A RELATIONSHIP BETWEEN PHOSPHATE SCALES AND SILICA FOULING IN WASTEWATER RO MEMBRANE SYSTEMS

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Abstract

Precipitation of calcium phosphate scale on RO membranes continues to be a major challenge for wastewater recycling facilities. In most cases, antiscalant is dosed in combination with sulfuric acid because calcium phosphate solubility improves at lower pH. Several waste water RO plants in California that have attempted to reduce the costly acid dosing have experienced fast scale formation that has offset any savings with downtime and expensive cleaning chemicals. On-line cleanings were attempted by reducing pH to 6 for one week in order to reduce downtime, however, they did not fully restore flux in the tail elements and performance progressively declined over time. When these membranes were autopsied, silica was surprisingly the predominant deposit on the membrane surface even though brine silica concentrations were only in the range of 130 – 160 ppm.   An extensive study was conducted to simulate these conditions in a laboratory setting. Tests were conducted using various antiscalants available on the market and compared against a control that used no antiscalant. For all cases where calcium phosphate scale formed, even when specialty silica antiscalants were used, Energy Dispersive X-Ray Spectroscopy (EDS) analysis indicated the presence of silica. Quantification revealed that silicon made up at least 30% of scales. When Prismatic Elemental Mapping (PEM) was performed, it was found that the silicon was present and evenly distributed in all areas where calcium and phosphorus had deposited. On the other hand, in areas where calcium phosphate had not deposited, no silicon was present. The performance of successful calcium phosphate inhibiting antiscalants was completely diminished when ferric ions were introduced into the water, even when ferric was only present in trace quantities. Since ferric chloride is used as part of the wastewater treatment process, preventing ferric ion carryover can be a challenge. This paper attempts to identify the cause of silica polymerization during formation of calcium phosphate scales at elevated pH, and investigates methods to inhibit this co-precipitation even when ferric ions are present in the feedwater of wastewater RO systems.

I. Introduction

In July 2008, an abrupt drop in permeate flow occurred in all trains of a 70 MGD (265,000 m^3/day) wastewater reuse RO plant in Orange County, California. The plant which employed Microfiltration (MF) pretreatment, antiscalant and sulfuric acid dosing, had been operating without any problems since November 2007. Initial investigations found that the in-line filters in the antiscalant dosing line had been clogged, reducing antiscalant dosing to less than half the dosage. An autopsy on a tail end element from the third stage determined the fouling to consist of about 65% organic materials and 35% inorganic materials. The inorganic components were found to consist mainly of calcium phosphate and silica, along with aluminum and iron (see Table 1). These results were consistent with a sudden increase of orthophosphate in the plant feedwater from <1 ppm to slightly more than 4 ppm (as PO_4).

The membranes were cleaned and placed back on-line, but within a few months, permeate flow was greatly reduced again and was not accompanied by an increase in pressure loss (delta P). Another membrane autopsy was performed, and again calcium phosphate and silica were identified, along with iron and organics.

Table 1:EDS results from autopsy on membrane from Orange County. Sulfur is from the polysulfone component of the membrane.

Element	Wt%	At%
C K	33.34	45.84
N K	5.41	6.38
O K	30.38	31.36
Na K	1.06	0.76
Mg K	0.29	0.20
Al K	2.40	1.47
Si K	9.75	5.74
P K	4.55	2.43
S K	6.16	3.17
Cl K	0.39	0.18
Ca K	5.42	2.23
Fe K	0.85	0.25

Table 2: EDS results from second autopsy on Membrane from Orange County showing high ratio of Si to Ca and P (These results were obtained from an analysis performed for the plant by a third party and the atomic percentages were not provided)

Element	WT%
Carbon	31.2
Oxygen	29.3
Sodium	0.5
Magnesium	1.0
Aluminum	6.1
Silicon	22.9
Phosphorous	1.1
Sulfur	1.2
Potassium	1.2
Calcium	1.6
Iron	4.1

Elemental analysis by Energy Dispersive X-Ray Spectrscopy (EDS) showed that silicon was now disproportionately high, about 20 times higher by weight than either calcium or phosphorous (see

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Table 2). It was likely that silica left behind on the membrane surface after cleaning was "seeding" further silica growth.

Similar trends were seen at another wastewater reuse RO facility in El Segundo, California with a production capacity of 17.1 MGD (~65,000 m^3/day). The orthophosphate in the feed water had increased to more than 9 ppm. Recognizing that calcium phosphate was contributing to the membrane fouling, the operators of this plant attempted on-line cleanings to increase run time. This was achieved by reducing the feed pH to 6 for one week, and then resuming operation at a pH of 6.8 for 3 weeks. Although the online cleanings were substantially effective, permeate production was incrementally lower after each cleaning event. When off-line cleanings were performed, a low pH cleaning with citric acid did little to restore membrane flux. Cleaning with a proprietary high pH cleaner gave acceptable but not entirely satisfactory results. A membrane autopsy at this site also revealed calcium phosphate and silica fouling on the membranes.

In reviewing the feedwater analysis of the first plant, which operated at 85% recovery, it was noted that the silica feedwater concentration had remained very consistent at around 18 - 22 ppm since plant start-up (concentrating to ~120 - 147 ppm in the tail element). However, no decline in performance had ever been detected until the orthophosphate levels increased.

This observation prompted a study to determine whether
1. calcium phosphate scale formation would somehow catalyze silica polymerization.
2. antiscalants that could successfully control phosphate salts would result in reduced silica deposition (which would indirectly support the theory that membrane scaling with phosphate salts would initiate silica scaling).

1.1 General Background:

Dissolved silica exists as monosilicic acid (Fig.1) at low concentrations. As silica concentration increases, polysilicic acid begins to form. Once formed, it will grow to spherical colloidal silica particles or to large polymerized silica networks depending on pH, temperature, silica concentration and TDS [2].

