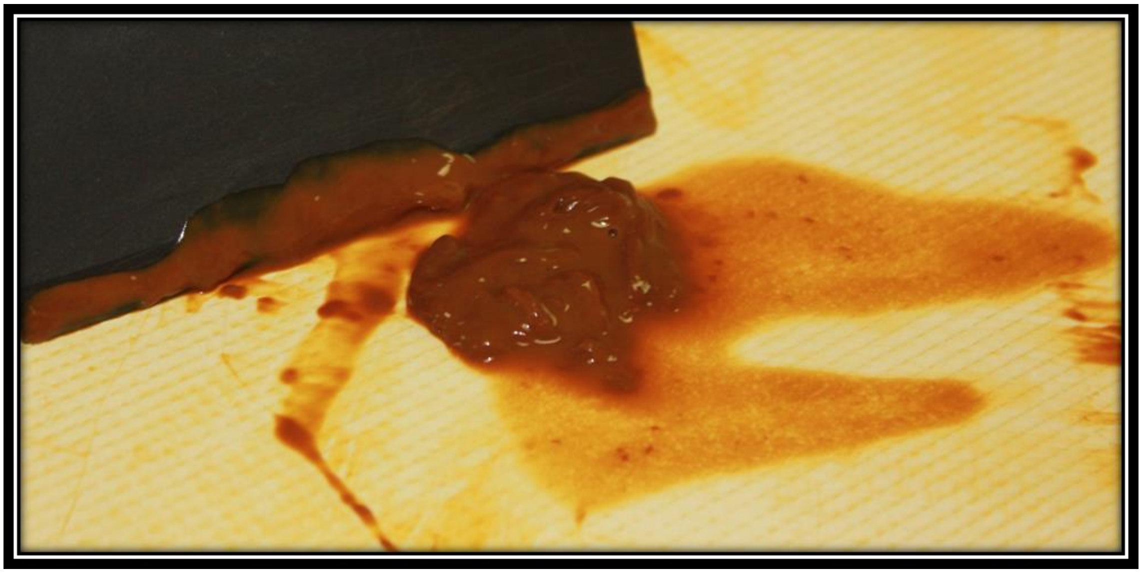


Figure 3: Foulant collected from tail element membrane surface during autopsy.

Table 1: Localized EDS analysis from membrane autopsy. Iron salts and silica were found to be the predominant foulants.

Element	Weight%	Atomic%
Na K	1.40	2.40
Mg K	2.96	4.78
Al K	1.35	1.96
Si K	15.66	21.89
P K	11.85	15.02
S K	4.38	5.37
Cl K	0.22	0.25
K K	0.28	0.29
Ca K	16.43	16.10
Fe K	45.47	31.96
Totals	100.00	

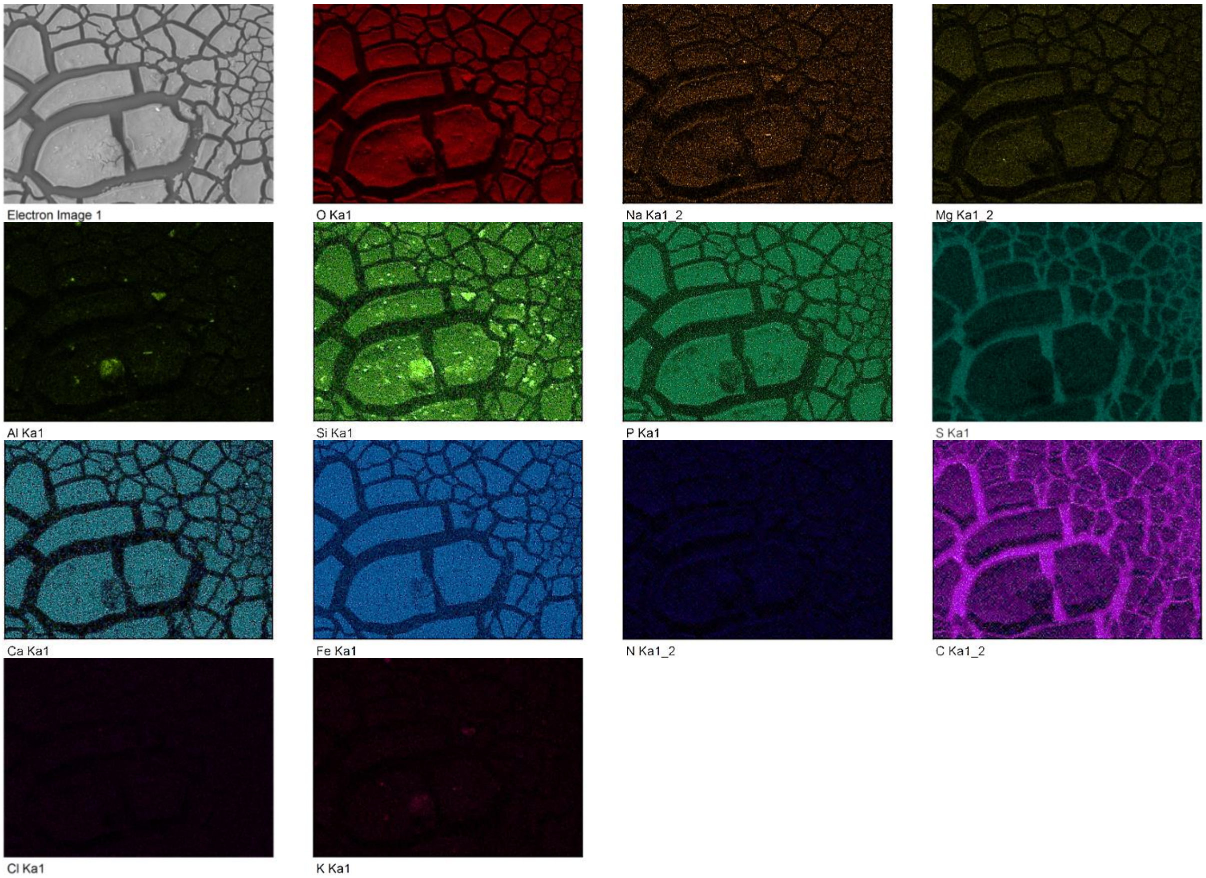


Figure 4: Prismatic Elemental Mapping of the membrane surface. Silica was clearly present in the same pattern as the ferric hydroxide and ferric hydroxyphosphate. Calcium carbonate scaling was also present, likely due to preferential adsorption of the antiscalant to the ferric salts.

Table 2: Localized EDS analysis from membrane surface. Silica buildup was extremely high in certain areas.

Element	Weight%	Atomic%
Na K	0.95	1.40
Mg K	1.23	1.72
Al K	0.63	0.79
Si K	51.81	62.77
P K	5.70	6.26
S K	1.99	2.11
Ca K	8.25	7.01
Fe K	29.44	17.94
Totals	100.00	

