CONTROLLING ALUMINUM SILICATE FORMATION IN MEMBRANE SEPARATION PROCESSES

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Abstract

Silica scaling is very common in reverse osmosis systems that operate at high recoveries. Whenever silica fouling/scaling occurs, autopsy results almost always reveal the presence of aluminum. The problem is most prominent in membrane plants that use aluminum coagulants, but is also found in plants with non-detectable levels of feed water aluminum.

A review of the literature found only a single study about aluminum silicate fouling in Reverse Osmosis (RO) and Nanofiltration (NF) membrane systems. It theorized that aluminum silicates that can form under the ambient conditions of an RO system would be Kaolinite and Muscovite. These clays are both crystalline and have ratios of 1:1 Al:Si. However, aluminum can interact with silica in many different ways. Its hydroxide can act as a substrate for silica polymerization on the membrane surface and aluminum ions can also adsorb onto surface sites when silicic acid and silica oligomers polymerize.

Numerous laboratory experiments were performed using various dissolved aluminum concentrations with reject silica concentration maintained at 167 ppm. The pH of the solution was always in the range of 7.5-8.5; typical of concentrate pH in the tail element of RO or NF systems operating without acid dosing. The precipitates were filtered and analyzed by SEM/EDS and Prismatic Elemental Mapping (PEM) to determine their morphology and stoichiometry. The results were then compared against SEM/EDS analysis of a membrane foulant from a plant that had experienced co-fouling of silica and aluminum.

This paper investigates the types of silica fouling that would occur in the presence of aluminum carryover from coagulant dosing, and evaluates multiple types of antiscalants to determine if such fouling can be prevented.

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I. INTRODUCTION

Many autopsy reports mischaracterize polymerized silica as aluminum silicate scaling when trace amounts of aluminum are inevitably found by Energy Dispersive X-ray Spectroscopy (EDS).

A search for prior work on aluminum silicate formation in Reverse Osmosis (RO) and Nanofiltration (NF) membrane systems yielded only one study that was performed at the Metropolitan Water District of Southern California (MWDSC), and funded by the US Bureau of Reclamation. The authors of the study (Gaeblich et al) had performed geochemical modeling and concluded that either Kaolinite or Muscovite clays could form. They theorized that sodium, calcium and potassium concentrations would determine the predominant clay species [9]. Kaolinite and Muscovite both have stoichiometric aluminum to silica ratios of 1:1. Gaeblich et al clearly stated that the objective of the MWDSC study was to determine whether the scaling could be inhibited by commercially available antiscalants. They therefore did not attempt to determine whether crystal growth of Kaolinite and Muscovite was kinetically possible during the short residence time in RO systems. All commercial antiscalants were determined to be ineffective at inhibiting aluminum silicate precipitation, even when combined with EDTA or citric acid. Many of the same antiscalants were evaluated in this paper.

Precipitated aluminum hydroxide, amorphous aluminum silicates, and any other hydroxide bearing surfaces[2] can act as substrates for silica polymerization on the membrane surface. This could mean that although aluminum silicates may precipitate, they may not be the primary foulants, but rather initiators for amorphous silica formation.

Aluminum ions and their hydroxides can also adsorb onto surface sites when silicic acid and silica oligomers polymerize. The resulting foulant would consist of amorphous silica with traces of aluminum.

The objective of this study was to:

1. Assess the impact of aluminum carryover from coagulant dosing in silica bearing waters, and to determine whether trace levels of aluminum ion could contribute to scale formation.
2. Differentiate between silica adsorbed onto aluminum hydroxide and aluminosilicate compounds that may have formed.
3. Determine the morphology of aluminosilicate compounds that may form in RO/NF membrane systems (amorphous materials vs. crystalline clays).
4. Identify commercially available antiscalants that can effectively inhibit the formation of aluminosilicate compounds.

II. BACKGROUND

Silica exists in water as silicic acid which has the formula $Si(OH)_4$. When the concentration of silica increases, it begins to polymerize into low molecular weight oligomers. These can continue to grow to larger colloidal polymeric species (Figure 1), and eventually, to an amorphous silica gel [2]. Polymerization typically occurs at concentrations above 100 ppm as SiO_2, with the extent and rate of

polymerization varying with temperature, pH, and TDS. The term "reactive silica" in water analysis reports, refers to silicic acid and very low molecular weight oligomers [2].

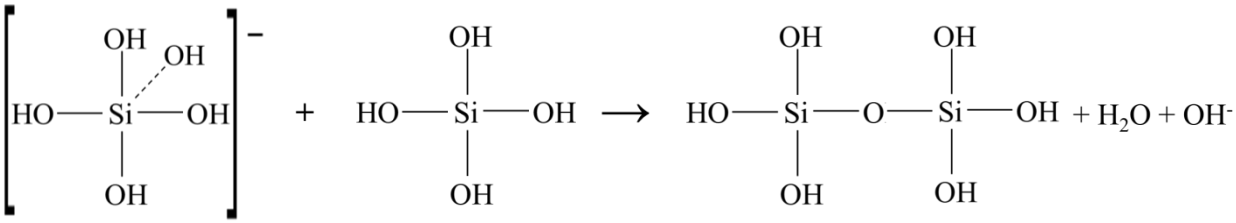


Figure 1 : Silica polymerization [4]

Since silica is a weak acid, it deprotonates with increasing pH. Its oligomers and polymers exhibit the same properties, gaining negative surface charges in proportion to rising pH. At a pH of 8.5, about 10% of silica is anionic [3]. This would theoretically increase its solubility by about 10% as those silica molecules repel each other, preventing the collisions necessary for polymerization.

(1) $$\mathbf{Si(OH)_4 + OH^- = H_3SiO^- + H_2O}$$

However polyvalent cations, such as calcium or aluminum, can act as coagulants that neutralize these repulsion charges [2]. This makes pH irrelevant to silica solubility in typical RO/NF feed water.

Aluminum ions in water are hydrated with increasing pH [7], with the majority of dissolved aluminum existing as $Al(OH)_4^-$ at neutral pH. $Al(OH)_3$ typically precipitates as an amorphous material [10] that has a very low solubility at neutral pH and crystallizes very slowly . Silicic acid strongly adsorbs onto the surface of precipitated aluminum hydroxide. The adsorbed silica then polymerizes with other silica in solution to form a substrate onto which further layers can grow [2]. This interaction with aluminum can cause amorphous silica fouling of the membrane surface even when the water is unsaturated with respect to pure amorphous silica.

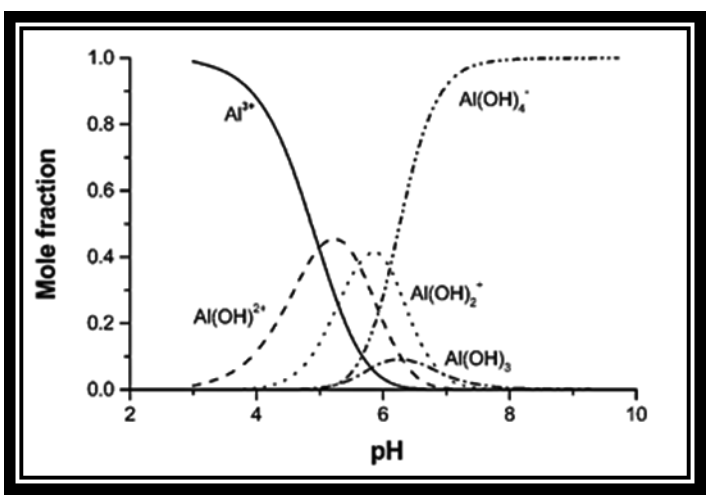


Figure 2: Aluminum hydrolysis products as a function of pH [7] (from Gregory et al, Hydrolyzing metal salts as coagulants, Pure Appl. Chem., Vol. 73, No. 12, 2001, Pages 2017–2026)

Dissolved aluminum can also react with monomeric silica to precipitate Halloysite or Kaolinite [2], which have the same chemical composition but different crystal structures. This process is extremely slow, however, and the following solubility products were obtained by reacting silica and alumina at various pH values for periods as long as 4 years [2]:

(2) $2Si(OH)_4 + 2\,Al^{3+} + H_2O = Al_2Si_2O_5(OH)_4 + 6H^+$, **Ksp = $10^{11.25}$ @ 25°C**

(3) $2Si(OH)_4 + 2\,Al(OH)_4^- + 2H^+ = Al_2Si_2O_5(OH)_4 + 7H_2O$, **Ksp = $10^{-32.98}$ @ 25°C**

III. EXPERIMENTAL SET-UP AND PROCEDURE

Cation and anion solutions were prepared from reagent-grade materials to replicate RO tail element concentrate where scaling potential would be highest. The cation and anion solutions were made in two separate batches and vacuum filtered through 0.45µm membranes to remove insoluble solids. The solutions were then heated to the target temperatures prior to mixing.

Anion and cation solutions were mixed together at a controlled rate for each of the tests. The solutions were stirred continuously on hotplates throughout the experiment at a speed of 200 rpm to maintain homogeneity and simulate laminar flow. The initial turbidity readings were collected immediately upon mixing, keeping in mind that residence time in a tail element would be no more than a few seconds. 200 mL of each solution were filtered through an absolute 100 nm polycarbonate filter for analysis. Turbidity readings were collected every 30 minutes thereafter. Any readings higher than the turbidity of de-ionized water indicated the formation of insoluble salts. Higher turbidity readings were directly correlated to heavier scale formation in RO/NF membrane systems.

The 0.1 µm filters were then analyzed by SEM/EDS and Prismatic Elemental Mapping (PEM) to determine morphology, composition and stoichiometry of the precipitates under the varying conditions.

Using the experimental set up described above, a series of experiments were conducted using a known water analysis from a 70 MGD membrane water reuse facility in Orange County, California. This particular analysis was selected because a previous autopsy performed by a third party determined the presence of aluminum silicate scaling on this plant's tail elements despite aluminum ion concentrations being below the detection limit. Orthophosphate was omitted from the analysis to eliminate phosphate salt formation which would catalyze amorphous silica scaling[1].

Aluminum and calcium concentrations and pH were all varied to observe their impact on the performance of various scale inhibitors and their dosages. When calcium was used, sulfates were always added to minimize calcium carbonate scale formation, so as to create an environment under which silicate salts could easily be identified by EDS.

The tests were performed with the following variations in water analysis:

1. Analysis in Table 1, without calcium or sulfate (Feed Al^{3+}=0.3 ppm and SiO_2 with HCO_3^-, Na^+ and Cl^-) – to identify stoichiometry of aluminum silicate compounds.

2. Analysis in Table 1, without silica, calcium or sulfate (Feed Al^{3+}=0.3 ppm with HCO_3^-, Na^+ and Cl^-) – to compare precipitation behavior and determine whether silica merely adsorbs to aluminum hydroxide salts.