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{OH} - \text{Si} - \text{OH} \\
| \\
\text{OH}
\end{array}
$$
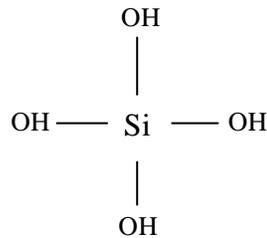
Fig.1: Monosilicic acid

According to Iler [1], silica polymerization at pH>2 is catalyzed by hydroxyl ions as follows: A hydroxyl ion and a silanol group simultaneously adsorb onto the silicon atom, temporarily changing its coordination number from 4 to 6. This destabilizes all the silicon-oxygen bonds causing rearrangements to occur. The ionized silica group then reacts with the non-ionized silanol group, and condensation results in siloxane bonds.

(1) $[(OH)_4SiOH]^- + HOSi(OH)_3 \rightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O + OH^-$
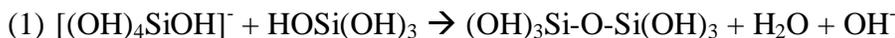
This type of polymerization can occur between silicic acid monomers, polysilicic acid or colloidal silica. Colloidal silica by definition is polysilicic acid with a diameter greater than 50 nm.

As pH increases, more hydroxyl catalysts become available, increasing the rate of silica polymerization. Above pH 6, silica polymerization occurs almost instantly, compared to extremely low pH where silica polymerizes in stages and never exceeds 2 – 3 nm in size [1].

Monosilicic acid and silanol groups on the surface of polymerized silica bodies are weak acids and they deprotonate above neutral pH, gaining an anionic charge. At pH > 7, the dissociation of silanol groups increases dramatically causing silica molecules to repel each other and preventing aggregation [1]. At pH > 9.5, negatively charged ions such as hydroxyl ions are repelled away from the ionized silica, preventing the adsorption of the catalyst and thereby inhibiting polymerization [2].

However, in a typical RO feedwater, there are never pure silica solutions. The presence of cations substantially reduces the repulsion charges of ionized silica, accelerating the rate of aggregation and polymerization [1] and increasing the possibility of silica adsorption onto the membrane surface. Once a monomolecular layer of silica is adsorbed onto a surface, dissolved silica will polymerize with that layer, building up a film of amorphous silica[1].

Magnesium silicate does not precipitate until pH 9.5[1], and since most membrane systems do not exceed pH 8 in the tail element, it is rarely encountered. On the other hand, hydroxides of aluminum, iron, manganese and magnesium co-precipitate with silica [3] and are commonly detected when performing elemental analysis of silica fouled membranes.

Dissolved silica is known to adsorb to hydroxide bearing surfaces [5]. It would therefore be safe to assume that ionized polysilicic acid and colloidal silica particles are likely to adsorb to precipitated hydroxides bearing salts in the tail element of a reverse osmosis system. Dissolved silica in the boundary layer could then form siloxane bonds with the surface adsorbed silica[1], and subsequent polymerization could lead to silica scaling. Based on this logic, the authors of this paper hypothesized that in the absence of the hydroxide salts, dissolved silica that polymerizes in suspension would exit with the RO concentrate rather than foul the membrane. This hypothesis was limited to silica reject stream concentrations between 100 ppm - 300 ppm (at neutral pH) where the authors have found no direct correlation between solution concentration and scaling tendency.

II. Experimental Procedure

An experiment was conducted using the water analysis of the waste water treatment RO plant. The water chemistry in the tail element was reconstituted by separately making anion (as sodium salts) and cation (as chloride salts) solutions, and filtering each of the solutions through 0.45μm filters to remove insoluble particles. When evaluating multiple antiscalants, anion solutions and cation solutions were made in large batches that would then be equally divided using volumetric flasks. The antiscalant was added into the anion solution in each case. The anion solution was then mixed with the cation solution in a beaker at a controlled rate of addition, pH and temperature for each of the tests. The mixing rate was set at 200 rpm for the duration of the test to simulate flow and to maintain a uniform temperature throughout the solution.

Turbidity measurements were taken immediately after addition, and every 30 minutes thereafter. The turbidity readings were compared against the turbidity of demineralized water. Any turbidity value in excess to that of demineralized water would indicate the formation of a second phase, most likely the precipitation of a sparingly soluble salt. In most cases, although precipitation was not visibly detectable, a slight increase in measured turbidity indicated the formation of colloidal sized particles. Such particles could deposit on the membrane surface and act as seeds, reducing the surface energy required for scale formation [10]. This could eventually lead to membrane scaling and loss of flux.

A variety of antiscalants were tested, based on products recommended by each antiscalant manufacturer during a previous antiscalant bid for the wastewater RO plant. The intent was to evaluate the effect of the various antiscalants on silica deposition when calcium phosphate formed and when it was inhibited. In each case, 100 ml of each of the the mixed solutions were filtered immediately upon

mixing using an absolute 0.1 μm filter. The captured precipitates were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

The experiments were performed in three parts:

1. The water analysis in Table 3 but excluding iron
2. The water analysis in Table 3 including iron (in the ferric state) but excluding calcium
3. The complete water analysis in Table 3 including both iron (ferric) and calcium

Table 3 : Feedwater analysis of wastewater reuse RO in Orange County, CA - Recovery=85%

	Raw	Feed	Reject*
Ca	80.70	80.70	538.00
Mg	25.20	25.20	168.00
Na	256.45	256.45	1709.67
K	18.80	18.80	125.33
Fe	0.12	0.12	0.80
Mn	0.05	0.05	0.33
Cl	252.00	252.00	1680.00
SO4	233.00	316.81	2112.07
HCO3	408.70	302.15	2014.33
PO4	4.35	4.35	29.00
SiO2	22.20	22.20	148.00
pH	7.80	7.00	7.50

*Reject values were calculated based on a conservative assumption of 100% salt rejection for all species

The first experiment was performed at 31°C, the highest feedwater temperature recorded at that plant. Calcium phosphate solubility is known to decrease with increased temperature, however, silica is known to be more soluble under those same conditions [11]. The intent was to establish a relationship between silica polymerization and phosphate salt formation under conditions that were more favorable for silica solubility. This first test was performed without iron to avoid any interferences from possible iron hydroxide formation and to avoid iron poisoning of the antiscalants.