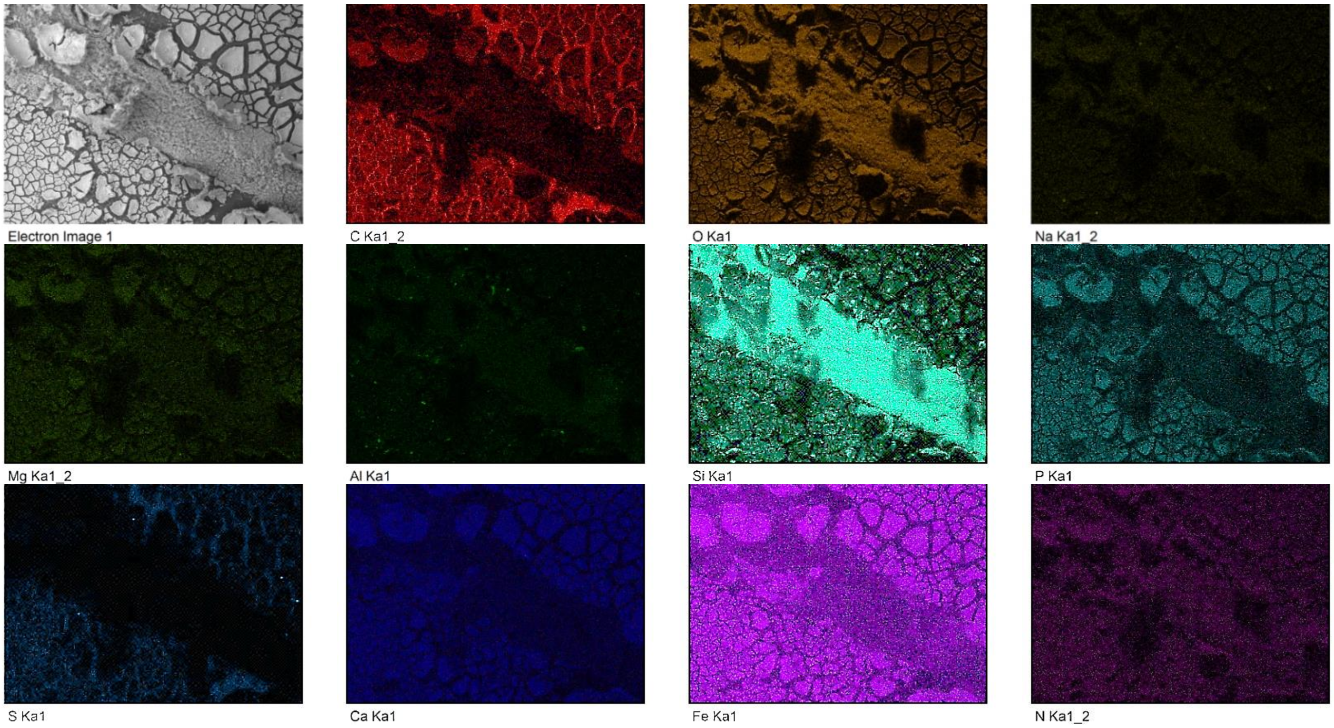


Figure 5: Prismatic Elemental Mapping (PEM): A thick layer of silica scale resulted in a reduced signal from the ferric salts beneath, as determined by a fainter color from the iron map in the region where silica scaling was heaviest.

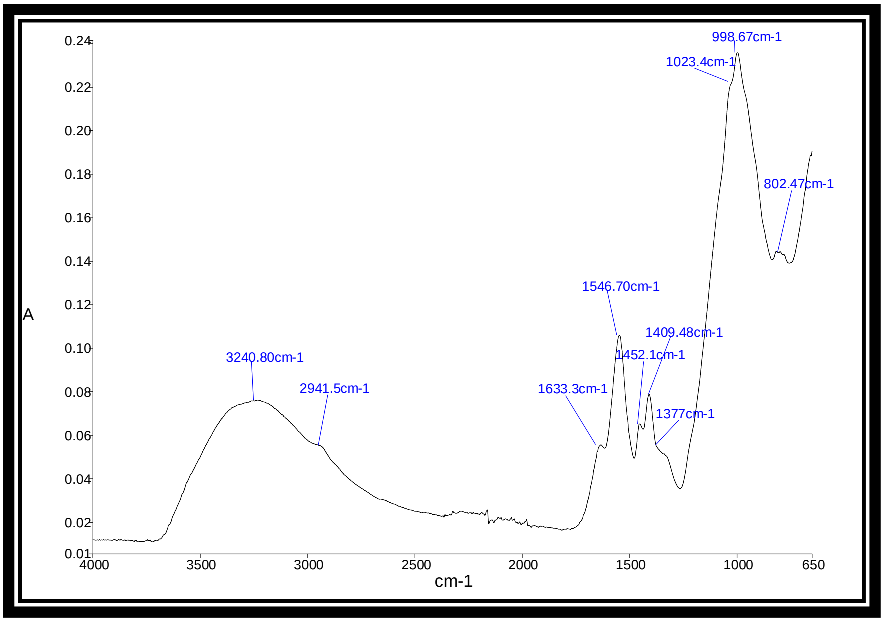


Figure 6: FTIR spectra from membrane autopsy shows biofouling and a strong siica peak.

Table 3: Interpretation of FTIR results from Figure 6

Wavenumber, cm^{-1}	**Band Assignment**
3240.80	O-H stretch, N-H stretch (overlap): Protein
2941.5	C-H stretch: Fatty acids
1633.3	C=O stretch: Protein amide I band
1546.70	N-H bending: Protein amide II band
1452.1	C-H bending: Proteins and Lipids
1023.4	C-O stretch: Polysaccharides
998.67	Si-O stretch: Silica or Silicates

An analysis of a heavy red deposit that coated the pretreatment cartridge filters found the foulant to consist primarily of iron salts and significant biological fouling. This was an indication that the fouling problem was starting ahead of the membranes. An effective solution therefore had to include control of already precipitated ferric salts.

Silicon-oxygen bonds that were identified by FTIR in the cartridge filter foulant were determined to be from silts based on SEM/EDS/PEM analysis of their morphology and chemical composition.

Figure 7: Cartridge filter from pretreatment is heavily fouled with iron.

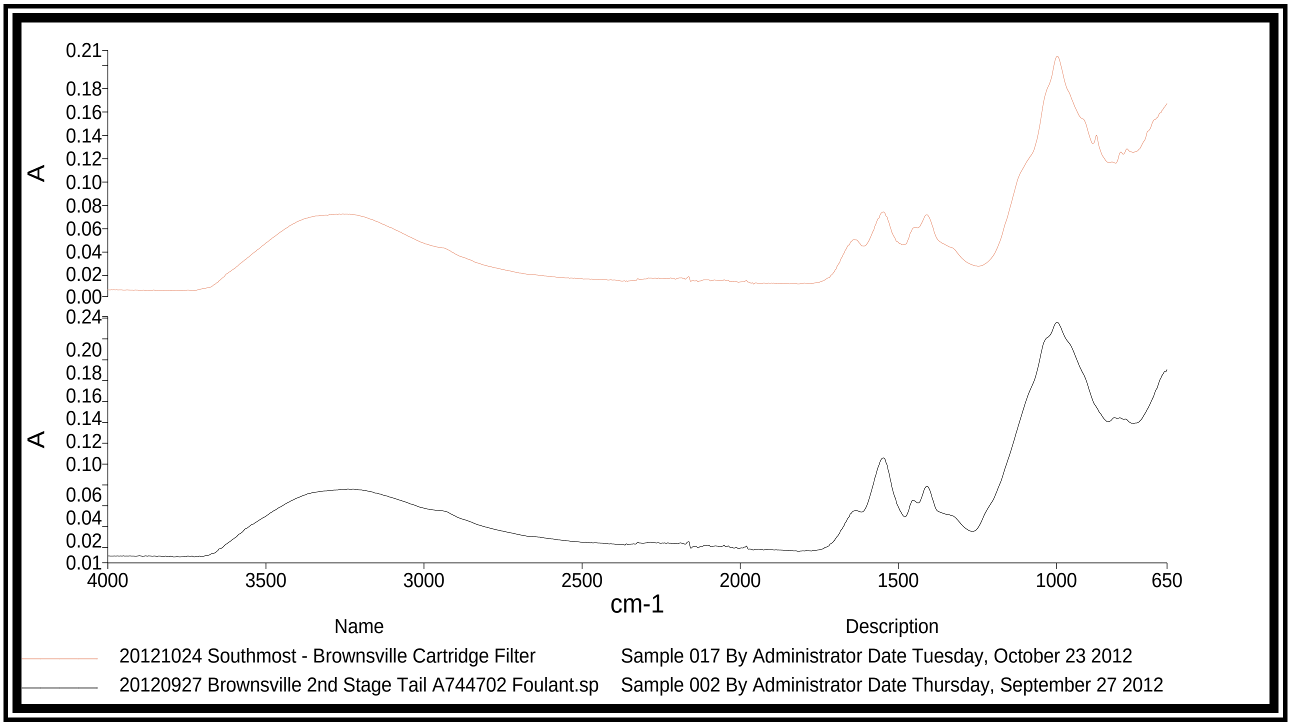


Figure 8: FTIR spectrum of the foulant collected from the cartridge filter compared with the foulant collected from the membrane surface (91.5% correlation)

1.1 General Background

Iron in the ferrous form is very soluble because only a small portion of it hydrolyzes to ferrous hydroxide at neutral pH[1]. In Table 4, the ferrous ion speciation is listed based on the hydrolysis constant [2]as a function of the pH, temperature, and ionic strength of the water in the tail elements of the subject RO plant.