3. Analysis in Table 1, without calcium or sulfate (Feed Al^{3+}=0.3 ppm and SiO_2 with HCO_3^-, Na^+ and Cl^-) at an increased concentrate pH of 8.6 – to compare precipitation behavior to Test #1, given that aluminum and silica are individually more soluble at higher pH.

4. Based on all constituents in Table 1, (Al^{3+} and SiO_2 with Ca^{2+}, HCO_3^-, Na^+ and Cl^-) with multiple tests performed using varying Al^{3+}– to determine the likelihood of aluminum salt formation at low Al^{3+} concentrations and to identify the most effective antiscalants and dosages at varying concentrations.

5. Based on all constituents in Table 1, (Al^{3+} and SiO_2 with Ca^{2+}, HCO_3^-, Na^+ and Cl^-) with multiple tests performed using varying Ca^{2+}– to determine the effect of calcium on antiscalant dosage.

In each of the tests, a control test (no antiscalant) was performed against 9 commercially available antiscalants. All antiscalants tested claimed good control of both silica and metal hydroxides.

Table 1: Feed water analysis

	Feed (ppm)	Concentrate (ppm)
Calcium	87 ppm	580
Aluminum	Variable	Variable
Sodium	487	3248
Chloride	558	3722
Bicarbonate (as $HCO3^-$)	192	1280
Sulfate	317	2113
Silica	25	167
pH	**7.1**	**7.6**
Temperature: 27 °C		
Recovery: 85%		

***Concentrate was calculated based on a concentration factor of 6.67 and an assumption of 100% salt rejection.**

The analytical results were finally compared to those of a membrane autopsy from a 2.7 MGD plant in Long Beach, CA where severe co-fouling of aluminum and silica were found as a result of prior alum coagulant overdosing. The comparison was performed to allow the authors to determine whether precipitates formed in the lab were of a similar nature to those in a membrane system.

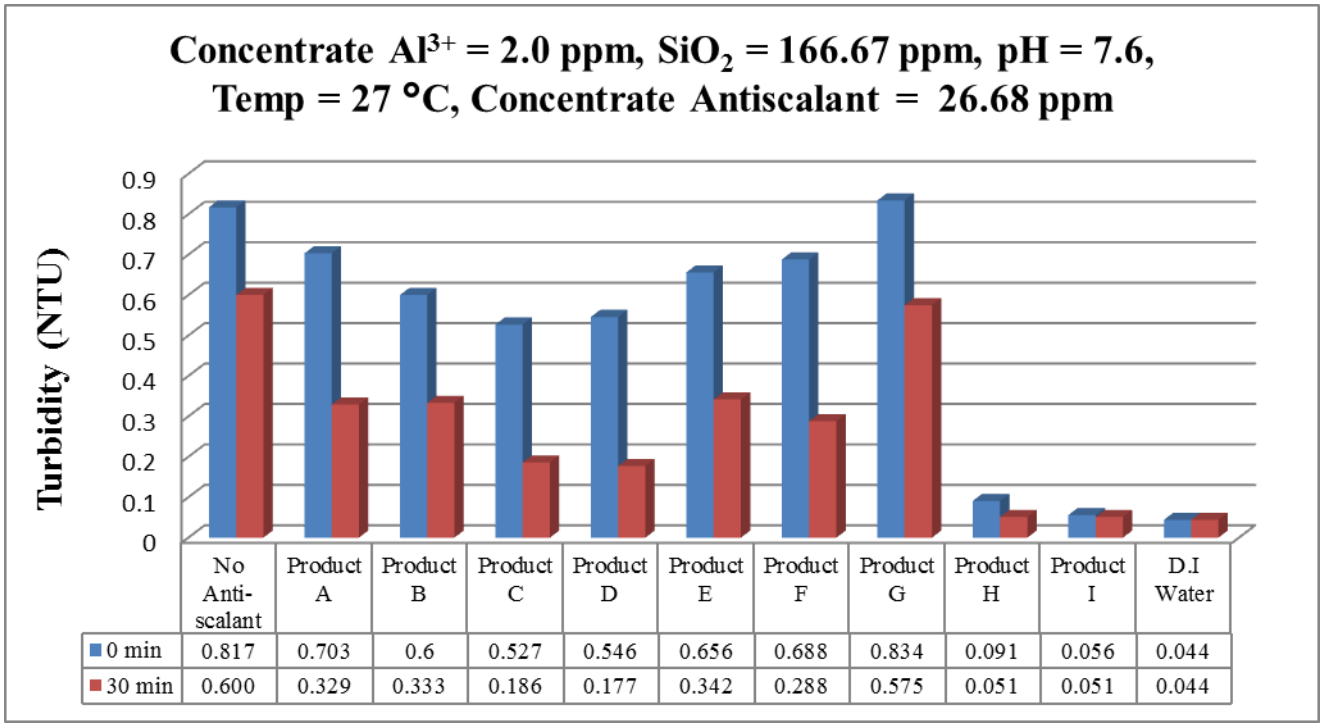
IV. RESULTS AND DISCUSSION

Experiment 1 (Analysis in Table 1, without calcium or sulfate)

In order to determine the potential for aluminum and silicate scale formation, the first experiment was performed without calcium or sulfate. This eliminated the possibility of interference by calcium salt formation.

A feed water aluminum concentration of 0.3 ppm was found to require a minimum antiscalant dosage of 4 ppm (based on the best performing antiscalant). Product H and Product I both exhibited almost complete scale inhibition, with solution turbidities comparable to those of deionized water. All other products failed upon mixing, resulting in heavy insoluble salt formation. Products E and F, both of which are promoted as silica antiscalants, were amongst the worst performers.

However, in all cases where scale had formed, including that of the control, turbidity improved after 30 minutes – an indication that some of the salts had partially redissolved. The authors of this paper do not believe that the partial salt re-dissolution that was observed over 30 minutes would have practical implications in a membrane system. Only antiscalants that exhibited inhibition immediately upon mixing were considered successful.



	No Anti-scalant	Product A	Product B	Product C	Product D	Product E	Product F	Product G	Product H	Product I	D.I Water
0 min	0.817	0.703	0.6	0.527	0.546	0.656	0.688	0.834	0.091	0.056	0.044
30 min	0.600	0.329	0.333	0.186	0.177	0.342	0.288	0.575	0.051	0.051	0.044

Figure 3: Comparison of inhibition by various antiscalants in the absence of calcium and sulfate ions, based on Feed Al^{3+}=0.3 ppm, Feed SiO_2=25 ppm, Feed pH=7.1, Temp=27°C, Antiscalant Dosage=4 ppm, Recovery=85%

SEM images of the precipitants from all samples were analyzed and found to consist of silica, aluminum and sodium. In all cases where scale was not inhibited, the stoichiometric ratio of the precipitant was approximately 1 Al: 2 Si, with a Al:Na ratio that varied between approximately 4 and 5 (and a corresponding Si:Na ratio of approximately 8 – 10).

$Al(OH)_4^-$ is geometrically similar to $Si(OH)_4$ and both have approximately the same atomic diameter [2]. The OH groups of $Al(OH)_4^-$ can interact with the silanol groups of silicic acid and condense to form Al-O-Si bonds. The result would be an aluminosilicate compound with an overall negative charge [2,12] (see Figure 13). The sodium would therefore act as a counter-ion, facilitating precipitation as a salt.

The higher number of aluminum atoms compared to the cationic sodium ion suggested that each aluminosilicate anion was a polymer consisting of multiple aluminum and silicon atoms that maintained a respective 2:1 ratio.

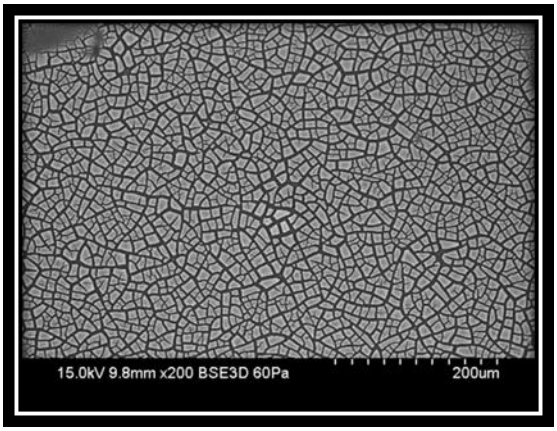


Figure 4: SEM Micrograph of Filter Deposit of Solution without Antiscalant, Al^{3+}=2 ppm w/SiO2, Ca^{2+}=0 ppm, Turbidity = 0.823 NTU

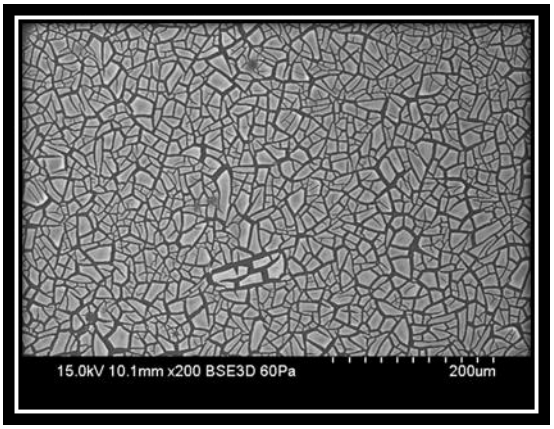


Figure 5: SEM Micrograph of Filter Deposit from Solution using Product E, Al^{3+}=2 ppm w/SiO2, Ca^{2+}=0 ppm, Turbidity = 0.460 NTU

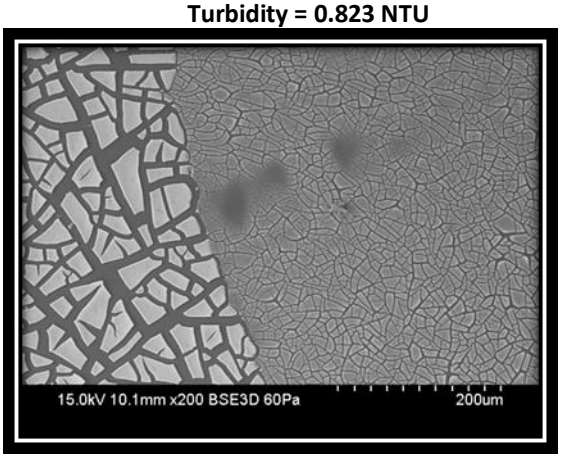


Figure 6: SEM Micrograph of Filter Deposit of Solution using Product F, Al^{3+}=2 ppm w/SiO2, Ca^{2+}=0 ppm, Turbidity = 0.598 NTU