The second experiment was performed with 0.8 ppm iron (equivalent to 0.12 ppm ferric in feed @85% recovery) but without calcium. The purpose of this was to determine whether an iron phosphate precipitate would form, and whether it could be controlled by antiscalant. The experiment was again conducted at 31°C.

The final experiment was performed with all constituents in Table 3, including calcium and iron in the water. The purpose was to simulate the normal operating conditions of the water reuse plant. The temperature was also reduced from 31°C to 27°C to reflect the feedwater temperature of the plant for the majority of the year. Only products that performed reasonably well in the first two experiments were tested.

In all cases, spectrophotometric analysis was used to compare reactive silica concentrations in the test solutions with that of their filtrate.

III. Results

Experiment 1 (Analysis in Table 3 without ferric ions):
The control test without antiscalant performed better than Products A, B, C and F, meaning that these products actually catalyzed calcium phosphate precipitation (see Fig.2). Products D, E and G appeared to have no effect on phosphate scale inhibition as they performed no differently than the

control. Only one antiscalant, Product H, substantially inhibited calcium phosphate formation as seen by the extremely low turbidity readings. At 30 minutes, calcium phosphate formation increased in the control but was still lower than in Products A, B, C and F.

The extent of material collected on the filters was directly proportional to the turbidity, and could theoretically be correlated to the extent of scaling in a cross-flow membrane system operating under the same conditions (see Fig.3 and Fig.4). An elemental analysis of the control shows that silicon accounted for the highest percentage of the deposits that covered the filter surface when calcium phosphate was not inhibited (See Fig.3 and Table 4). On the other hand, when the calcium phosphate was substantially inhibited by product H, only a few submicron spherical particles formed that actually had relatively low silicon content (See Fig.4 and Table 6).

Concentrate PO$_4$=29 ppm, Fe=0, pH=7.5, Temp=31°C, Concentrate Antiscalant=33.3 ppm

Turbidiy (NTU)

	No Anti-scalant	Product A	Product B	Product C	Product D	Product E	Product F	Product G	Product H	Demin Water
■ 0 mins	0.175	0.551	0.6	0.551	0.172	0.189	0.273	0.163	0.089	0.069
■ 30 mins	0.351	0.7	0.724	0.717	0.231	0.285	0.391	0.193	0.113	0.069
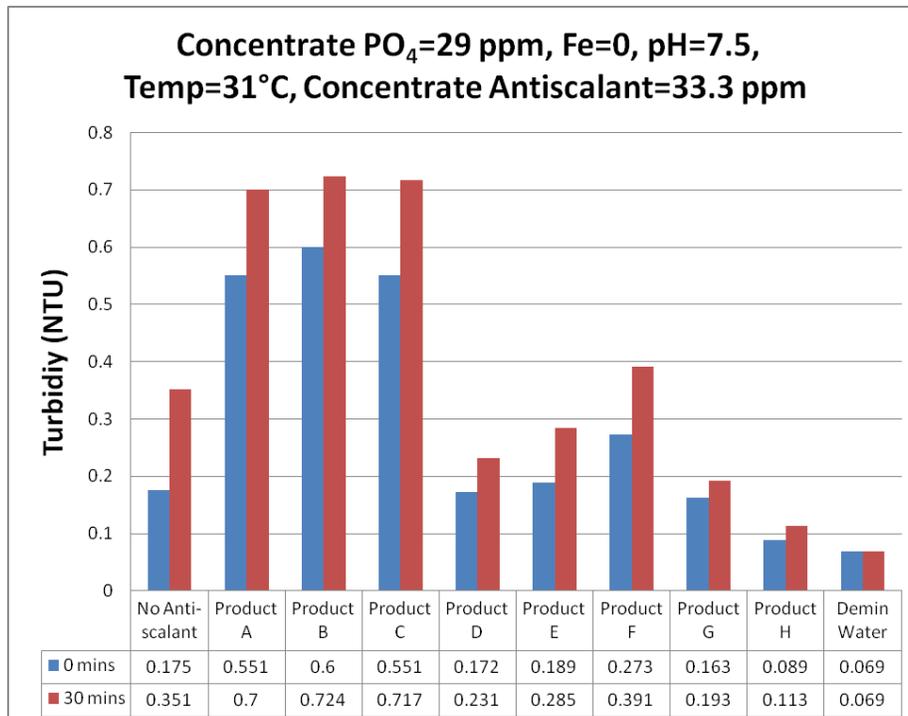
Fig.2: Comparison of calcium phosphate inhibition by various antiscalants in the absence of ferric ions, based on Feed PO$_4$=4.35 ppm, Fe=0, Feed pH=7.0, Temp=31°C, Antiscalant Dosage=5 ppm, Recovery=85%
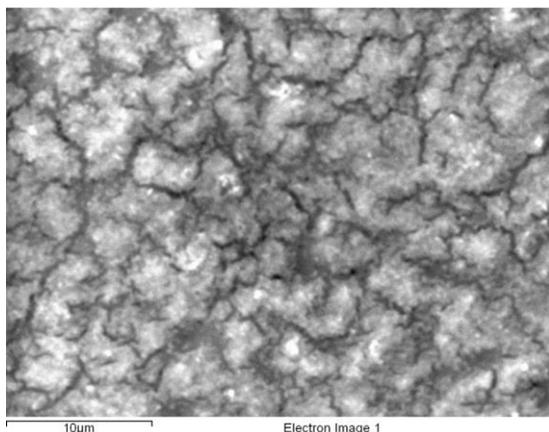
Fig.3: Filtered deposit from solution without antiscalant (Control), turbidity reading= 0.175 NTU
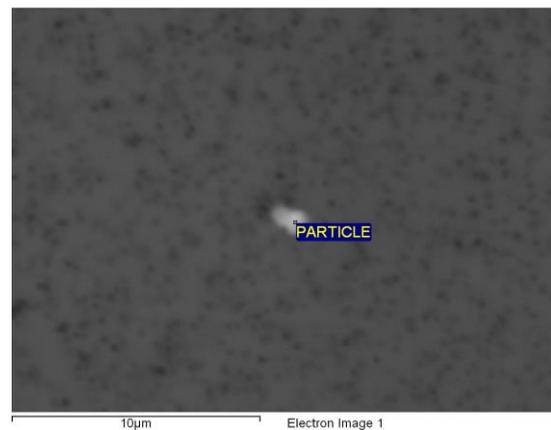
Fig.4: Filtered deposit from solution using Product H, turbidity reading= 0.089 NTU