Although the monovalent ferrous ions can react with alkalinity to form carbonate salts[3], their concentration was calculated to be <0.01 ppm.

Table 4: Ferrous hydrolysis speciation in the reject stream (prior to implementation of chlorine oxidation) as a function of pH, temperature and ionic strength

Reject	**Mols**	**mg/L as Fe2+**
Fe^{2+}	4.271E-05	2.3853
$Fe(OH)^{+}$	1.093E-07	0.0061
$Fe(OH)_2$	1.953E-12	0.0000
$Fe(OH)_3^{-}$	1.241E-18	0.0000

Iron in the ferric state is much less soluble because more of it hydrolyzes to an insoluble ferric hydroxide at neutral pH [4]. In Tables 5 and 6, ferric ion speciation based on the hydrolysis constant as a function of pH, temperature and ionic strength, shows that a significant amount of the iron will precipitate as ferric hydroxide.
Furthermore, the monovalent ferric hydroxide species that forms can react with phosphate to form ferric hydroxyphosphate, which is completely insoluble (pKsp =97 [5]).

Table 5: Ferric hydrolysis speciation in the feedwater (post chlorination) as a function of pH, ionic strength and temperature

Feed	**Mol/L**	**mg/L as Fe3+**
Fe^{3+}	8.536E-14	0.0000
$Fe(OH)^{2+}$	9.496E-09	0.0005
$Fe(OH)_2^{+}$	8.812E-06	0.4921
$Fe(OH)_3$	1.789E-06	0.0999
$Fe(OH)_4^{-}$	1.339E-07	0.0075

Table 6: Ferric hydrolysis speciation in the reject stream (post implementation of chlorine oxidation) as a function of pH, ionic strength and temperature

Reject	**Mol/L**	**mg/L as Fe3+**
Fe^{3+}	5.655E-14	0.0000
$Fe(OH)^{2+}$	1.013E-08	0.0006
$Fe(OH)_2^{+}$	2.950E-05	1.6475
$Fe(OH)_3$	1.129E-05	0.6305
$Fe(OH)_4^{-}$	2.021E-06	0.1128

Antiscalants are known to have a higher affinity to ferric ions than to calcium ions based on a comparison of the complexation factors and electronegativities of the two ions [6]. The antiscalant is therefore likely to be consumed by ferric ions that would otherwise adsorb to crystal nuclei for threshold inhibition of carbonate scales.

It is well documented that silica adsorbs to hydroxide bearing surfaces [7], and the presence of ferric hydroxide precipitates will catalyze silica polymerization and allow silica polymers to attach to the membrane surface.

1.2 Study Objectives

The objectives of this study were as follows:

1. Identify the most appropriate cleaning chemicals for efficient removal of silica and iron scales
2. Verify that formation of ferric salts was directly related to silica scaling
3. Identify an antiscalant that would prevent formation of ferric salts and preferably re-dissolve ferric salts that had already formed in the feed water.

II. Procedures

2.1 Membrane Cleaning

A tail end element from the last stage of the RO plant was tested under the manufacturer's standard test conditions (1500 ppm NaCl solution at 150 psi) for the membrane type (Hydranautics ESPA2-365).

The membrane was then cleaned with various cleaning chemicals, and tested under the same standard condion after each cleaning. The high pH cleaning chemicals that were tested were a gentle high cleaner for biofouling (AWC C-237), and a more aggressive high pH cleaner for silica removal (AWC C-236). A low pH cleaning (AWC C-234) was then performed for hydroxide and carbonate scales.

2.2 Review of Water Analysis

The feed water analysis was collected and tested on September 18, 2012. A second feed water analysis was collected by the City's consulting engineer on October 18, 2012 when a different combination of wells were in use, and tested using a different environmental lab. Both analyses were then compared to a water analysis that had been performed on October 20, 2005, about 18 months after plant start-up.

2.3 Lab Simulations and Antiscalant Selection

The feed water analysis from the plant was multiplied by a concentration factor (C.F.) of 4 (based on 75% recovery) and the reject stream was reconstituted accordingly using sodium salts of anions and chloride salts of cations. A C.F. of 4 would only truly apply to trivalent ions since other ionized and non-ionized species would have lower membrane rejection. However, the use of the maximum C.F. was determined to be a more conservative method. An analysis of the concentrate stream was deemed unreliable due to the likelihood of significant precipitation on the membranes.

2.4 Full Scale Testing

Based on the outcome of the lab simulations, a 3 month full scale trial was implemented. The normalized data was reviewed weekly by the author to determine whether the recommended antiscalant was more effectively inhibiting scale formation.

III. EXPERIMENTAL SETUP

Cation and anion solutions were prepared using reagent grade salts to reconstitute the water quality in the reject stream. The cation and anion solutions were each made in large batches to allow for 11 simultaneous tests (10 different products and a control) without variation in dissolved ion content. The cation and anion solutions were then each vacuum filtered through 0.45µm membranes to remove insoluble solids. Finally, the solutions were heated to the target reject water temperature.

The filtered cation and anion solutions were mixed at a controlled rate for each of the tests, followed by continuous stirring on hotplates at 200 ppm for the remainder of the experiment to maintain homogeneity and simulate laminar flow.

The initial turbidity readings were collected immediately upon mixing to capture precipitates that would form in a dynamic system with continuous flow. 200 mL of each solution were filtered through an absolute 100 nm polycarbonate filter for analysis by SEM/EDS and Prismatic Elemental Mapping (PEM). Turbidity readings were collected every 30 minutes thereafter. The readings were compared to those of de-ionized water. Turbidities higher than those of deionized water were associated with formation of sparingly soluble salts. Higher turbidity readings were directly correlated to heavier scaling/fouling in RO/NF membrane systems.

Table 7: Water analysis collected on two separate dates while different well combinations were in use

		9/18/2012	10/18/2012	Average	Calculated Reject based on Avg. Analysis
Ca	mg/L	140	128	134	536
Mg	mg/L	56	53.2	54.6	218.4
Na	mg/L	920	878	899	3596
K	mg/L	12	17.3	14.65	58.6
Ba	mg/L	0.016	0.0156	0.0158	0.0632
Sr	mg/L	4.1	3.67	3.885	15.54
Fe	mg/L	0.6	0.56	0.58	2.32
Mn	mg/L	0.091	0.0812	0.0861	0.3444
Al	mg/L	ND	ND	ND	ND
Alkalinity	mg/L	377.8	419	398.4	1593.6
SO4	mg/L	1065.4	1150	1107.7	4430.8
Cl	mg/L	840	812	826	3304
F	mg/L	1.357	2.32	1.8385	7.354
PO4	mg/L	0.13	-	0.13	0.52
SiO2	mg/L	35.03	37.9	36.465	145.86
PH	Units	7.16	7.2	7.18	7.42
Temp	°C	26.1	27.8	26.95	27

IV. RESULTS

3.1 Cleaning Study Results

The cleaning study found that the membrane performance could be recovered to productivity levels very similar to those measured by the membrane manufacturer prior to installation and use. However, these results were only obtained with the use of the more aggressive silica cleaner , AWC C-236, which was also effective at chelating iron at high pH.

The cleaning protocol consisted of repeatedly alternating circulation for one hour with soaking for 30 minutes for the entire duration of the cleaning process. The membrane cleaning study found that a minimum of 4 hours were required to achieve acceptable cleaning results. However, optimal results with a flux similar to that obtained during the manufacturer's original wet test were obtained after 6 hours of total cleaning time. Based on this outcome, a minimum cleaning time of 4 - 6 hours was recommended for the high pH cleaning in order to substantially remove silica from the membrane surface.