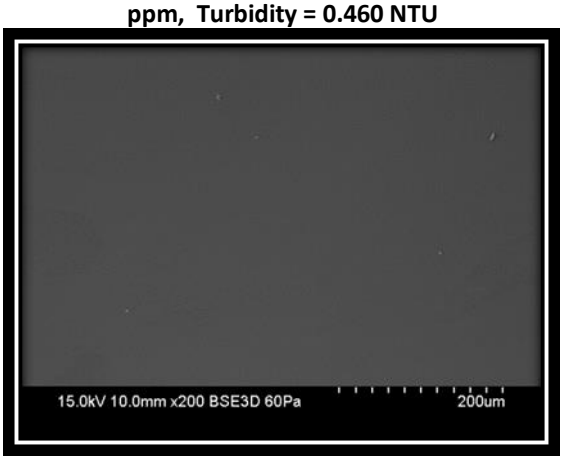


Figure 7: SEM Micrograph of Filter Deposit of Solution using Product I, Al^{3+}=2 ppm w/SiO2, Ca^{2+}=0 ppm, Turbidity = 0.056 NTU

Table 2: Elemental Composition (Mol %) of Precipitate from Solution Containing Only Al, Si, Na, Cl, HCO_3 with Concentrate Al^{3+}=2ppm at a concentrate pH of 7.6

Feed Antiscalant Dosage = 4 ppm	Al	Si	Na	P	Si : Al Ratio	Si : Na Ratio	Al : Na Ratio
No Antiscalant	28.93	63.99	7.8	-	2.21 : 1	8.20 : 1	3.71 : 1
Product A	25.88	55.58	4.78	13.62	2.15 : 1	11.63 : 1	5.41 : 1
Product B	28.57	59.97	5.33	5.93	2.10 : 1	11.25 : 1	5.36 : 1
Product C	23.89	55.62	8.84	11.06	2.33 : 1	6.29 : 1	2.70 : 1
Product D	27.20	54.81	5.19	12.38	2.02 : 1	10.56 : 1	5.24 : 1
Product E	27.91	59.94	5.02	6.73	2.15 : 1	11.94 : 1	5.56 : 1
Product F	28.17	59.17	7.90	4.65	2.10 : 1	7.49 : 1	3.57 : 1
Product G	30.72	62.73	4.79	-	2.04 : 1	13.10 : 1	6.42 : 1

Several of the precipitates that formed in the presence of phosphonate based antiscalant also contained phosphorous. It was unclear whether the antiscalants had precipitated as aluminum salts, or had simply adsorbed onto the precipitated aluminum. Phosphonates are known to have a strong affinity for metals and their hydroxides. All phosphonate based antiscalants outperformed Product G which was a phosphorous free product. Interestingly, the CAS number listed as the active ingredient of Product G in its MSDS was for an acrylic/maleic copolymer. Maleic based polymers have historically been touted as being effective inhibitors of silicate salts and polymerized silica.

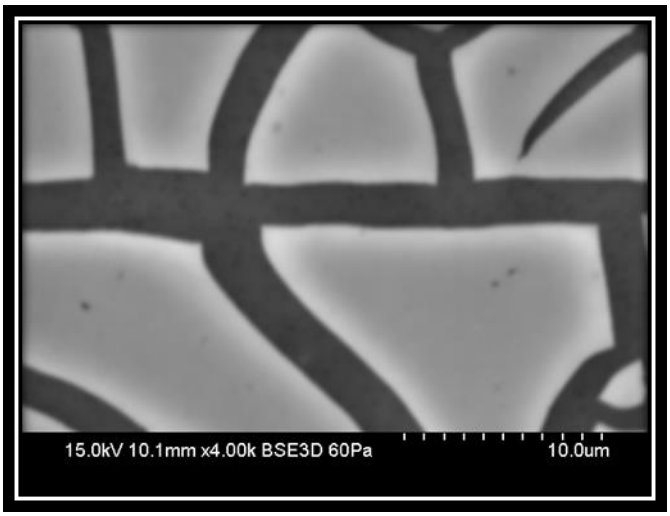


Figure 8: SEM Micrograph of Filter Deposit of Solution using Product F at 4000X Mag

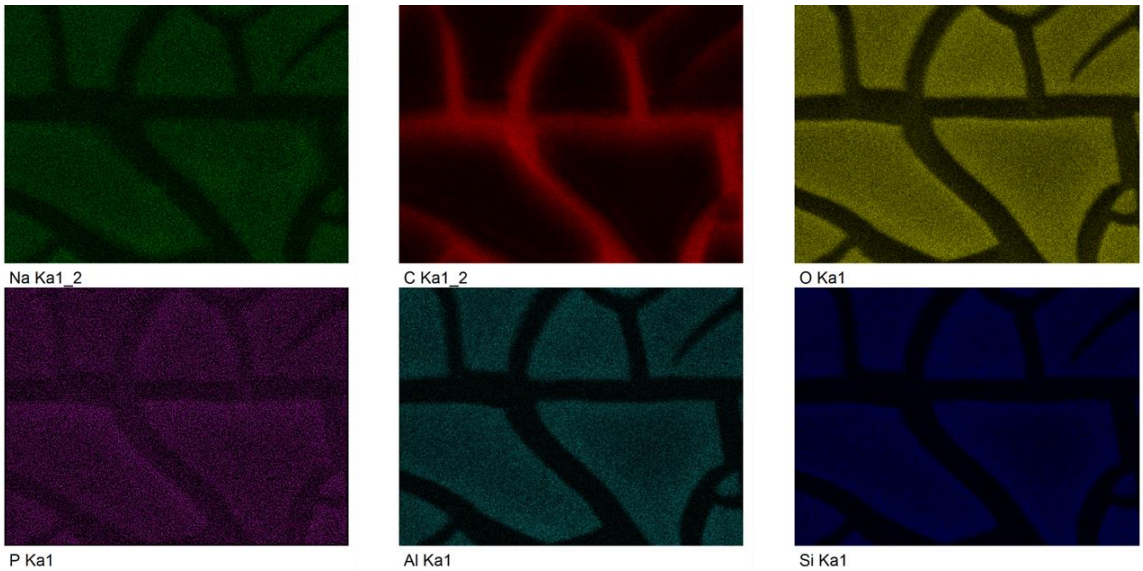


Figure 9: Prismatic Elemental Mapping (PEM) of deposits from solution using Product F, a silica antiscalant. Silica was clearly not inhibited and had co-precipitated with aluminum.

The morphology of the material on the filters appeared amorphous, but the amount of precipitant was insufficient to verify crystal structure by X-Ray Diffraction (XRD). Product H and Product I, which had

the lowest turbidities, were verified by SEM and PEM to have inhibited scale formation most effectively. Only a few small particles were trapped on the 100 nm filter, none exceeding 5µm in size.

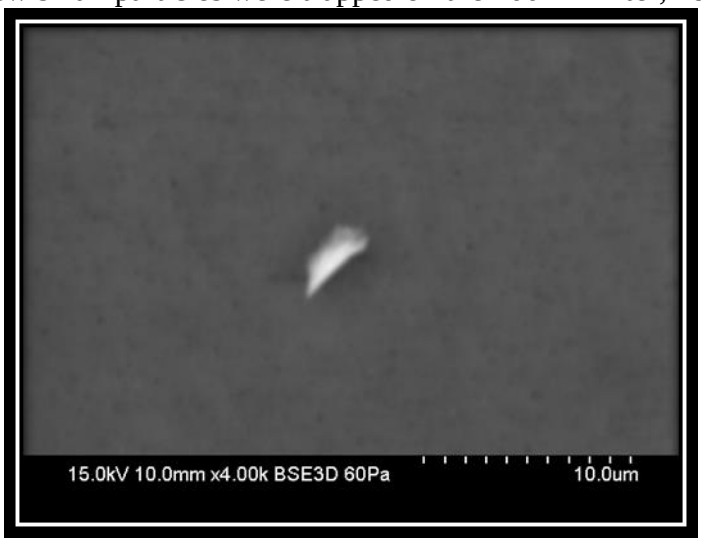


Figure 10: SEM Micrograph of Filter Deposit of Solution using Product I at 4000X Mag

Table 3: Elemental analysis of a particle found on filter from solution using Product I. Si:Al ratio is not consistent with composition of heavier precipitates.

Element	Weight%	Atomic%
Na K	4.39	5.33
Al K	3.52	3.64
Si K	90.88	90.18
K* K	1.20	0.86

***Potassium was likely introduced as an impurity from the reagents used in making the test solutions**

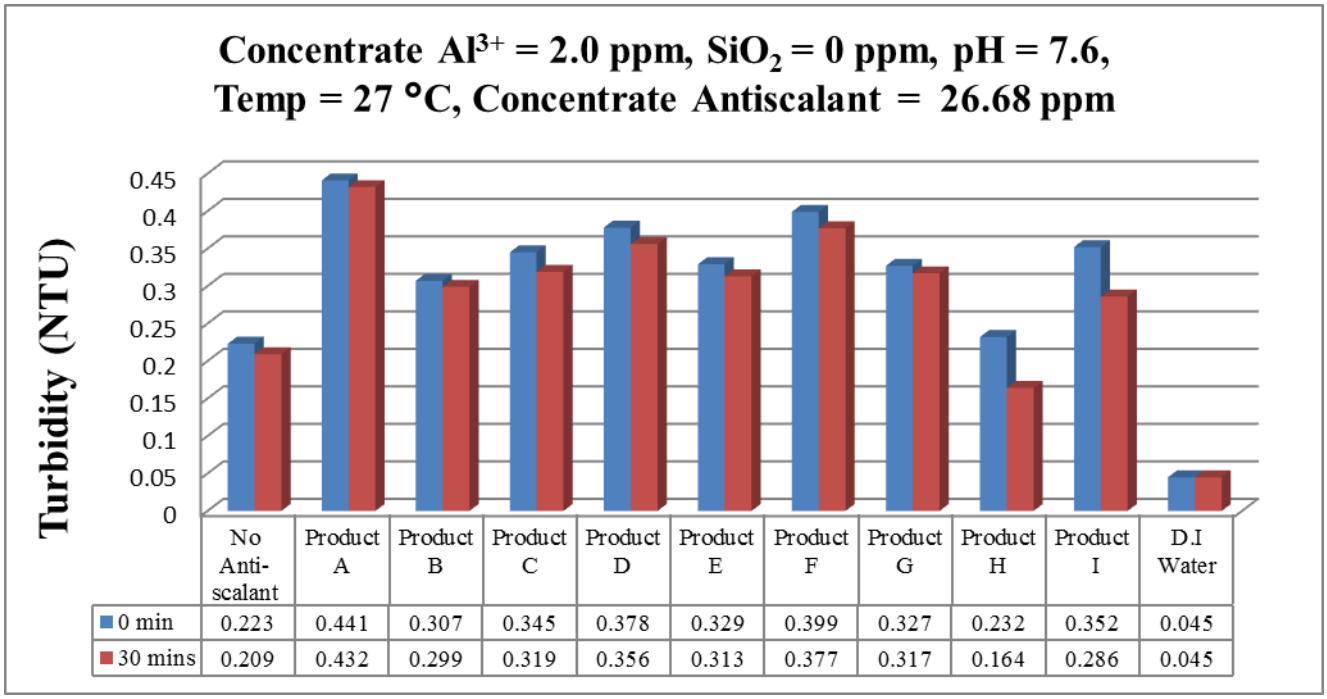
Experiment 2 (Analysis in Table 1, without silica, calcium or sulfate)

The same experiment was repeated without silica in order to compare the behavior of aluminum hydroxide under the same conditions. The purpose was to validate the theory that tetrahedral aluminum was substituting within silica oligomers to form an aluminosilicate compound, as opposed to silica merely adsorbing to precipitated aluminum hydroxide.