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Table 4: Elemental analysis of filtered deposit from the Control in Fig.4

Element	Weight%	Atomic%
Na K	6.78	9.18
Mg K	2.03	2.60
Al K	1.93	2.23
Si K	36.79	40.77
P K	15.33	15.40
S K	2.54	2.47
Cl K	4.92	4.32
Ca K	29.66	23.03

Table 5: Localized elemental analysis of colloidal particle in Fig.5

Element	Weight%	Atomic%
Mg K	0.48	0.76
Al K	1.93	2.73
Si K	7.88	10.72
P K	1.14	1.40
Ca K	88.57	84.39

Experiment 2 (Analysis in Table 3 with ferric ions but without calcium ions):

Product B, a phosphonate-free antiscalant with a dendritic polymer structure (according to its marketing literature), performed worse than the control upon mixing (see Fig.5). This indicated possible iron poisoning which is typical with polymer based antiscalants. Phosphate salts of iron, aluminum and magnesium were detected together with high amounts of silica (see Table 6) despite this product's literature claims of silica inhibition up to 300 ppm. The control (no antiscalant) and most products showed improved performance over time, as evidenced by reduced turbidity readings. There were no deposits at the bottom of the beakers, eliminating the possibility that turbidity had improved due to coagulation and subsequent removal of the colloidal particles from suspension. The turbidity decrease was interpreted to be a gradual re-dissolution of iron hydroxyphosphate and iron hydroxide. Being that precipitation occurred instantaneously and redissolution occurred over a 30 minute time frame, the redissolution mechanism would be of little benefit in a cross-flow membrane system.

Concentrate PO_4=29 ppm, Concentrate Fe=0.8 ppm, Ca=0, pH=7.5, Temp=31°C, Concentrate Antiscalant=33.3 ppm

	No Anti-scalant	Product A	Product B	Product C	Product D	Product E	Product F	Product G	Product H	Demin Water
0 mins	0.739	0.497	0.88	0.332	0.191	0.207	0.082	0.102	0.076	0.066
30 mins	0.686	0.313	0.794	0.141	0.099	0.111	0.078	0.114	0.076	0.066

Turbidiy (NTU)
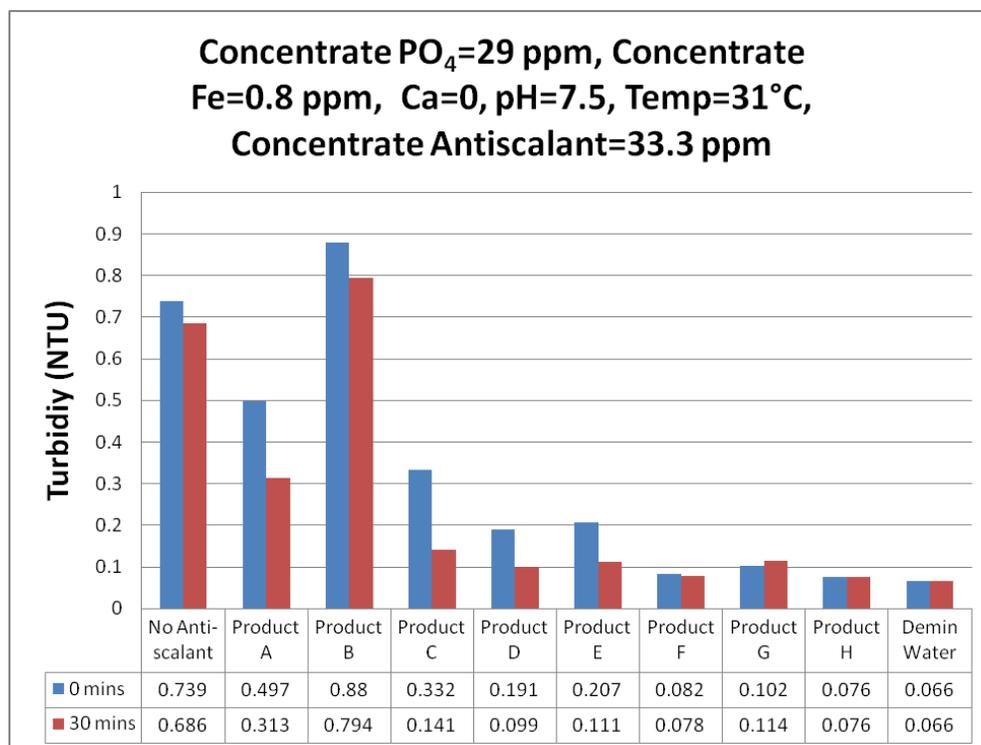
Fig.5: Comparison of ferric hydroxyphosphate inhibition by various antiscalants in the absence of calcium, based on Feed PO_4=4.35 ppm, Feed Fe=0.12 ppm, Ca=0, Feed pH=7.0, Temp=31°C, Antiscalant Dosage=5 ppm, Recovery=85%

Table 6 : Elemental analysis of material trapped on filter from solution using Product B

Element	Weight%	Atomic%
Mg K	10.93	16.41
Al K	2.16	2.92
Si K	18.82	24.45
P K	22.33	26.31
Fe K	45.75	29.90

Experiment 3 (Analysis in Table 3 simulating normal feed water conditions):

Only the better performing products were included in the final test, eliminating Products A, B and C.