The low pH cleaning did not further improve membrane productivity, but it was beneficial in recovering salt rejection lost after the high pH cleaning. Based on this outcome, it was determined that carbonate salts found during membrane autopsy most likely formed as a result of dehydration of moisture within the foulant. Dehydration is a necessary sample preparation step for both SEM and ATR-FTIR.

Table 8: A cleaning study found that use of a silica cleaner was more effective than a standard high pH cleaner. The low pH cleaning helped recover salt rejection but did not result in improved recovery.

	Manufacturer Specification	Manufacturer Wet Test Results
Permeate Flow (GPD)	8200	7466.00
Recovery (%)	15.0%	13.67%
Salt Rejection (%)	99.50%	99.60%
Specific Flux	0.15	0.14
Differential Pressure (PSI)	N/A	N/A

	AWC Wet Test Pre-Cleaning Result @ 1500 ppm (Normalized for 25°C)	AWC Wet Test Post 1st High pH Cleaning (AWC C-237) Result @ 1500 ppm (Normalized for 25°C)	AWC Wet Test Post 2nd High pH Cleaning (AWC C-236) Result @ 1500 ppm (Normalized for 25°C)	AWC Wet Test Post Low pH Cleaning (AWC C-234) Result @ 1500 ppm (Normalized for 25°C)
Permeate Flow (GPD)	5224.03	5977.30	7099.55	7107.38
Recovery (%)	10.19%	11.45%	13.39%	13.36%
Salt Rejection (%)	98.32%	97.81%	97.39%	98.05%
Specific Flux	0.10	0.11	0.13	0.13
Differential Pressure (PSI)	3.0	2.2	2.0	2.0

A review of the Plant's internal cleaning protocol found that high pH cleaning chemicals were only circulated for 45 minutes and then drained. The Low pH cleaning was also performed based on a similar length of time. pH was measured upon chemical mixing, but was not being monitored during the membrane cleaning process. The RO plant operators were provided with a cleaning procedure and hands-on training based on the exact protocol that was found to be most effective during the cleaning study.

3.2 Water Analysis Results

Two water analyses collected on different days and tested by different environmental laboratories were compared to a water analysis taken 7 years prior. The new water analyses, collected one month apart in late 2012 were very similar showing a relatively stable feed water quality despite the use of different well combinations. Most parameters taken in late 2005 were also found to be very similar.

However, there appeared to be a significant increase in both alkalinity and silica. The feed silica concentration was almost double the value measured in 2005. Orthophosphate was also found to be present in the feedwater sample collected on September 18, 2012. The client had not requested orthophosphate testing for the samples that they had collected, so no comparative data was available from the other water analyses. The presence of even low amounts of phosphate at neutral pH could be problematic due to the extremely low solubility of ferric hydroxyphosphate.

Although silica levels had increased, the silica in the reject stream was calculated to be in the range of 140 – 150 ppm. Such concentrations of silica are not typically considered to be excessive. However, silica adsorbs to hydroxide bearing surfaces [7] and precipitating ferric hydroxide would therefore attract silica to the membrane surface.

Table 9: A comparison of a water analysis from 2005 to more recent analyses performed in 2012 found significantly higher silica values than previously reported.

		10/20/2005	9/18/2012	10/18/2012
Ca	mg/L	145.54	140	128
Mg	mg/L	52.65	56	53.2
Na	mg/L	886	920	878
Ba	mg/L	0.01	0.016	0.0156
Sr	mg/L	3.98	4.1	3.67
Fe	mg/L	0.59	0.6	0.56
Mn	mg/L	0.07	0.091	0.0812
Alkalinity	mg/L CaCO3	358.25	377.8	419
SO4	mg/L	1092	1065.4	1150
Cl	mg/L	769.27	840	812
F	mg/L	0.83	1.357	2.32
PO4	mg/L	Not Tested	0.13	Not Tested
SiO2	mg/L	18.5	35.03	37.9
pH	Units	7.12	7.16	7.21
Temp	°C	23	26.1	27.8

3.3 Experimental Results

Lab simulations were performed to identify an antiscalant and dosage at which precipitation in the tail element membranes could be inhibited. The optimal dosage was found to be 8 ppm using AWC A-108Fe (Product J).