The results of the experiment showed that in the absence of antiscalant, insoluble salt formation was much lower in silica-free solutions that contain aluminum ions (compare turbidities of the control tests in figures 3 and 11). SEM observations showed that all the formed salts were amorphous in nature. Speciation calculations at pH 7.6 based on the hydrolysis constants of aluminum (as a function of temperature and ionic strength) found that the 2 ppm total reject aluminum ion (Al^{3+}) concentration existed almost entirely as soluble $Al(OH)_4^-$. Only 0.010 ppm existed as insoluble $Al(OH)_3$. This explained the extremely low precipitation in the absence of silica, and further reinforced the theory that $Al(OH)_4^-$ was reacting with silicic acid to form an anionic aluminosilicate compound.

The behavior of the solutions containing antiscalants was completely unexpected. Product H performed no differently than the control, while all the other antiscalants actually made precipitation worse.

Therefore, although solutions containing aluminum ions formed less precipitate in the absence of silica, the salts that were formed could not be inhibited by antiscalants. Product H and Product I had both been able to almost completely inhibit precipitation when silica was present, but could not do so in its absence. Altogether, this was further evidence that aluminum and silica do in fact interact to form an amorphous aluminum silicate compound that could more easily be controlled by antiscalants.



	No Anti-scalant	Product A	Product B	Product C	Product D	Product E	Product F	Product G	Product H	Product I	D.I Water
0 min	0.223	0.441	0.307	0.345	0.378	0.329	0.399	0.327	0.232	0.352	0.045
30 mins	0.209	0.432	0.299	0.319	0.356	0.313	0.377	0.317	0.164	0.286	0.045

Figure 11: Comparison of inhibition of $Al(OH)_3$ by various antiscalants in the absence of calcium and sulfate ions, based on Feed Al^{3+}=0.3 ppm, Feed SiO_2=0 ppm, Feed pH=7.1, Temp=27°C, Antiscalant Dosage=4 ppm, Recovery=85%

Experiment 3 (Analysis in Table 1, without calcium or sulfate, concentrate pH increased to 8.6)

In order to verify that the aluminum silicate compound would consistently have a 2Si:1Al ratio, Experiment 1 was repeated at a higher reject pH of 8.6.
The most striking observation was that the antiscalants, Product H and Product I, both of which had previously inhibited precipitation under the same conditions but at lower pH, were no longer as effective and now allowed some formation of insoluble salts. Contrary to the common belief that aluminum silicate would be more soluble at a higher pH, it appeared that more precipitation occurred and that the same dosage of antiscalant was no longer effective. Both aluminum and silica are known to be more soluble in deionized water at a pH of 8.6 due to an increase in concentration of their anionic species.

Based on the theory that $Al(OH)_4^-$ was interacting with silica to form an anionic aluminum silicate compound, the increase in concentration of $Al(OH)_4^-$ in the presence of excess silica would therefore result in higher concentrations of anionic aluminum silicate compounds. The stoichiometrically excessive sodium in solution would then react with the aluminosilicate anions to form insoluble salts. In other words, the decreased solubility at higher pH, coupled with the SEM images, and EDS and PEM data, provided further evidence that an amorphous anionic aluminum silicate compound was forming.

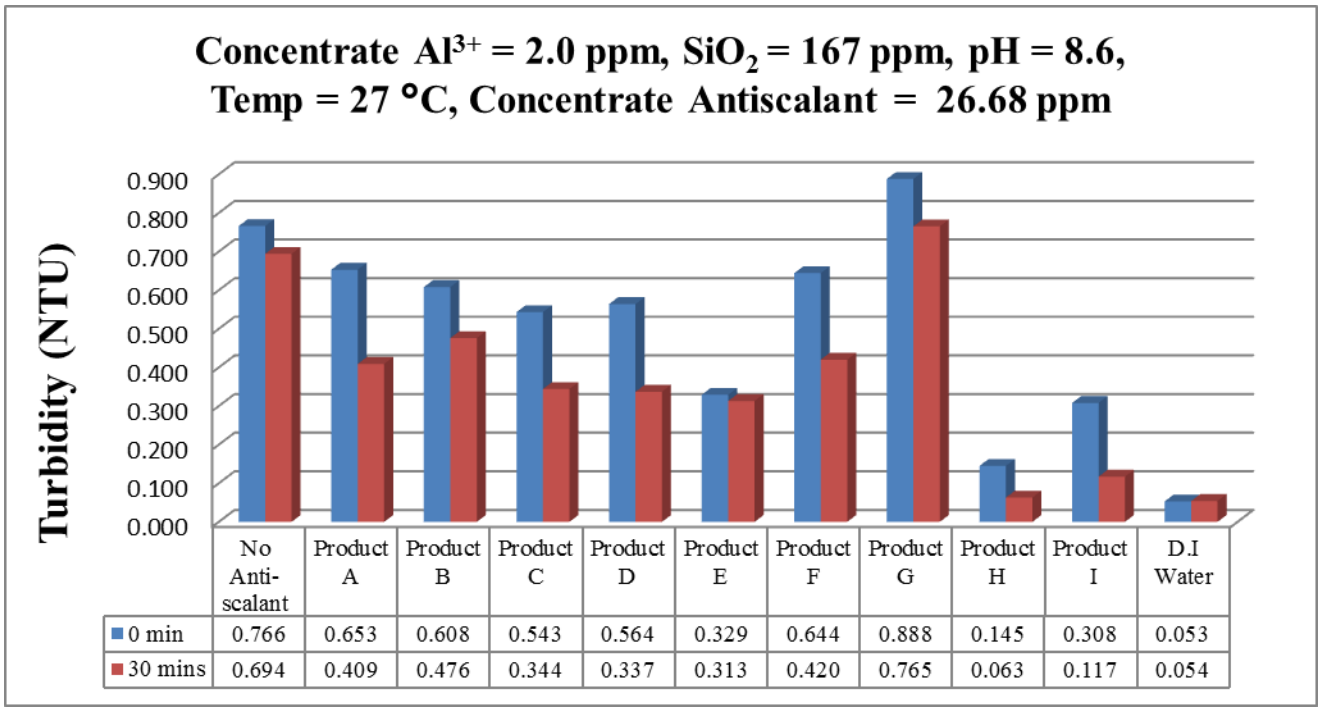


Figure 12: Comparison of inhibition by various antiscalants in the absence of calcium and sulfate ions, based on Feed Al^{3+}=0.3 ppm, Feed SiO_2=25 ppm, Feed pH=8.1, Temp=27°C, Antiscalant Dosage=4 ppm, Recovery=85%

Table 4: Elemental Composition (Mol %) of Precipitate from Solution Containing Only Al, Si, Na, Cl, HCO_3 with Concentrate Al^{3+}=2ppm at a concentrate pH of 8.6

Feed Antiscalant Dosage = 4 ppm	Al	Si	Na	P	Si:Al Ratio	Si:Na Ratio	Al:Na Ratio
No Antiscalant	30.85	59.36	9.79	-	1.92 : 1	6.06 : 1	3.15 : 1
Product A	28.75	52.37	9.08	9.76	1.82 : 1	5.77 : 1	3.17 : 1
Product B	29.12	56.49	9.75	4.20	1.94 : 1	5.79 : 1	2.99 : 1
Product C	23.58	59.87	10.25	6.12	2.54 : 1	5.84 : 1	2.30 : 1
Product D	25.39	57.18	10.10	7.08	2.25 : 1	5.66 : 1	2.51 : 1
Product E	27.07	59.65	8.45	4.44	2.20 : 1	7.06 : 1	3.20 : 1
Product F	28.03	57.40	10.96	3.50	2.05 : 1	5.24 : 1	2.56 : 1
Product G	29.66	62.70	7.62	-	2.11 : 1	8.23 : 1	3.89 : 1
Product H	19.62	68.60	6.84	4.51	3.50 : 1	10.03 :1	2.87 : 1
Product I	24.09	54.07	13.50	6.19	2.24 : 1	4.01 : 1	1.78 : 1

With the exception of Product H which formed a precipitate that had almost completely re-dissolved within 30 minutes, all precipitates maintained the same 1Al : 2Si ratio that had previously been observed at a reject pH of 7.6. This confirmed that anionic aluminum silicate compounds precipitating in RO/NF membrane separation systems would consistently have a 2:1 Si:Al ratio in the pH range at which such systems are typically operated.

However, the ratio of Al:Na was reduced to approximately 3:1. This suggested that at higher pH, the polymerized aluminosilicate anion would incorporate fewer aluminum and silicate atoms while maintaining its valence.

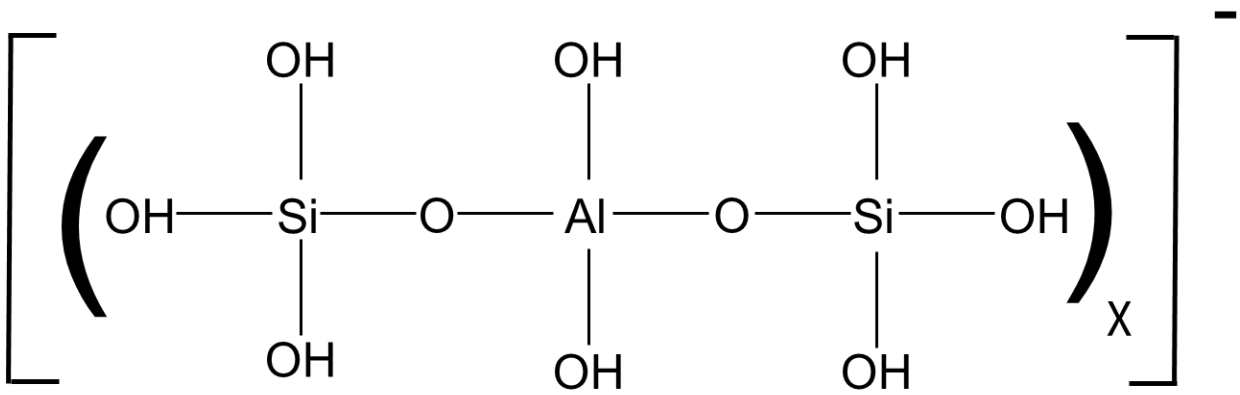


Figure 13: Aluminum silicate ion is anionic and constantly maintains a 2:1 ratio of Si:Al in the near neutral pH range at which RO/NF systems are typically operated

Experiment 4 (Analysis in Table 1 including all constituents) with varying Al^{3+} concentrations

In order to determine the interaction of aluminum with silica in typical RO/NF feed waters, the experiments were finally repeated at the original reject pH of 7.6, in the presence of calcium and sulfate (in addition to the silica, aluminum, alkalinity, sodium and chloride used in the initial tests).