The turbidities for the control and all products drastically increased, resulting in values higher than those measured in either of the two previous experiments. The presence of ferric ions clearly exasperated calcium phosphate formation. Product F, which had previously shown excellent control of iron hydroxyphosphate in the absence of calcium now appeared to be catalyzing precipitation (See Fig.6). Product I performed very well, giving turbidity readings remarkably close to demineralized water.

Product G, a popular silica antiscalant, was among the worst performers for calcium phosphate control when ferric ions were introduced (see Fig.6). In interpreting the atomic ratios from the EDS analysis, it seems that both amorphous calcium phosphate and iron hydroxyphosphate were present (see Fig.8, Table 8). Silicon was present in the highest percentage compared to the other elements of which the deposit was comprised.

Concentrate PO$_4$=29 ppm, Concentrate Fe=0.8 ppm, pH=7.5, Temp=27°C, Concentrate Antiscalant=33.3 ppm

	No Anti-scalant	Product D	Product E	Product F	Product G	Product H	Product I	Demin Water
0 mins	1.05	0.669	0.71	1.39	0.995	0.643	0.103	0.069
30 mins	1.21	0.735	0.794	1.71	1.07	0.711	0.114	0.069
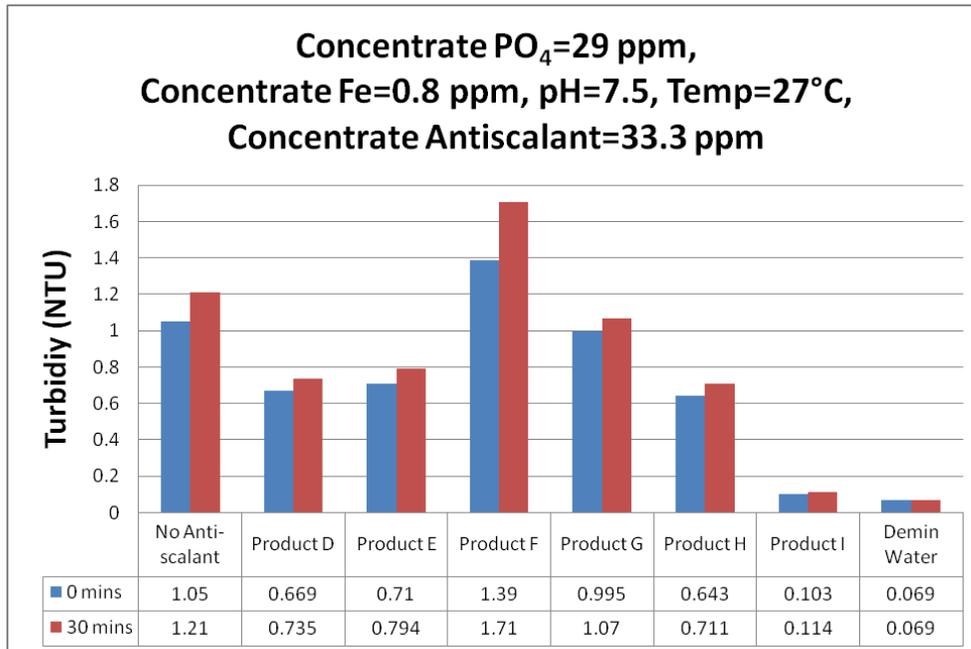
Fig.6: Comparison of calcium phosphate inhibition by various antiscalants in the presence of ferric iron based on Feed PO$_4$=4.35 ppm, Feed Fe=0.12 ppm, Feed pH=7.0, Temp=27°C, Antiscalant Dosage=5 ppm, 85% Recovery

Si Ka1
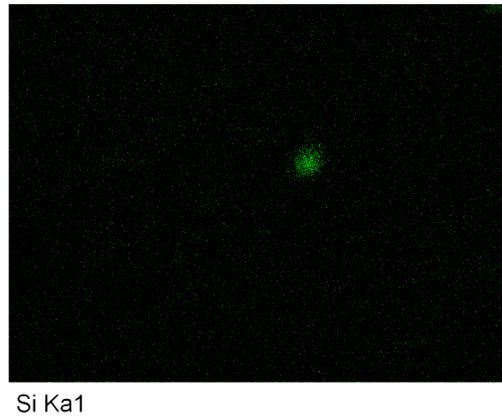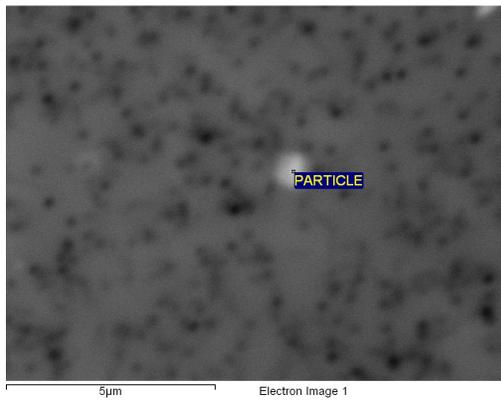
Table 7: Localized elemental analysis of colloidal particle in Fig.8

Element	Weight%	Atomic%
Na K	3.46	4.19
Al K	3.12	3.22
Si K	93.42	92.59

When Prismatic Elemental Mapping (PEM) was performed it was apparent that Product G, a product claimed to inhibit silica up to 250 ppm in the concentrate, was not able to inhibit silica formation when phosphate scales were allowed to form. Higher silica concentrations were directly correlated to higher concentrations of calcium, iron, and aluminum salts of phosphate (see Fig.9) based on the brightness of the elements in the PEM images. This is in contrast to the sporadic deposition of colloidal particles on the filter from the solution using Product I where calcium phosphate scale was substantially inhibited (Fig.7, Table 7).