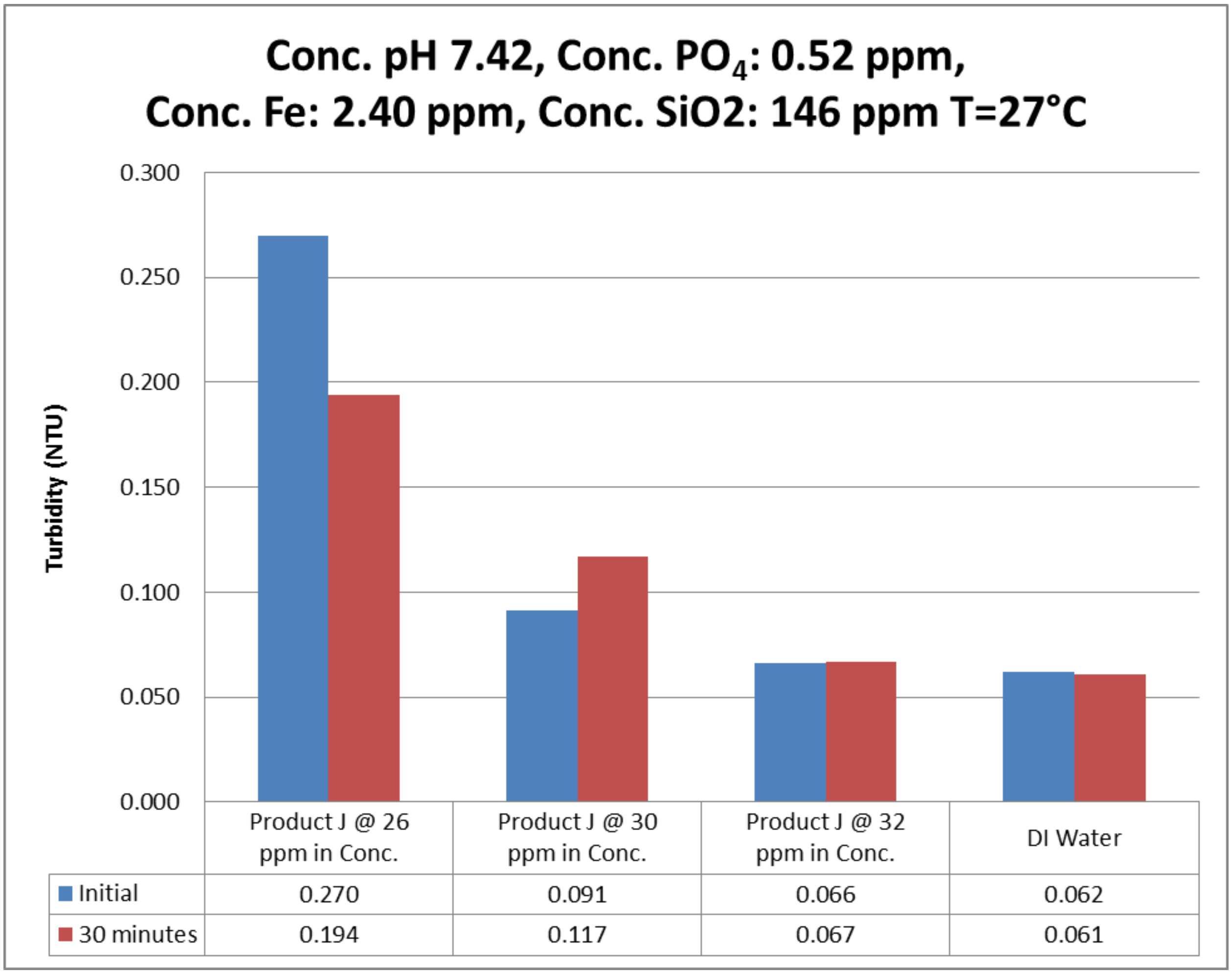
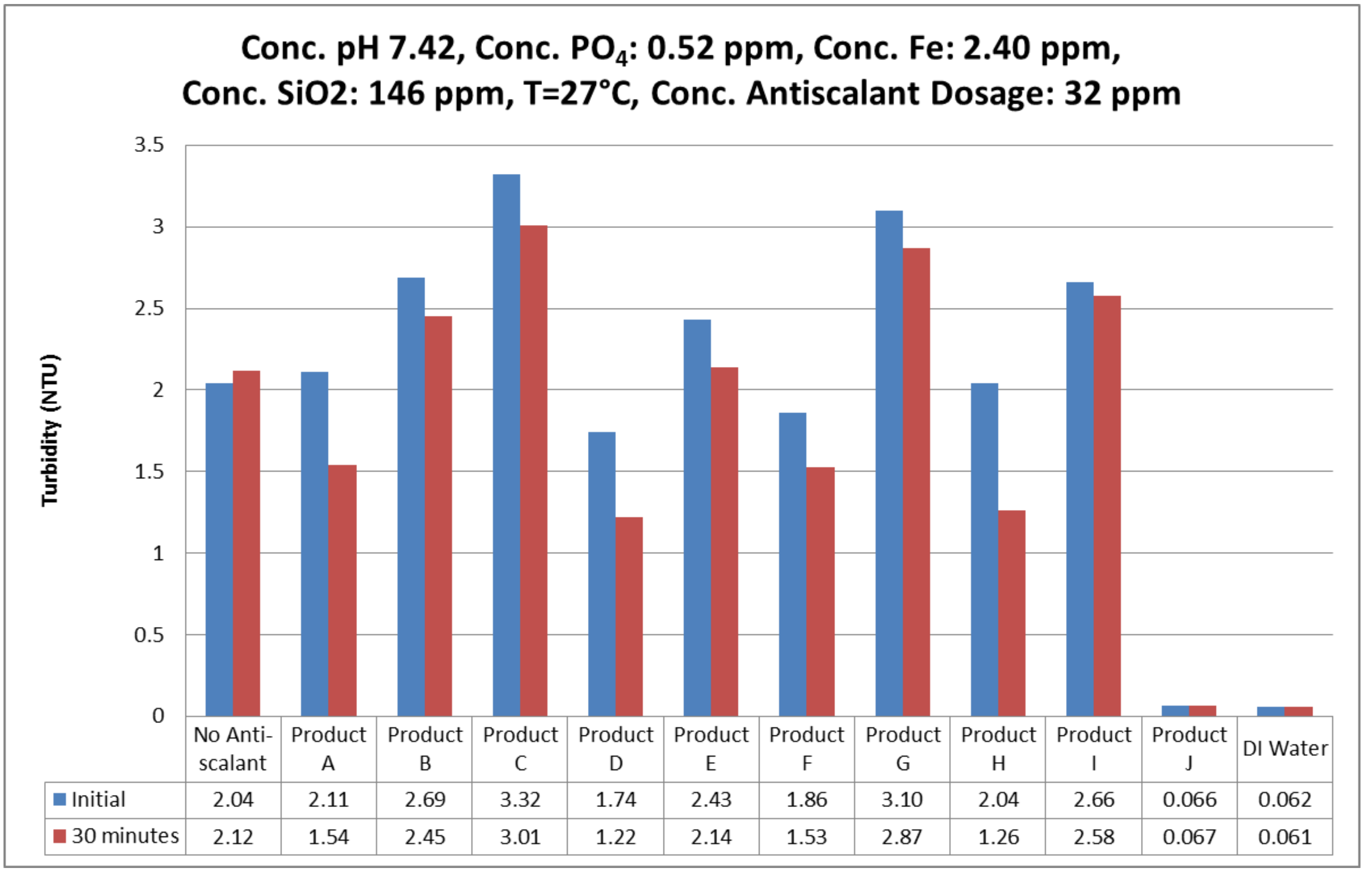


Figure 9: Dosage optimization testing found Product J to completely inhibit scaling and ferric salt formation at a feed dosage of 8 ppm (32 ppm in the reject stream based on 75% recovery)

Nine commercially available antiscalants were then compared to A-108Fe (Product J) at the same dosage. None were found to be effective and many appeared to actually increase precipitation when compared to the control. Product B, a silica antiscalant, was among the products that resulted in heavier foulant formation. SEM/EDS analysis with Prismatic Elemental Mapping (PEM) found the precipitation collected from product B to consist primarily of iron and silica. By contrast, AWC A-108Fe (Product J) formed no precipitation and neither iron nor silica were identified.



	No Anti-scalant	Product A	Product B	Product C	Product D	Product E	Product F	Product G	Product H	Product I	Product J	DI Water
🟦 Initial	2.04	2.11	2.69	3.32	1.74	2.43	1.86	3.10	2.04	2.66	0.066	0.062
🟥 30 minutes	2.12	1.54	2.45	3.01	1.22	2.14	1.53	2.87	1.26	2.58	0.067	0.061

Figure 10: A comparison of 9 commercially available antiscalants with A-108Fe (Product J)

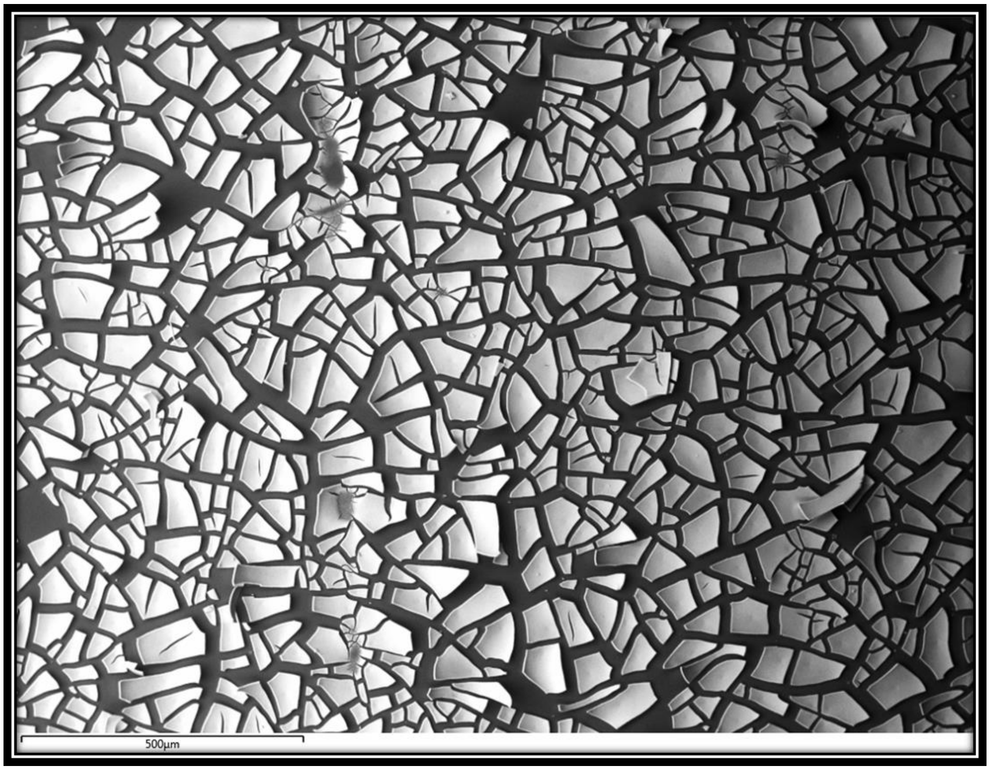


Figure 11: Filtered precipitate from Product B (a silica antiscalant) test (Turbidity=2.69 NTU)

Table 10: EDS Analysis of precipitate from Product B test shows silicon to make up the majority of the precipitate, along with iron.