Precipitation could not be controlled at a feed water aluminum ion concentration of 0.3 ppm when calcium was present. All antiscalants were tested at feed dosages as high as 10 ppm without any success. Based on this outcome, the experiments were repeated at various concentrations of aluminum (see Table 5) to determine the threshold based on the water analysis in Table 1.

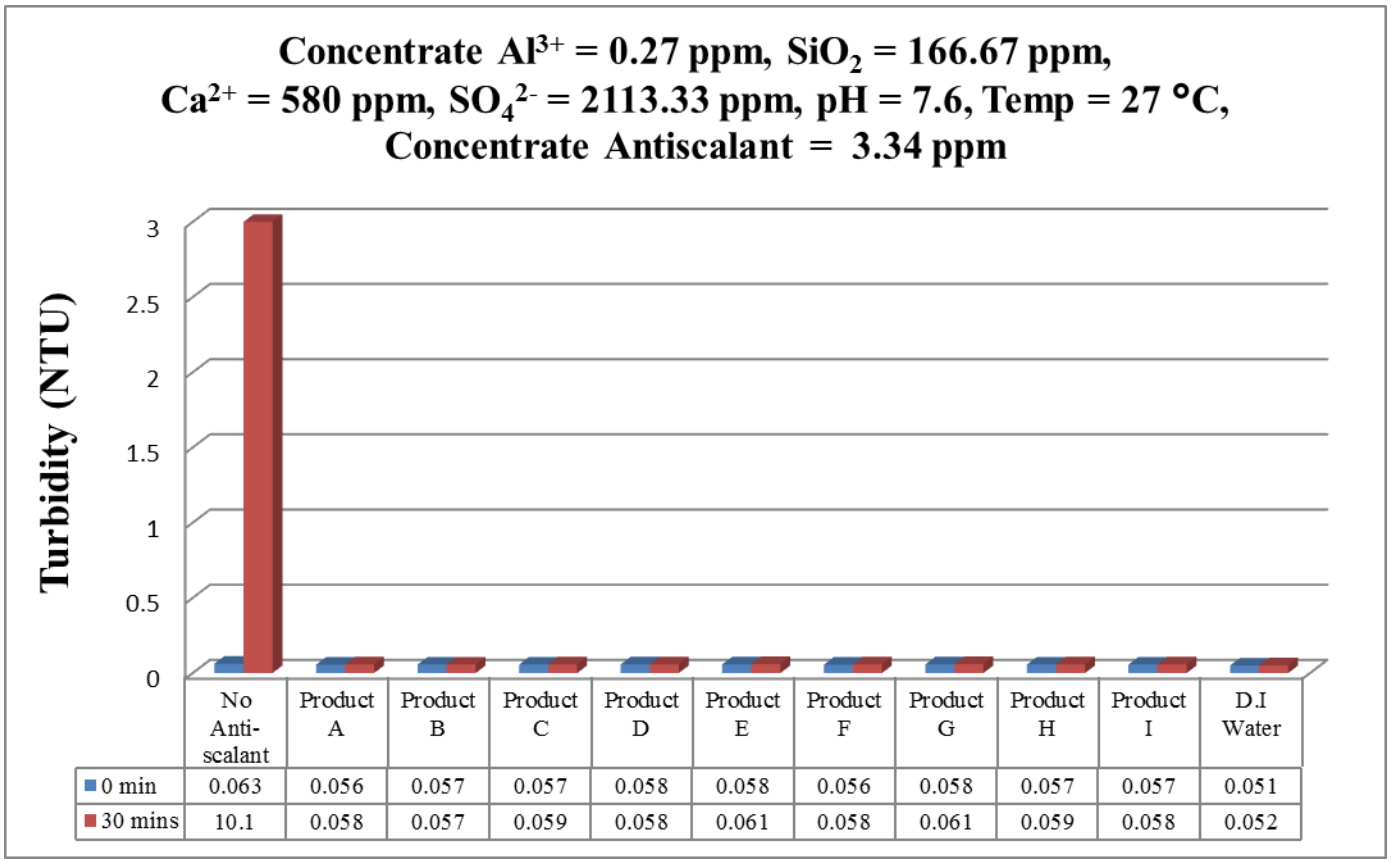
Table 5: Varying Aluminum Concentrations (ppm) in Feedwater

Experiments	Feed (ppm)	Concentrate (ppm)
1	0.02	0.13
2	0.04	0.27
3	0.06	0.40
4	0.08	0.53
5	0.1	0.67
6	0.2	1.33
7	0.3	2.00

***Concentrate was calculated based on a concentration factor of 6.67 and an assumption of 100% salt rejection**

All products were effective at a dosage of 0.5 ppm when Al^{3+} concentration was 0.04 ppm, with even the control (no antiscalant) showing no significant formation of aluminum silicate salts. Analysis of the material precipitated from the control found relatively large spheres, varying in diameter from 3 to 15µm and consisting primarily of tricalcium silicate.

The results of this experiment are of great significance because the typical MDL (Minimum Detection Limit) for Al^{3+} by Inductively Coupled Plasma – Atomic Absorption (ICP-AA) is 0.05 ppm. This is evidence that aluminum silicate is unlikely to precipitate in RO systems operating at 85% recovery and neutral pH with a feed water Al^{3+} concentration that is below the MDL. Plant operators should therefore be wary of membrane autopsy reports concluding the presence of aluminum silicate scales when Al^{3+} is undetectable in their feedwater. This is a frequent occurrence when autopsies are performed by inexperienced technicians who do not have a strong understanding of water chemistry, or worse, misidentify silt or clay fouling as precipitated aluminosilicate scale.



	No Anti-scalant	Product A	Product B	Product C	Product D	Product E	Product F	Product G	Product H	Product I	D.I Water
0 min	0.063	0.056	0.057	0.057	0.058	0.058	0.056	0.058	0.057	0.057	0.051
30 mins	10.1	0.058	0.057	0.059	0.058	0.061	0.058	0.061	0.059	0.058	0.052

Figure 14: Comparison of inhibition by various antiscalants, Feed Ca^{2+}=87 ppm, Feed SO_4^{2-}=317 ppm, Feed Al^{3+}=0.04 ppm, Feed SiO_2=25 ppm, Feed pH=7.1, Temp=27°C, Antiscalant Dosage=0.5 ppm, Recovery=85%

When the experiments were repeated with a feed water Al^{3+} concentration of 0.1 ppm, Product H and Product I were the best performers and were effective at a minimum dosage of only 1.5 ppm. Product F also performed well, with only a slightly higher rate of salt formation.

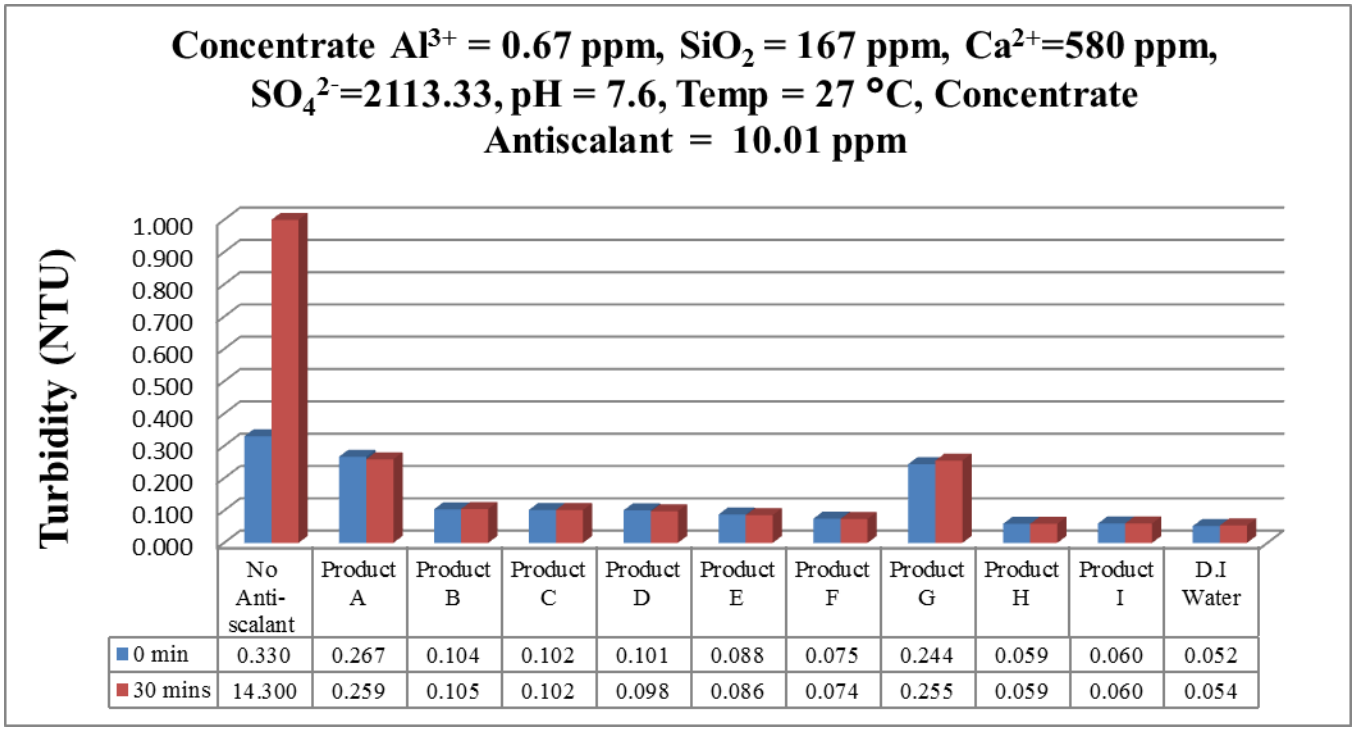


Figure 15: Comparison of inhibition by various antiscalants, Feed Ca^{2+}=87 ppm, Feed SO_4^{2-}=317 ppm, Feed Al^{3+}=0.1 ppm, Feed SiO_2=25 ppm, Feed pH=7.1, Temp=27°C, Antiscalant Dosage=1.5 ppm, Recovery=85%

Table 6 : Elemental Composition (Mol %) of Amorphous Precipitate from Solution Consisting of the Concentrate Water Analysis in Table 1, with reject concentration of Al = 0.67 ppm

Feed Antiscalant Dosage = 1.5ppm	Al	Si	Na	Ca	P	Si:Al Ratio	Si:Ca Ratio	Al:Ca Ratio
No Antiscalant	5.62	86.53	1.61	4.16	-	15.40 : 1	20.80 : 1	1.35 : 1
Product A	9.45	80.14	0.55	5.36	3.92	8.48 : 1	14.95 : 1	1.76 : 1
Product B	5.92	87.31	0.66	3.52	2.08	14.75 : 1	24.80 : 1	1.68 : 1
Product C	5.45	88.08	0.55	3.51	1.82	16.16 : 1	25.09 : 1	1.55 : 1
Product D	6.54	85.99	0.76	3.86	2.47	13.15 : 1	22.28 : 1	1.69 : 1
Product E	6.94	83.85	0.85	3.90	3.18	12.08 : 1	21.50 : 1	1.78 : 1
Product F	8.11	80.78	0.72	5.41	3.70	9.96 : 1	14.93 : 1	1.50 : 1
Product G	5.96	87.22	1.25	3.95	-	14.63 : 1	22.08 : 1	1.51 : 1

However, when the experiments were finally repeated with an Al^{3+} concentration of 0.2 ppm, Product F (marketed as a specialty silica antiscalant) failed along with most other products, with the solutions having a very high turbidity that indicated heavy insoluble salt formation.