Table 8: Elemental analysis of material trapped on filter from solution using Product G
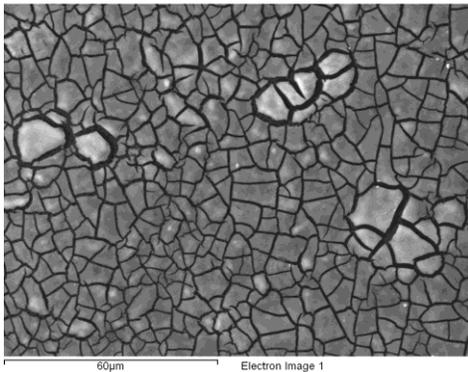
Element	Weight%	Atomic%
Na K	1.18	1.84
Mg K	1.83	2.69
Al K	1.83	2.43
Si K	22.65	28.84
P K	23.10	26.66
S K	1.51	1.68
Ca K	20.68	18.44
Fe K	27.22	17.43

Fig.8: Filtered deposit from solution using Product G

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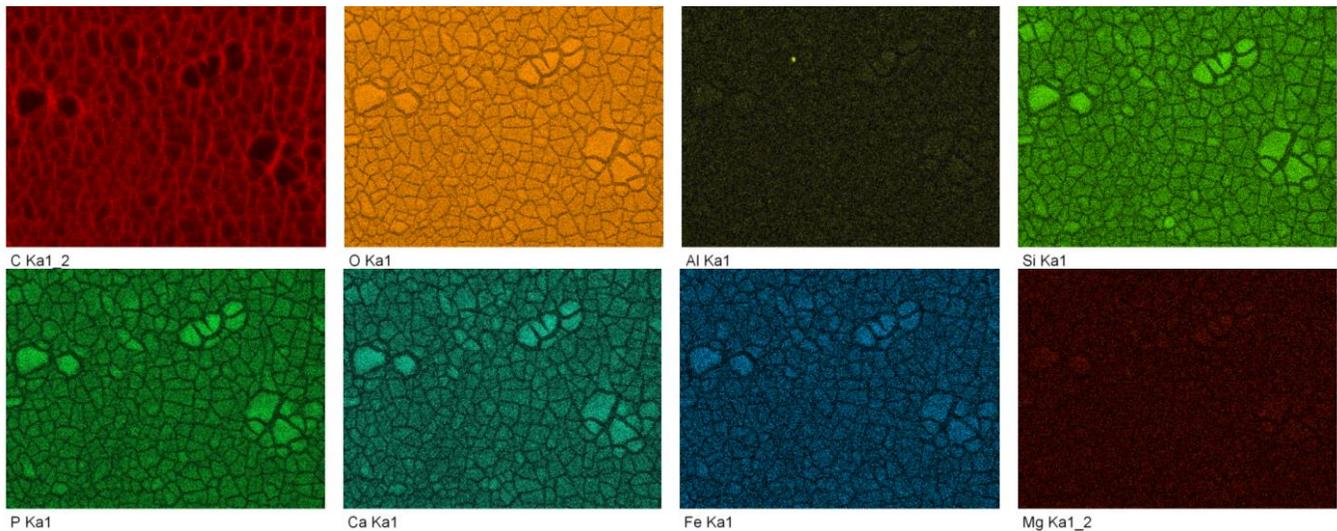
Fig.9: PEM of deposits from solution using Product G, a silica antiscalant. Silica was not inhibited when phosphate salts were allowed to precipitate. The brightest areas indicate the highest concentrations of each element.

In all cases, when silica was measured in the filtered solution by UV/Visible spectrometry, there was no detectable change in reactive silica. The mass of silica that had polymerized was therefore determined to be negligible, indicating that the silica identified by PEM had formed an extremely thin layer.

A supersaturated solution of calcium and orthophosphate above a neutral pH is known to produce amorphous calcium phosphate (ACP) as an initial phase with a Ca/P ratio of approximately 1.5 [4]. The amorphous nature of the collected precipitates was verified by X-ray diffraction (see Fig.10). However, based on the experiments performed without calcium, amorphous ferric hydroxyphosphate [6] also formed, and similarly, amorphous aluminum hydroxyphosphate could have formed. It is widely believed that phosphates adsorb onto soluble hydrolyzed iron and aluminum hydroxides, forming hydroxyphosphates, as opposed to precipitating as iron phosphate or aluminum phosphate[6,9].

The ACP deposit in the SEM images is visibly amorphous and has deposited much like a compacted powder. Most importantly, PEM showed that silica was found to have deposited wherever phosphate salts had deposited, in contrast to the sporadic deposition of silica containing particles seen when phosphate scaling were inhibited.
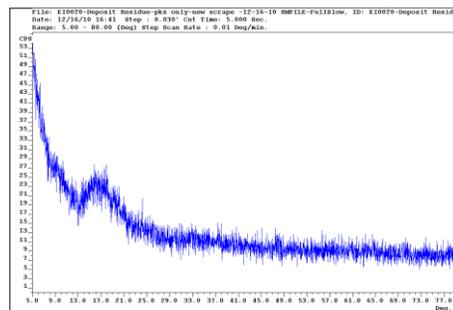
Fig.10: X-ray diffraction of precipitate from solution using Product D, no crystalline material could be identified

IV. Comparison of Filtered Deposit with Scale from Various Autopsies

The authors of this study performed several autopsies on membranes from plants where phosphate salts were not well controlled and feed water silica was concentrating to between $120 - 140$ ppm in the tail elements. PEM imaging consistently showed that silica preferentially adsorbed to phosphate salt deposits (See Appendix).