Element	Weight%	Atomic%
Na K	1.70	2.62
Mg K	0.60	0.88
Al K	0.43	0.56
Si K	50.05	63.14
P K	2.45	2.81
S K	0.64	0.71
Cl K	0.77	0.77
Ca K	4.01	3.54
Fe K	39.34	24.96
Totals	100.00	

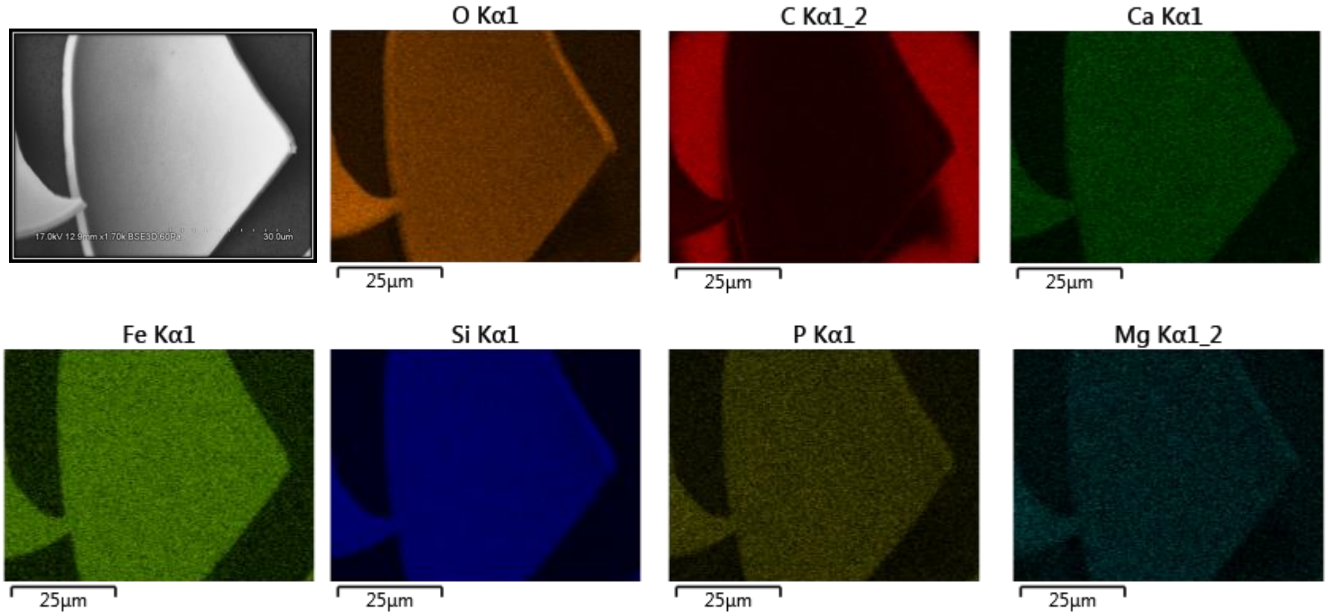


Figure 12: Prismatic Elemental Mapping (PEM): Filtered precipitate from Product B (a silica antiscalant) test shows silica co-deposited with iron on filter surface

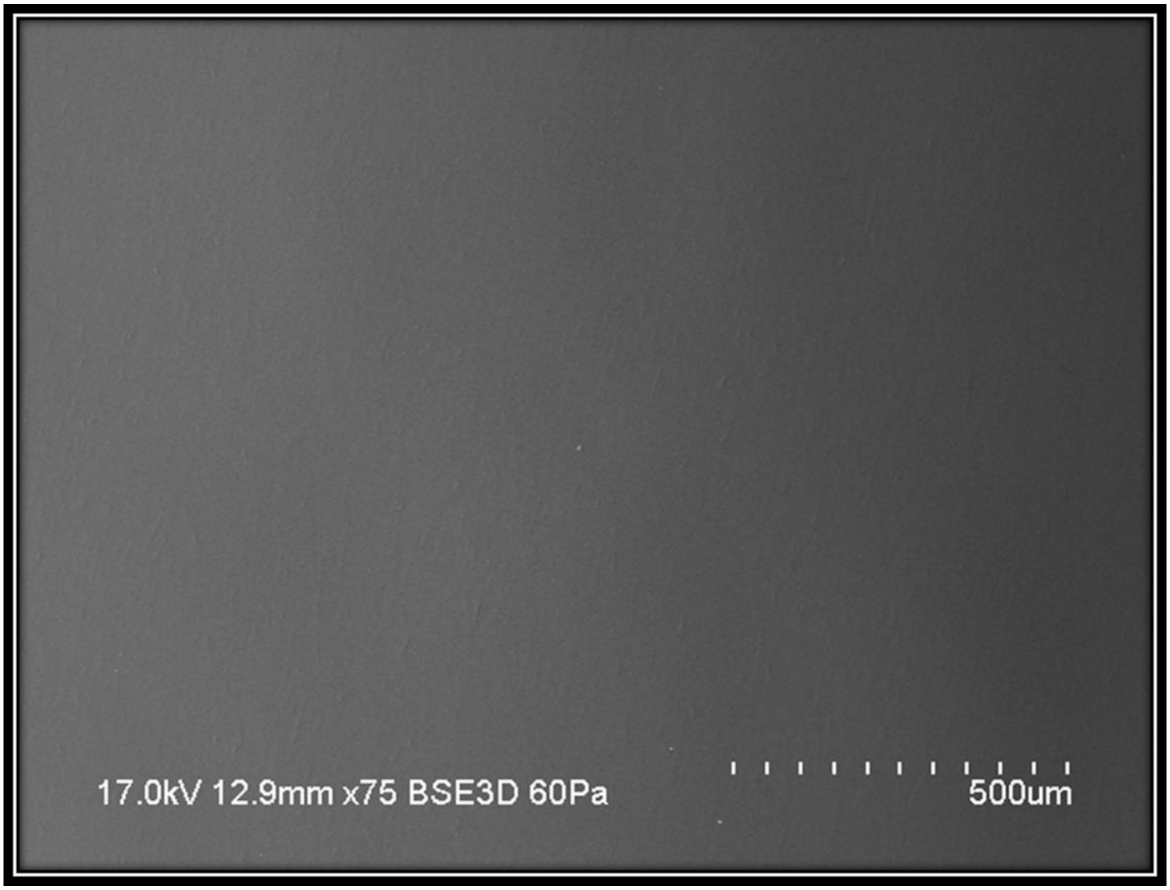


Figure 13: SEM image of filter surface from test using Product J (Turbidity = 0.066 NTU)

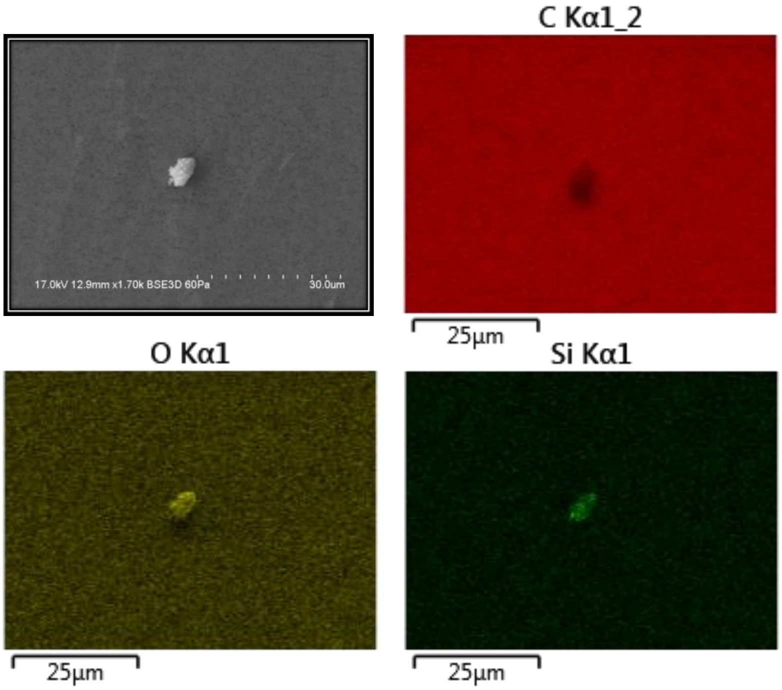


Figure 14: The small deposit found upon filtering the Product J test solution was found to consist primarily of iron and silica. No silica was deposited in areas of the filter surface where iron had not deposited.