Only Product H and Product I were effective at inhibiting aluminum silicate salt formation (Figure 16) at a minimum antiscalant dosage of 8 ppm. Based on the combined test results, it was determined that precipitation could not be inhibited using a feasible antiscalant dosage beyond a feed water concentration of 0.2 ppm Al^{3+} (assuming 85% recovery).

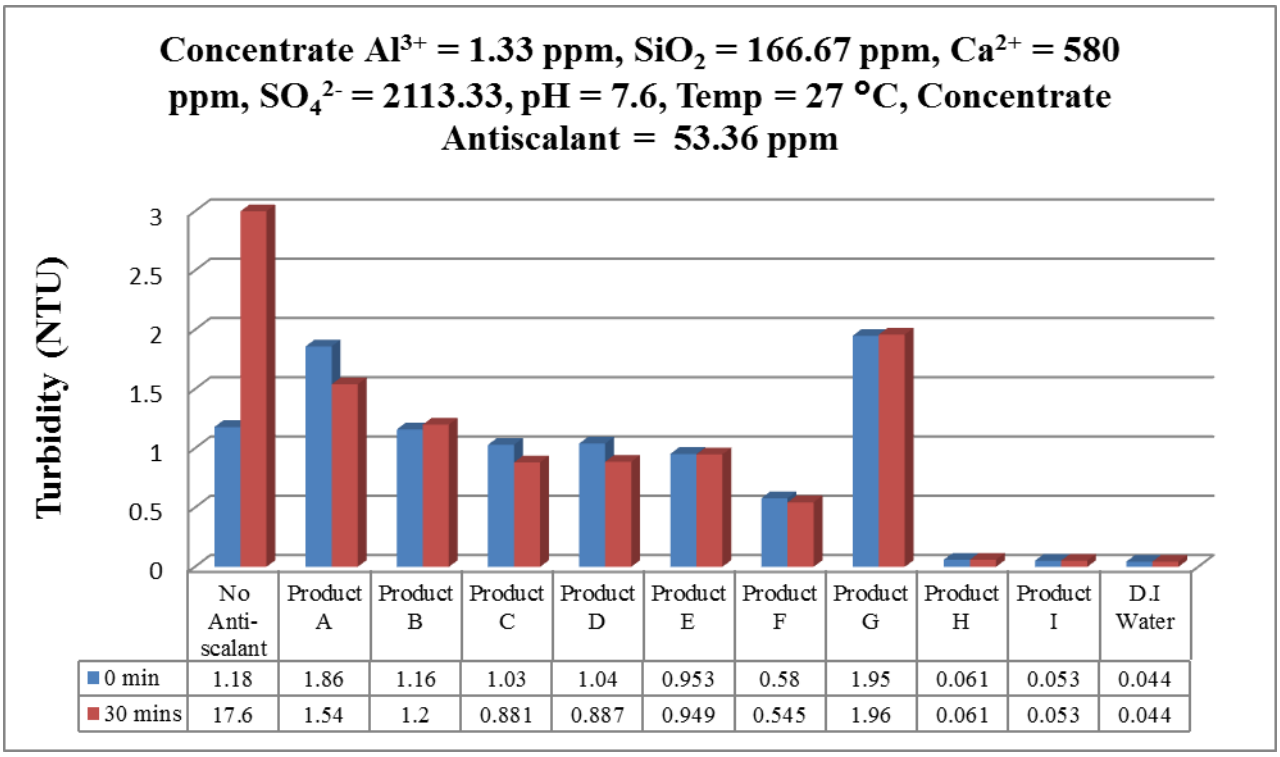


Figure 16: Comparison of inhibition by various antiscalants, Feed Ca^{2+}=87 ppm, Feed SO_4^{2-}=317 ppm, Feed Al^{3+}=0.2 ppm, Feed SiO_2=25 ppm, Feed pH=7.1, Temp=27°C, Antiscalant Dosage=8 ppm, Recovery=85%

In the control experiments with 0.2 ppm Al^{3+}, the filtered precipitate consisted of a layer of a dehydrated amorphous foulant in addition to spheres of calcium silicate. Elemental analysis of the amorphous foulant determined it to comprise mainly of calcium aluminum silicate and amorphous silica (Table 7).

EDS analysis of the core of the spheres showed a stoichiometric ratio of 3 Ca: 1 Si, consistent with tricalcium silicate. A detailed look at the Prismatic Elemental Mapping (PEM) image showed a calcium silicate core surrounded by a spherical calcium carbonate shell. Calcium aluminum silicate appeared to be precipitated in a thin layer on the outer surface of the spheres.

The calcium carbonate/calcium silicate spheres were completely inhibited by all the antiscalants that were tested. However, the amorphous layer continued to appear on filters where precipitation had occurred. In all cases, the amorphous layer was determined to consist mostly of amorphous silica.

It is evident from the elemental analysis acquired by EDS that ratios of silica to aluminum and silica to calcium varied widely. The higher valence of calcium relative to sodium most likely reduced repulsion between ionized silica molecules and ionized aluminosilicate molecules, allowing a higher rate of polymerization. It can therefore be hypothesized that a low solubility amorphous calcium aluminosilicate compound acted as a substrate for amorphous silica polymerization.

In all cases where antiscalants were used, there was a consistent Al:Ca ratio of 1.5:1, suggesting that the aluminosilicate polymers consisted of shorter chains when calcium was present.

The higher Al:Ca ratio in the absence of antiscalant may have been a result of reduced available Ca^{2+} due to calcium carbonate and calcium silicate formation. In the majority of the precipitates, sodium aluminum silicate formation appeared minimal, most likely due to the higher affinity of the anionic aluminosilicate compound to divalent ions.

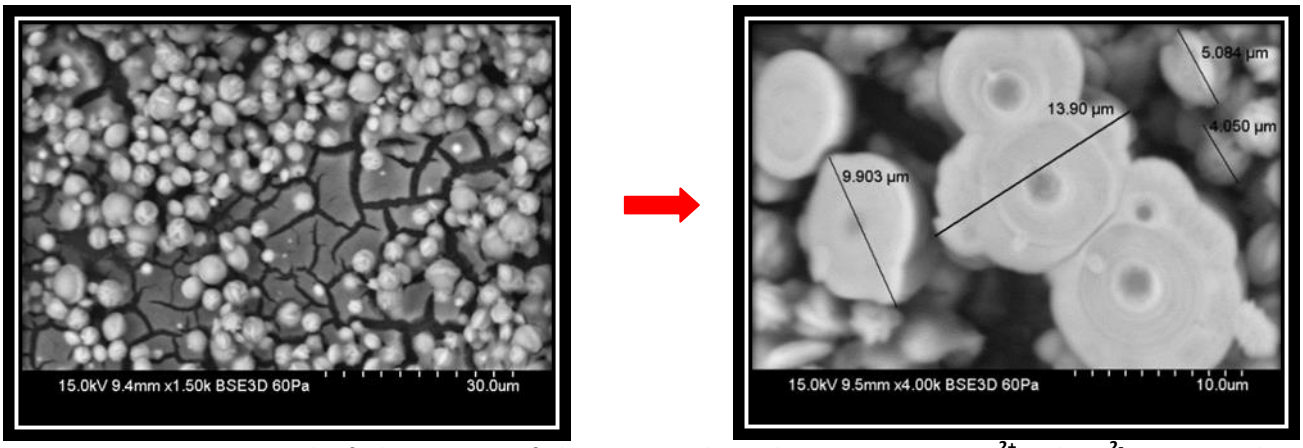


Figure 17: SEM Micrograph of Filter Deposit of Aluminum – Silica Solution Containing Ca^{2+} and SO_4^{2-} ,No Antiscalant (1.33 ppm Al^{3+} in reject water)

Table 7: Elemental analysis of amorphous deposit trapped on filter deposit without Antiscalant (Fig.17)

Element	Weight%	Atomic%
Na K	0.57	0.70
Al K	19.52	20.69
Si K	70.53	71.82
S K	0.40	0.35
Cl K	0.26	0.21
Ca K	8.73	6.23

Table 8: Elemental analysis of spheres trapped on filter deposit without Antiscalant (Fig.17)

Element	Weight%	Atomic%
Al K	1.47	2.02
Si K	16.72	22.06
S K	1.28	1.48
Ca K	80.53	74.44

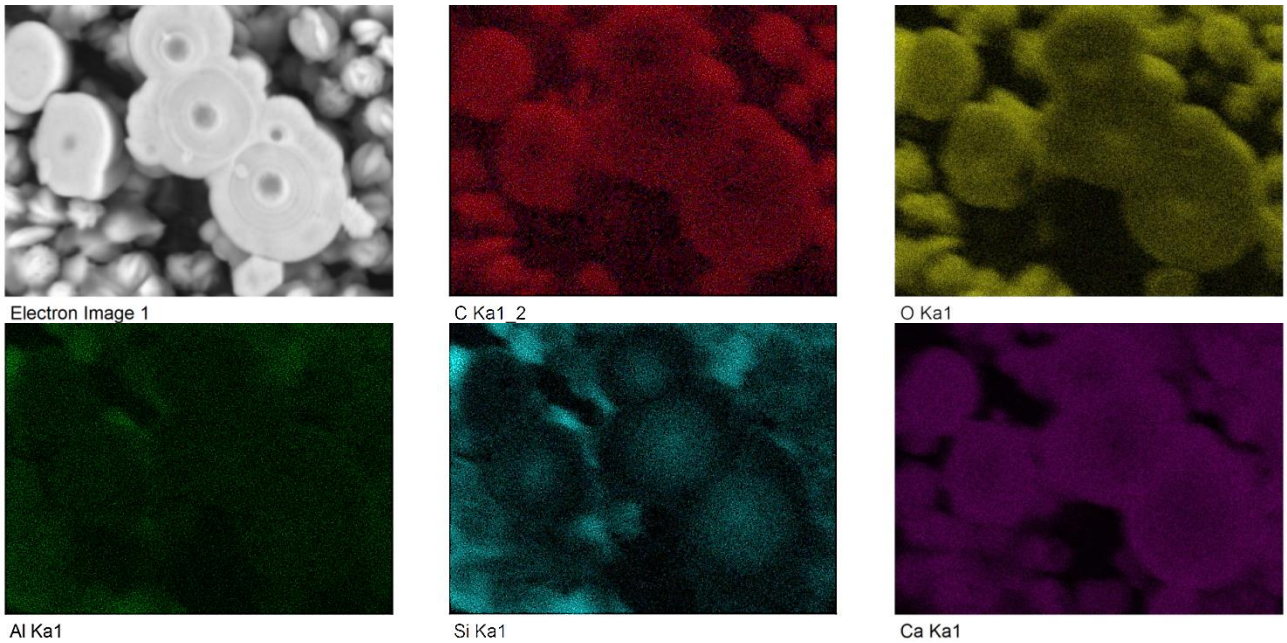


Figure 18: Prismatic Elemental Mapping (PEM) of the filter surface from the control solution at 4000X magnification