In an autopsy performed on a membrane from a one month pilot in Clearwater, Florida, it was found that a very small amount of calcium phosphate scale had formed on the membrane (Fig. 11,Table 9). In reviewing the PEM images, the silica deposition was the same pattern as that of calcium phosphate, but was covering a slightly larger area. This indicated that silica had initially adsorbed onto the calcium phosphate scale and then continued to polymerize in all directions resulting in a larger area of coverage on the membrane. What is most noteworthy is that despite the high concentration of silica in the reject stream (225 ppm as SiO_2) at a pH of 7.8, there was absolutely no silica deposition in areas where no scale had formed. Silica is known to be least soluble in the pH range of 7 – 8 [12]. The findings from the autopsies agreed with the results of the experiments performed in this study – amorphous silica adsorbed to phosphate salts but did not deposit in areas where hydroxide bearing scales were not present.
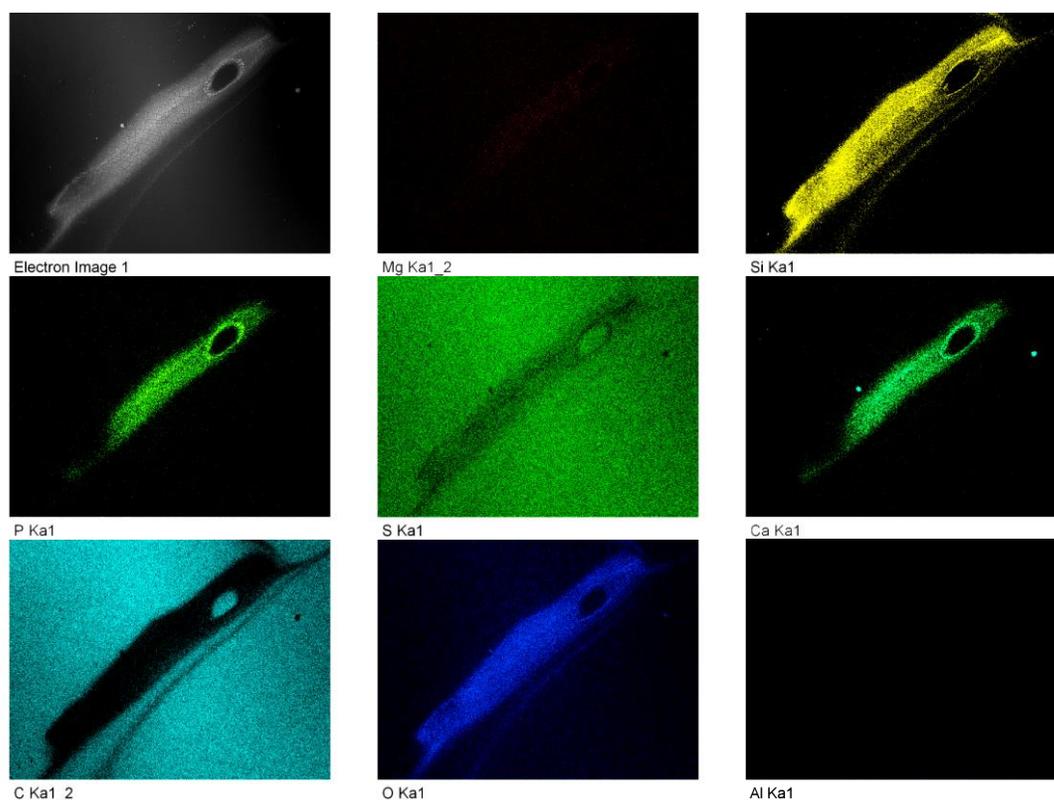
Fig.11: PEM of scale on membrane from Clearwater, FL RO pilot – silica is present only where phosphate salts have formed

Table 9: Elemental analysis of deposit on RO membrane from Fig.17

Element	Weight%	Atomic%
Na K	1.27	1.82
Mg K	1.69	2.30
Al K	0.32	0.39
Si K	18.92	22.27
P K	21.15	22.58
S K	22.76	23.46
Cl K	2.25	2.10
Ca K	29.48	24.31
Fe K	0.61	0.36
I L	1.55	0.41

V. Discussion of Experimental Results and Membrane Autopsy Findings

Whether phosphate salts are precipitated synthetically and filtered or formed as scale on the tail end of a RO membrane element, silica in solution appears to adsorb to the areas where the phosphate salts have formed. Furthermore, based on quantification values obtained by EDS, deposited silica appears to continue to polymerize with dissolved silica, resulting in growth of silica scale.

Silica may be adsorbing to phosphate salts by bonding with hydroxyl functional groups on their surfaces. The chemical formula for ACP is $Ca_9(HPO_4)_x(PO_4)_{6-x}(OH)_x$ [4]. Silicic acid is known to condense with any solid surface that bears OH groups with which it can react [1,5]. As such, silanol bonds can condense with OH groups on the ACP forming P-O-Si-OH bonds.

Similarly, silica can bond with amorphous ferric hydroxyphosphate $[Fe_2PO_4(OH)_3]$ and amorphous aluminum hydroxyphosphate $[Al_2PO_4(OH)_3]$. Ferric calcium hydroxyphosphate salts with the formula $Fe_{1.66}CaPO_4(OH)_4$ are also believed to form [6] which may account for some of the elemental co-existence of iron, calcium and phosphorus in some of the PEM images.

Various studies have also shown that silicon phosphate compounds can form as a reaction product of silica and orthophosphate [7] or polyphosphates [8], which is not surprising since phosphate polymers are structurally very similar to those of silica.

The silanol groups in the adsorbed monolayer of silica on the phosphate salts would condense with dissolved silica (and colloidal silica) in the boundary layer to form siloxane bonds, resulting in multidirectional growth of silica scales. This would explain the disproportionately high percentage of silicon as measured by EDS when compared to Ca and P at the wastewater RO plants as well as the lab simulations.

The mass of phosphate salts that can form is stoichiometrically limited by the phosphate concentration in the water. The feed waters reviewed in this study never exceeded 10 ppm orthophosphate (as PO_4). Furthermore, despite silica being identified by EDS and PEM in all the laboratory experiments, spectrophotometric analysis did not show a measurable decrease in silica concentrations of the test solutions – this indicated that a very thin layer of silica was depositing.