3.4 Full-Scale Trial Results

The plant had 6 – 1 MGD trains named alphabetically A – F. A cleaning was performed on Train E prior to the start of the full scale trial.

The antiscalant trial was performed at only 6.5 ppm. Although the lab results found 8 ppm to be the most effective dosage, such a dosage was not economically feasible. Furthermore, the assumption was made that a portion of the precipitated ferric hydroxide and ferric hydroxyphosphate would be trapped on the cartridge filters and in the first stage elements. This would reduce iron loading on the tail elements where the silica concentrations were high enough for polymerization to occur.

At exactly 60 days a power outage occurred that shut down the well pumps. When the power returned, the dosing pumps which had been temporarily set to run independently of the flow-meters, started to dose even though the plant had not been restarted. As a result, antiscalant was dosing into stagnant water in the main header that supplied water to all the trains. This resulted in a severe antiscalant overdose that was labeled in the normalization graph. All the trains showed a severe downward trend upon this occurrence, although Train E appeared to be less impacted by the incident. There were no major increases in differential pressure across Train E (normalized data was not available for the individual stages) and the trial was therefore continued without membrane cleaning. At the end of the 90 day period, the antiscalant trial was determined to be successful and the plant continued use of the AWC A-108Fe.
Soon after the completion of this trial, the membranes were replaced with 400 ft^2 membranes in order to increase the capacity of the plant. For this reason, no long term normalized data was available beyond the 3 months at which Train E was observed.

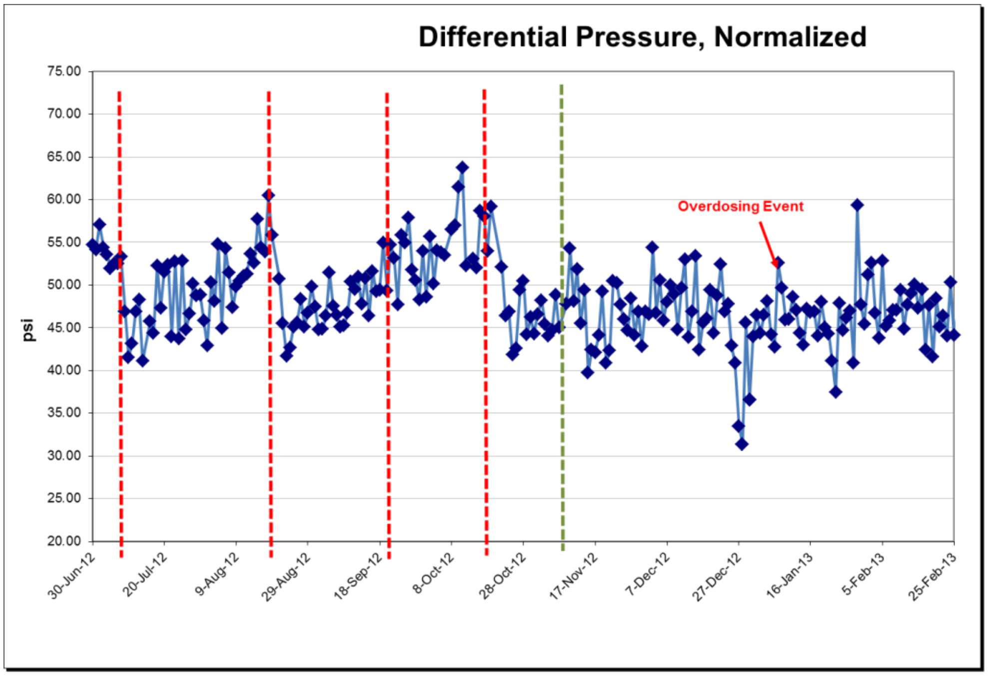


Figure 15: Normalized differential pressure (N∆P) during full scale trial using AWC A-108Fe

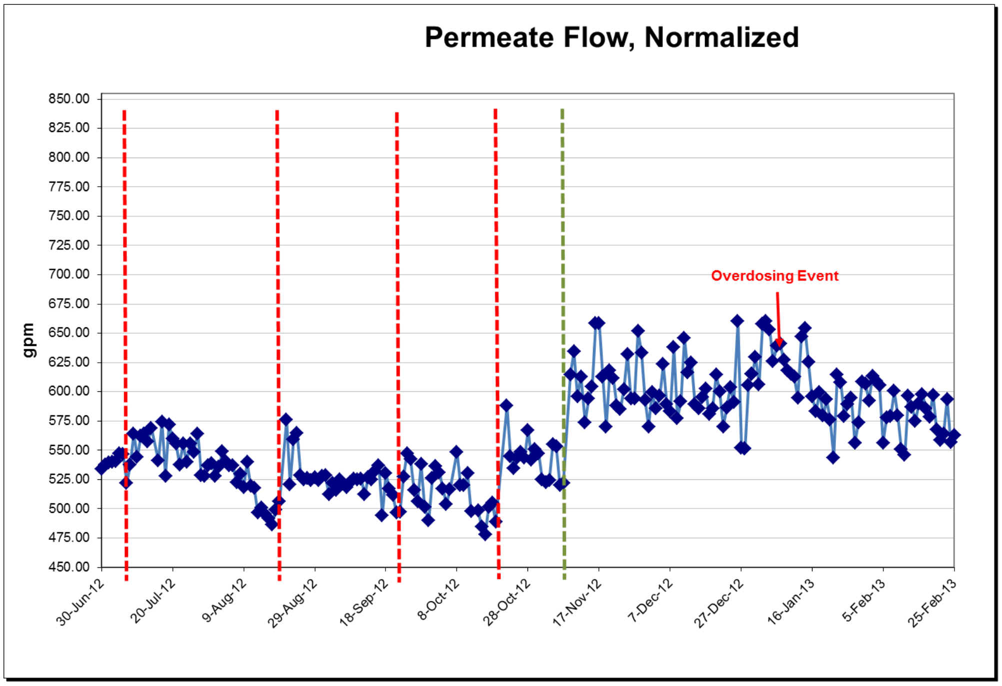


Figure 16: Normalized permeate flow (NPF) data during the full scale trial using AWC A-108Fe. Performance was relatively consistent for over 90 days despite an antiscalant dosing event that resulted in heavy front-end fouling. No cleaning was performed on this specific train.

The new higher surface area membranes allowed the plant to operate at 80% recovery instead of the 75% recovery at which it had operated for the past 8 years. There was initially some concern because planned retrofits were delayed and the cross flow in the second stage was less than optimal.

Despite the more strenuous operating conditions, a membrane autopsy performed on the new membranes about 6 months after their initial installation found no traces of any ferric or silica scaling on the membrane surface. Foulants were found to consist entirely of suspended solids and organic matter (Fig 17,18). Unfortunately, there were numerous instrumentation issues that interfered with the ability to collect reliable normalized data during that time. However, the membrane autopsy and a single element wet test performed at the membrane manufacturer's standardized conditions confirmed that the antiscalant had completely inhibited all scale formation.