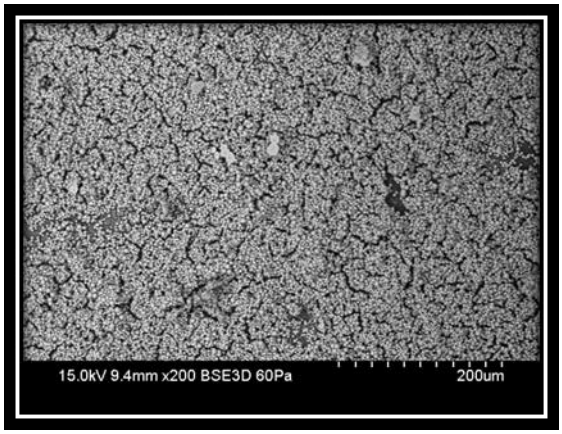


Figure 19: SEM Micrograph of Filter Deposit of control Solution, 1.33 ppm Al^{3+} w/ SiO2, 580 ppm Ca^{2+}, Turbidity = 1.45 NTU

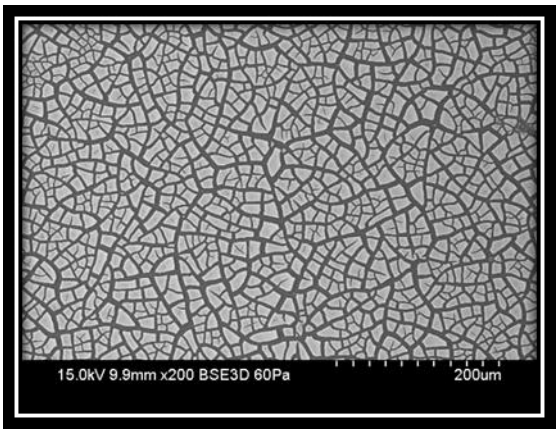


Figure 20: SEM Micrograph of Filter Deposit of Solution using Product E, 1.33 ppm Al^{3+} w/ SiO2, 580 ppm Ca^{2+}, Turbidity = 0.463 NTU

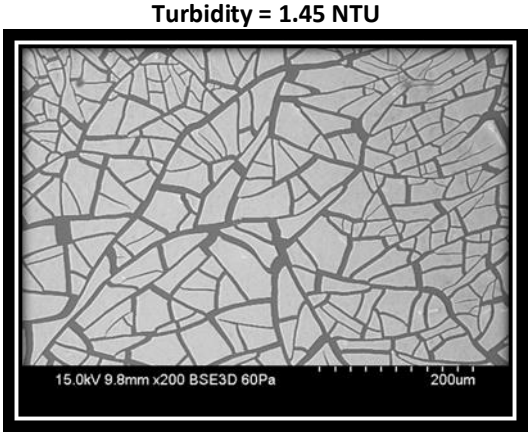


Figure 21: SEM Micrograph of Filter Deposit of Solution using Product F, 1.33 ppm Al^{3+} w/ SiO2, 580 ppm Ca^{2+}, Turbidity = 0.140 NTU

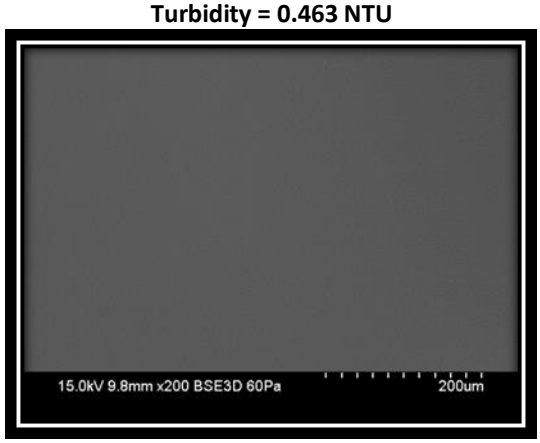


Figure 22: SEM Micrograph of Filter Deposit of Solution using Product I, 1.33 ppm Al^{3+} w/ SiO2, 580 ppm Ca^{2+}, Turbidity = 0.050 NTU

Table 9 : Elemental Composition (Mol %) of Amorphous Precipitate from Solution Consisting of the Concentrate Water Analysis in Table 1, with reject concentration of Al = 1.33 ppm

Feed Antiscalant Dosage = 8ppm	Al	Si	Na	Ca	P	Si:Al Ratio	Si:Ca Ratio	Al:Ca Ratio
No Antiscalant	20.69	71.82	0.7	6.23	-	3.47 : 1	11.53 : 1	3.32 : 1
Product A	11.51	67.14	0.88	8.35	11.71	5.83 : 1	8.04 : 1	1.38 : 1
Product B	8.14	71.75	5.04	5.88	2.85	8.81 : 1	12.20 : 1	1.38 : 1
Product C	9.64	79.00	0.42	5.79	4.64	8.20 : 1	13.64 : 1	1.66 : 1
Product D	11.92	72.67	0.59	7.13	7.52	6.10 : 1	10.19 : 1	1.67 : 1
Product E	9.23	72.05	4.44	5.77	3.63	7.81 : 1	12.49 : 1	1.60 : 1
Product F	10.43	76.78	1.22	7.86	3.42	7.36 : 1	9.77 : 1	1.33 : 1
Product G	13.69	76.56	0.40	8.91	-	5.59 : 1	8.59 : 1	1.54 : 1

Experiment 5 (Analysis in Table 1 including all constituents) with reduced Ca^{2+} concentrations

In an attempt to determine the impact of calcium on the polymerization of silica in the presence of the aluminosilicate salts, the experiment was finally repeated with the reject calcium concentration reduced

to 58 ppm. Despite the calcium having been reduced to 1/10th of the concentration of the previous experiment, the necessary antiscalant dosage to inhibit precipitation was only reduced by half to 4 ppm.

This underscored how much more impact aluminum had on the antiscalant dosage as compared to calcium. The precipitates that formed were very similar in composition to the previous experiments, consisting of aluminum silicate salts and polymerized silica. However, the presence of sodium aluminum silicate was now more pronounced. The reduced calcium concentration had apparently allowed for more interaction of the anionic aluminosilicate compound with sodium.

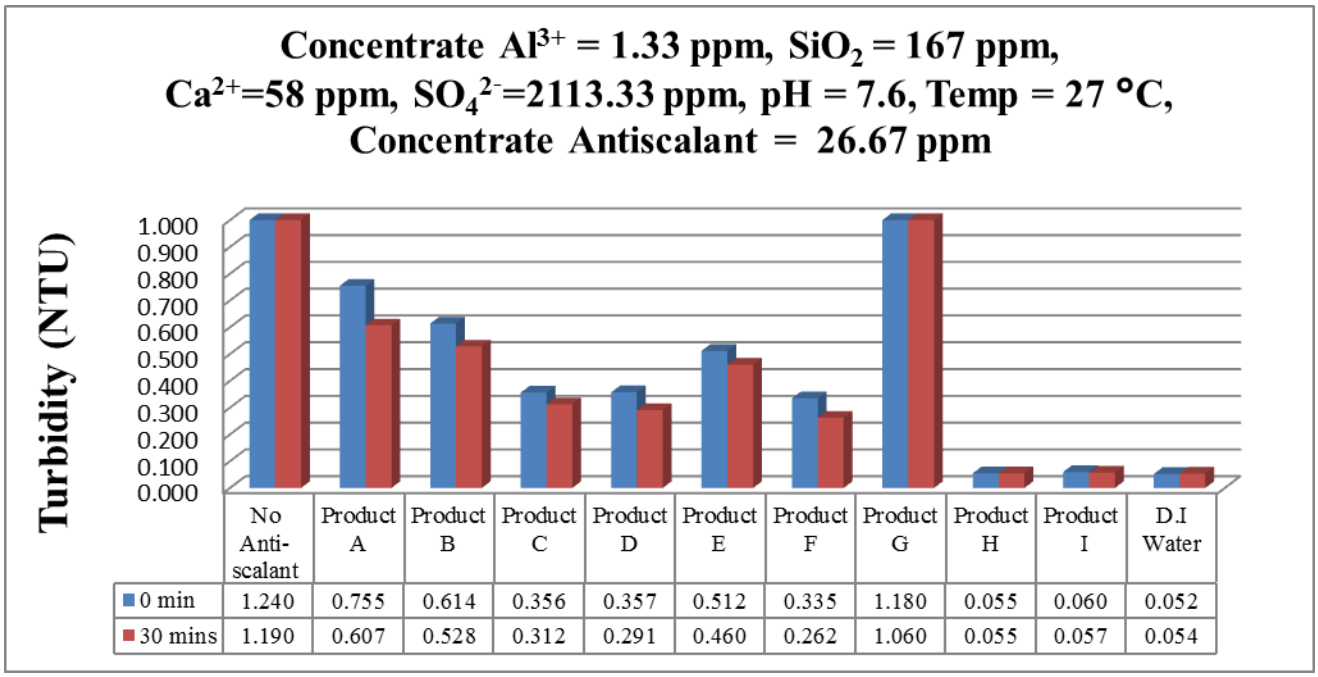


Figure 23: Comparison of inhibition by various antiscalants, Feed Ca^{2+}=8.7 ppm, Feed SO_4^{2-}=317 ppm, Feed Al^{3+}=0.2 ppm, Feed SiO_2=25 ppm, Feed pH=7.1, Temp=27°C, Antiscalant Dosage=4 ppm, Recovery=85%

Table 10 : Elemental Composition (Mol %) of Amorphous Precipitate from Solution Consisting of the Concentrate Water Analysis in Table 1, with reject concentration of Al^{3+} = 1.33 ppm and reject concentration of Ca^{2+} reduced to 1/10th of the previous experiment

Feed Antiscalant Dosage = 4ppm	Al	Si	Na	Ca	P	Si:Al Ratio	Si:Ca Ratio	Al:Ca Ratio	Al:Na Ratio
No Antiscalant	12.94	81.05	3.30	2.30	-	6.26 : 1	35.24 : 1	5.63 : 1	3.92 : 1
Product A	13.42	70.23	3.33	4.24	8.33	5.23 : 1	16.56 : 1	3.17 : 1	4.03 : 1
Product B	11.70	75.67	4.99	2.91	3.01	6.47 : 1	26.00 : 1	4.02 : 1	2.34 : 1
Product C	9.27	80.94	4.06	2.36	2.53	8.73 : 1	34.30 : 1	3.93 : 1	2.28 : 1
Product D	11.01	78.16	4.46	2.89	3.18	7.10 : 1	27.04 : 1	3.81 : 1	2.47 : 1
Product E	10.66	79.39	3.77	2.58	3.01	7.45 : 1	30.77 : 1	4.13 : 1	2.83 : 1
Product F	11.46	75.93	4.22	4.67	2.45	6.63 : 1	16.26 : 1	2.45 : 1	2.72 : 1
Product G	13.17	78.92	4.12	3.07	-	5.99 : 1	25.71 : 1	4.29 : 1	3.20 1

V. Comparison of Filtered Deposit with Scale from an Autopsy on Membrane with alum pretreatment

The analysis results from the lab experiments were then compared against an autopsy for a RO water reuse facility in Long Beach, CA. Autopsy results suggested that any attempted membrane cleanings had been unsuccessful. The facility had been using product E for scale control throughout the plant's history. The facility was operating at 85% recovery and its feedwater contained 20 ppm silica and 59 ppm calcium, with variable alum due to carryover.