These observations were in agreement with all the autopsy findings. In all cases, the described phosphate-silicate scales were found to have formed a very thin layer on the membrane surface, drastically reducing permeate production without restricting flow through the feed channels. This would explain the symptoms experienced at all plants where this type of scaling was found - the complete loss of productivity without any increase in differential pressure (ΔP).

VI. Conclusion

Amorphous calcium phosphate scale and most phosphate salts will cause silica deposition on membrane surfaces in RO and NF systems. When phosphate scales are cleaned offline with low pH cleaners or online by periodic drops in pH, the phosphate salt deposits are dissolved from the membrane surface. However, the silica that has polymerized within and around the phosphate salt deposits remains intact so that optimal permeate production is never recovered.

Although polymer based antiscalants are claimed to prevent iron and silica fouling by dispersion, they were instead found to catalyze iron phosphate precipitation, resulting in heavier silica scaling. Certain antiscalants that are known to be effective at inhibiting calcium carbonate appeared to catalyze calcium phosphate scaling and resulted in heavier silica scale formation.

Antiscalants that can individually inhibit calcium phosphate scale and iron phosphate scale were found to lose their efficacy when both calcium and iron were present together with phosphate. Since these products performed effectively in controlling iron phosphate, and did not exhibit symptoms of iron

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poisoning, it is proposed that amorphous ferric calcium phosphate may have formed. It is possible that calcium phosphate inhibitors may not be effective at inhibiting amorphous ferric calcium phosphates. However there is also a possibility that a higher dosage of antiscalant may simply have been required. Further studies would be necessary to determine whether this was the case.

Silica antiscalants were found to be ineffective at preventing silica formation in the presence of amorphous phosphate scales. This study showed that the most effective method of preventing silica deposition in RO systems with orthophosphate in their feedwater is by inhibiting formation of any phosphate salts.

Appendix

Product A	King Lee PTP100
Product B	PWT Spectraguard
Product C	Avista Vitec 3000
Product D	Genesys LF
Product E	Nalco PC-191
Product F	Flocon 260
Product G	Avista Vitec 4000
Product H	AWC A-109
Product I	AWC A-110
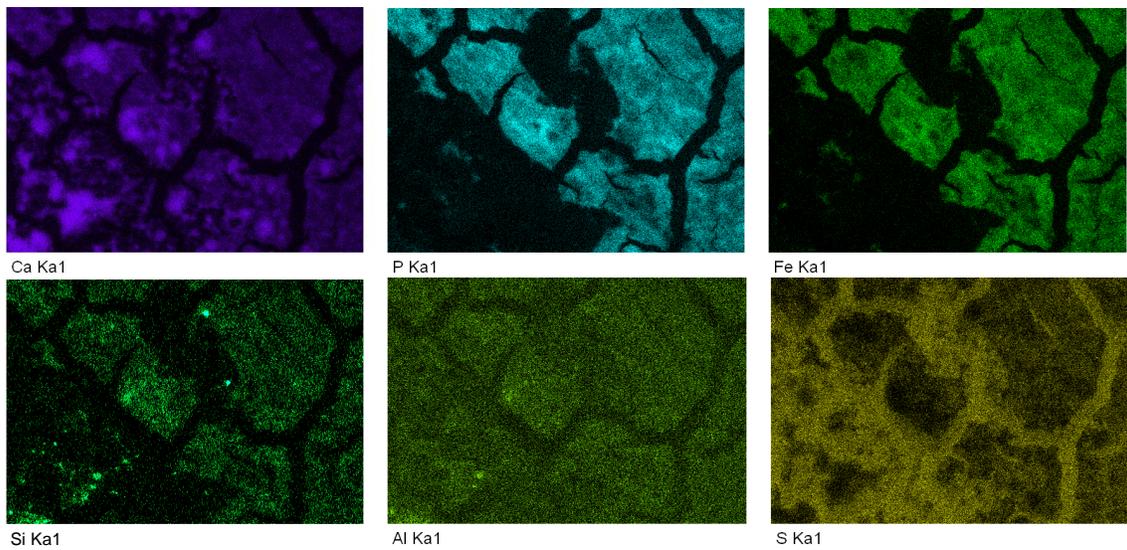
Fig.12: PEM images of scale on membrane surface - Potable RO system in Palm Coast, FL
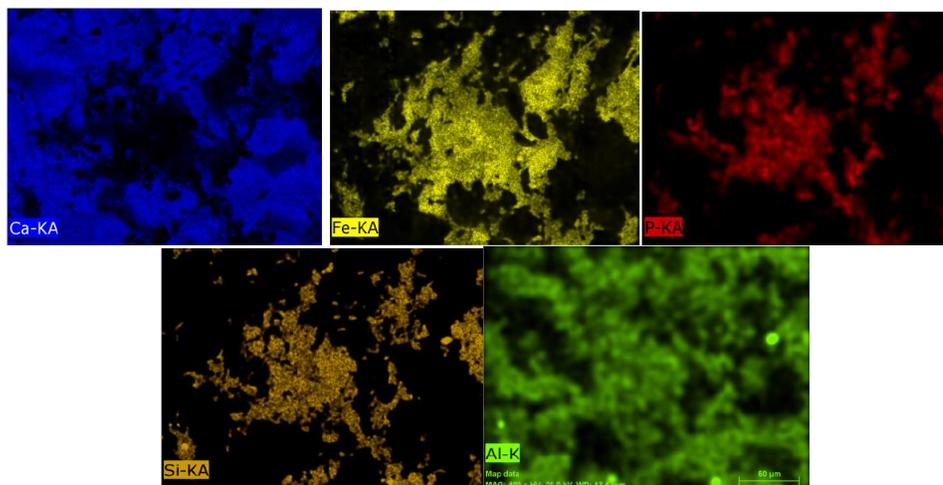
Fig 13: PEM of scale on membrane surface - Potable RO system in Rancho Viejo, TX

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