Table 11: Pre-autopsy full element wet test compared with the Manufacturer's original wet test results found no loss in productivity (within margin of error for paddle-type flowmeters)

	Manufacturer Specification	Manufacturer Wet Test Results	AWC Wet Test Result (Normalized for 25°C)
Permeate Flow (GPD)	10000.0	9474.0	9171.15
Recovery (%)	15.00%	14.21%	13.77%
Salt Rejection (%)	99.60%	99.60%	99.66%
Flux (GFD)	25.00	23.69	22.93
Specific Flux	0.17	0.16	0.15

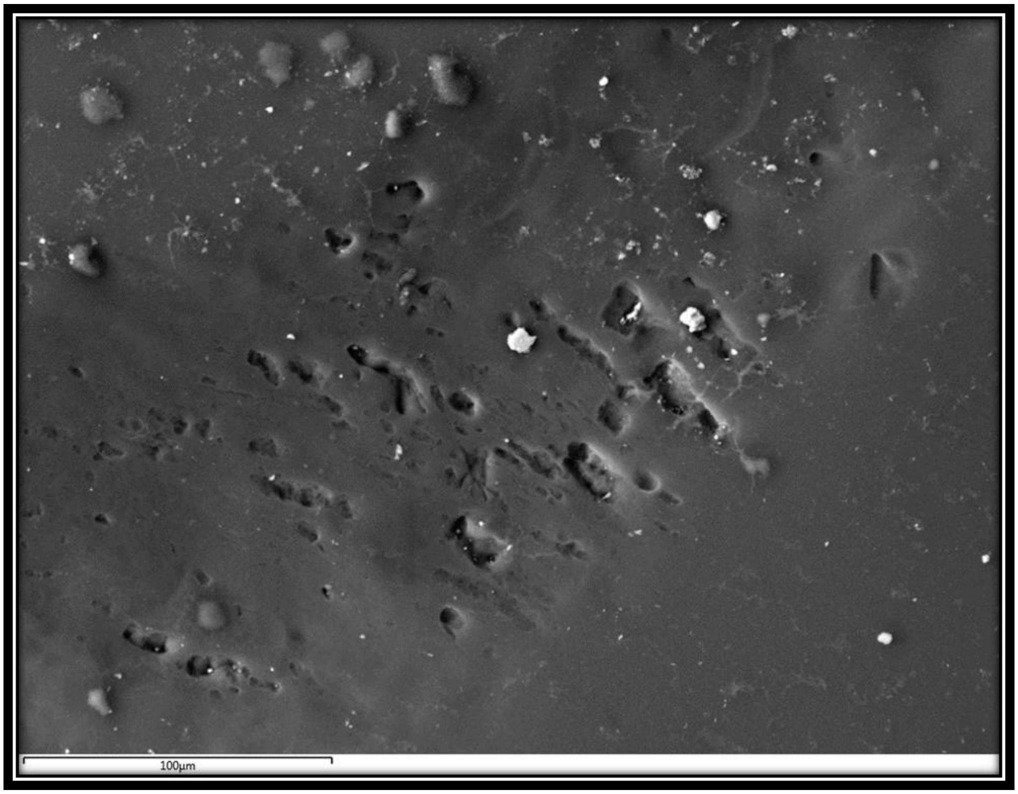


Figure 17: Membrane surface had no scaling after 6 months of operation using the AWC A-108Fe. The surface was so clean that membrane surface damage from suspended solids was clearly visible.

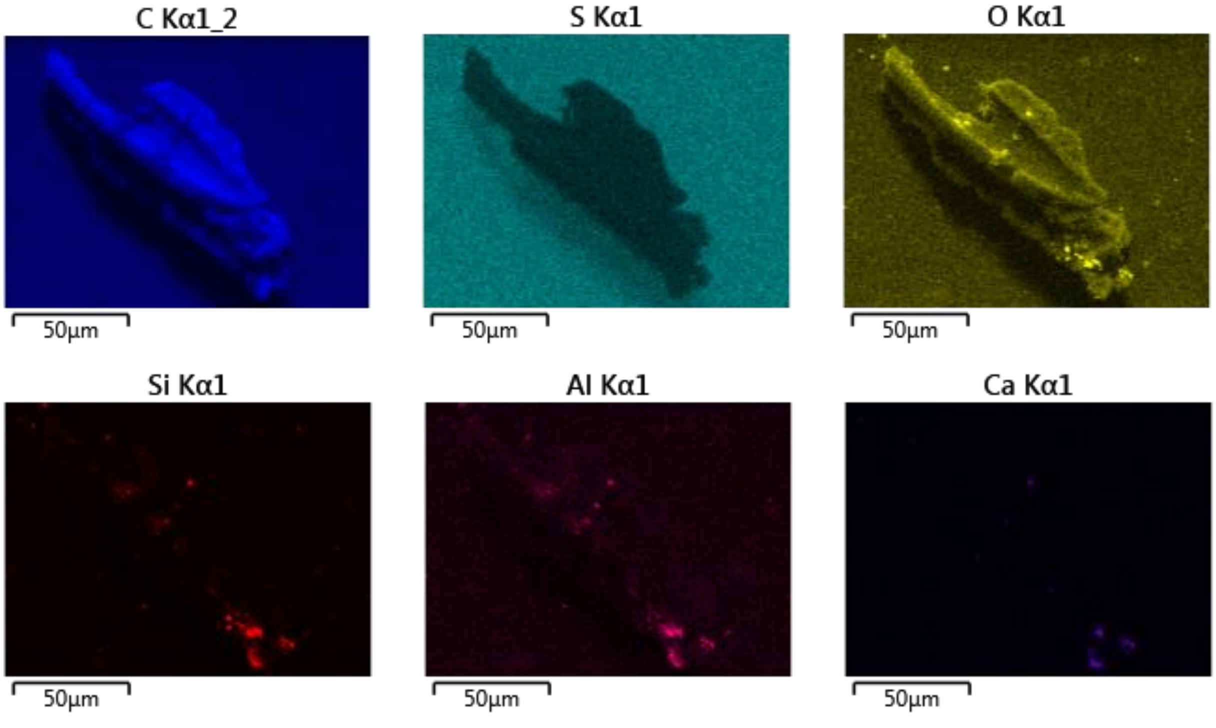


Figure 18: Prismatic Elemental Mapping (PEM) of new membrane surface during an autopsy shows organic deposits and calcium aluminum silicate silts (Garnett).

V. CONCLUSION

Oxidation of iron from the ferrous state to ferric was found to directly result in silica scale formation in reverse osmosis systems, despite silica concentrations being at levels that would normally not be considered problematic.

The use of an antiscalant that was capable of inhibiting ferric hydroxide precipitation resulted in significant improvement in performance and reduced cleaning times. Normalized data from a 90 day full scale trial on the existing membrane elements operating at 75% recovery found the use of a novel antiscalant for ferric ion control to be highly effective at maintaining system productivity. An autopsy on a newly installed membrane after 6 months of continuous operation at 80% recovery revealed that there was no recurrence of silica fouling while the ferric hydroxide was being controlled, despite operation at higher recovery and lower cross-flow.

VI. APPENDIX

PRODUCT DESIGNATION	COMMERCIAL PRODUCT NAME
No Antiscalant	**Control**
Product A	**Avista Vitec 3000**
Product B	**Avista Vitec 4000**
Product C	**Flocon 260**
Product D	**Genesys LF**
Product E	**King Lee Pretreat Plus 100**
Product F	**King Lee Y2K**
Product G	**Nalco 1850**
Product H	**Nalco PC 191**
Product I	**PWT Spectraguard**
Product J	**AWC A-108FE**
DI Water	**DI Water**

VI. REFERENCES

1. R. Cornelis, Handbook of Elemental Speciation II, Wiley (2005)

2. F. Sweeton, C. Baes, The solubility of magnetite and hydrolysis of ferrous ion in aqueous solutions at elevated temperatures, Journal of Chemical Thermodynamics - J Chemical Thermodynamics 2(4):479-500 (1970)

3. R.D. Braun, Solubility of Iron(II) Carbonate at Temperatures Between 30 and 80°,Takmta, 38(2): 205-211 (1991)

4. F.J. Millero, D.Pierrot, The activity coefficients of Fe(III) complexes with hydroxide in NaCl and NaClO4 solutions. Geochim Cosmochim Acta 71:4825–4833(2007)

5. D.W. De Haas et al, The Use Of Simultaneous Chemical Precipitation In Modified Activated Sludge Systems Exhibiting Biological Excess Phosphate Removal Part 4: Experimental Periods Using Ferric Chloride, Water SA, 26, 4 (2000)

6. S. Friedfeld, The Temperature and Ionic Strength Dependence of the solubility product of Ferrous Phosphonate, Rice University (1997)

7. R.K. Iler, The Chemistry of Silica, Wiley (1979)