As can be seen in the SEM images, the precipitates that formed in the membranes were very similar to what was produced in the lab, in both their amorphous morphology and their chemical composition. Prismatic Elemental Mapping (PEM) of the deposits on the membrane show that they consisted primarily of polymerized amorphous silica and calcium aluminum silicate. The silica to aluminum ratio varied from 8:1 to 15:1 at various areas that were analyzed on the membrane surface; this again suggested silicic acid monomers and silica oligomers polymerizing with a precipitated aluminosilicate salt substrate.

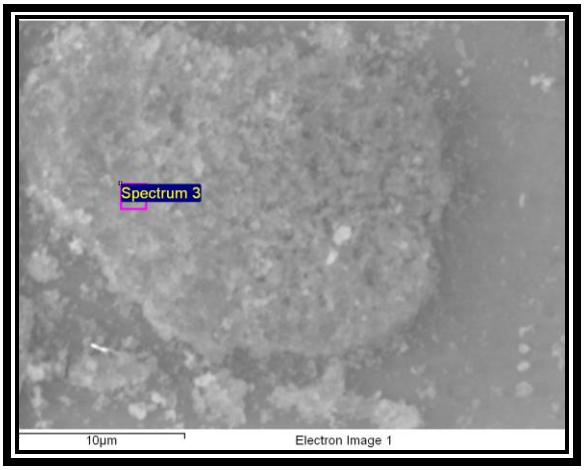


Figure 24: SEM Micrograph from RO Water Reuse Facility using Product E at 4000X Mag

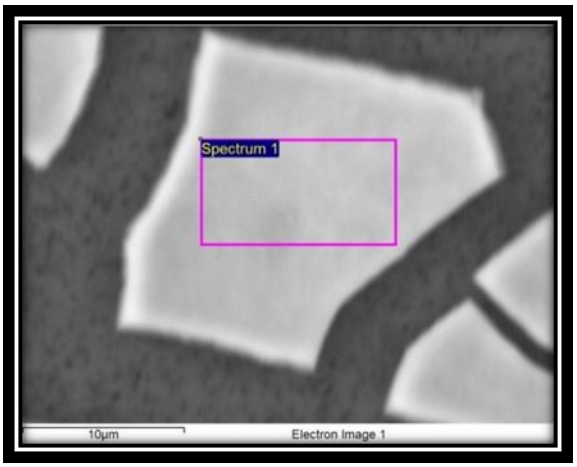


Figure 25: SEM Micrograph of filter surface from lab simulation using Product E at 4000X Mag

Table 11: Elemental analysis of membrane surface deposits from water reuse plant using Product E. The Silica to Aluminum Ratio of the deposit in this particular region of the membrane was ~8:1.

Element	Weight%	Atomic%
Na K	0.65	0.85
Al K	4.83	5.41
Si K	40.63	43.74
S K	45.74	43.13
Cl K	3.76	3.21
Ca K	2.83	2.14
P K	0.65	0.63
K K	0.51	0.39
Mg	0.39	0.49

The foulant was scraped off the surface and was analyzed by X-Ray Diffraction (XRD). The material was entirely amorphous, with only one small sharp peak at 62 degrees 2-theta that suggested a very

minor presence of crystalline matter. The peak could not be identified, but was likely from silts or clays that were introduced as suspended solids.

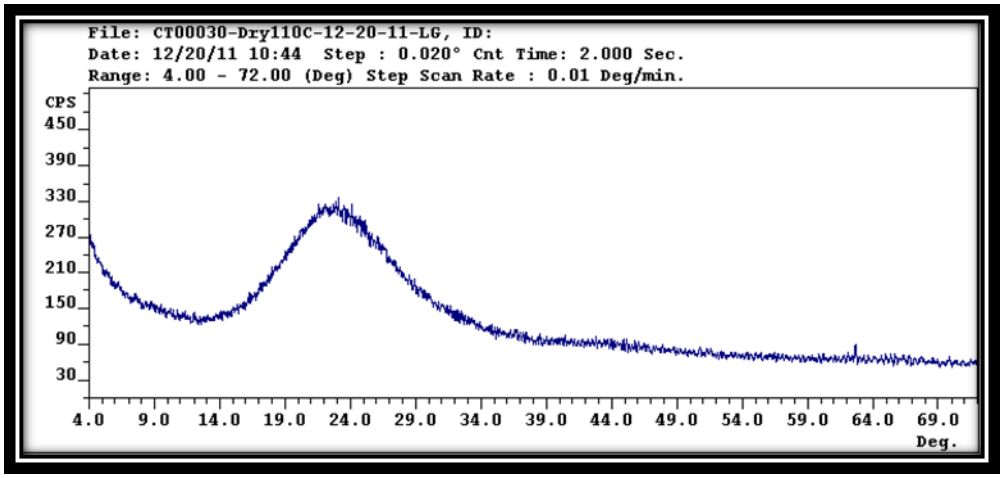


Figure 26: X-ray diffraction of the membrane foulant from the wastewater reuse RO facility using Product E

VI. CONCLUSION

Aluminum carryover from coagulation processes did not result in aluminum hydroxide precipitation when silica was present in stoichiometrically excess amounts. Silica was therefore not merely adsorbing to precipitated aluminum hydroxides, but was actually forming amorphous aluminosilicate compounds in the presence of dissolved aluminum. Hydrated aluminum ions ($Al(OH_4)^-$) and silanol groups condensed to form an aluminosilicate anion [2,12] (Figure 13) that had the potential to precipitate when combined with counterions such as sodium or calcium. The aluminosilicate compounds that formed in conditions typical of membrane systems were determined to be polymers with a consistent ratio of 2Si:1Al.

Solutions containing sodium without calcium resulted in the formation of a sodium salt of an aluminosilicate polymer. Precipitation of sodium aluminum silicate actually increased at higher pH, which supported the theory that higher concentrations of $Al(OH_4)^-$ in the presence of excess silica led to an increased formation of aluminosilicate anions . However, the polymers that formed at higher pH appeared to be of shorter chain length, incorporating fewer aluminum and silicon atoms.

When calcium was also present, a calcium aluminum silicate formed preferentially and appeared to make the polymer chain lengths shorter, as determined by an Al:Ca ratio of only 1.5, as compared to an Al:Na ratio of 4 – 5 in the absence of calcium.

Amorphous silica polymerization was initiated in the presence of calcium, as determined by the high ratio of silica to aluminum. The fact that this phenomenon only became pronounced when divalent cations were added indicates that neutralization of anionic repulsion charges likely allowed the necessary interaction between anionically charged aluminosilicates and deprotonated silica monomers and oligomers. The calcium therefore acted as a catalyst for polymerization of silanol bonds of the aluminosilicates with the silanol bonds of silica monomers and oligomers.

The more effective antiscalants completely inhibited formation of aluminosilicate compounds, and in turn, amorphous silica. None of the antiscalants that were marketed as silica inhibitors were effective at preventing aluminosilicate salt precipitation or silica polymerization when aluminum was present in high concentrations.

The valence of the cations also significantly impacted the antiscalant dosage necessary for inhibition of the aluminosilicate compounds. In solutions containing sodium, aluminosilicates were inhibited with a dosage of only 4 ppm when 0.3 ppm Aluminum ion (Al^{3+}) was present in the feed water at 85% recovery. When a feed water concentration of 87 ppm calcium was present in addition to the sodium and 0.3 ppm Al^{3+} at 85% recovery, aluminosilicates could not be controlled even with a dosage as high as10 ppm.

Aluminum ion (Al^{3+}) concentration had the most pronounced effect on the required antiscalant dosage. An 8 ppm dosage was necessary to control aluminosilicates at a reduced feed water Al^{3+} concentration of only 0.2 ppm at 85% recovery. When Al^{3+} was reduced to 0.1 ppm under the same conditions, only 1.5 ppm of antiscalant was necessary for aluminosilicate inhibition. A feed water Al^{3+} concentration of 0.04 ppm (below MDL) was easily controlled by 0.5 ppm antiscalant dosage – this low dosage was effective using all antiscalants, even those that failed to performed under all other test conditions. By contrast, when the feed water calcium concentration was reduced by 10 times to 8.7 ppm while maintaining a feed water Al^{3+} concentration of 0.2 ppm at 85% recovery, the required antiscalant dosage was only reduced by half.

Calcium silicate consistently formed in the control tests, verifying that ionic interactions between calcium and silica were in fact taking place. Calcium silicate was easily controlled by all scale inhibitors. However, only Products H and Product I were effective inhibitors of aluminosilicate compounds when Al^{3+} was present in significant concentrations .

An autopsy of a membrane from a plant that had used alum coagulants had similarly high molar ratios of silica to aluminum. X-ray diffraction found the foulant to be entirely amorphous and no crystalline aluminum silicates could be positively identified. Clays are unlikely to form in RO/NF processes – a search revealed that most studies that successfully precipitated crystalline clays involved experiments that ranged from 40 days to 4 years.

In conclusion, calcium in typical RO/NF feed water catalyzes the formation of aluminosilicates and causes them to polymerize with amorphous silica thereby forming substrates for silica scaling. Increasing pH allows more anionic aluminosilicate polymers to form, thereby resulting in heavier precipitation with cations and consequent amorphous silica deposition. However, inhibiting the formation of these salts using an effective antiscalant would clearly prevent silica scaling of membranes. The efficacy of the antiscalant appears to be dose dependent, with the dosage being directly correlated to aluminum ion and calcium ion concentrations.

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VIII. Appendix A: List of Products Tested

No Antiscalant	Control
Product A	Avista Vitec 3000
Product B	King Lee PTP 100
Product C	Nalco PC191
Product D	Genesys LF
Product E	King Lee Y2K
Product F	Avista Vitec 4000
Product G	PWT Spectraguard
Product H	AWC A-108
Product I	AWC A-110