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The role of dissolved aluminum in silica chemistry for membrane processes

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Abstract

The use of aluminum sulfate (alum) coagulation prior to reverse osmosis (RO) treatment has been shown to be problematic. Membrane fouling was theorized to occur through soluble aluminum (Al^{3+}) reacting with ambient silica (H_4SiO_2) to form kaolinite ($Al_2Si_2O_5(OH)_4$) within the RO unit. Chelating agents (citrate at 34 mg/L and ethylenediaminetetraacetic acid [EDTA] at 16 mg/L) were tested for their efficacy in controlling aluminum silicate fouling. The results of bench-scale testing demonstrated that both citrate and EDTA did control aluminum silicate formation, citrate more so than EDTA. Additional aluminum-based fouling was encountered when a commercial, phosphonate-based antiscalant — used to control barium sulfate scaling — reacted with the excess aluminum despite the presence of either citrate or EDTA.

Keywords: Aluminum; Silica; Silicate; Membrane; Fouling

1. Introduction

Membrane technologies (e.g., reverse osmosis [RO], nanofiltration [NF]) have found wider acceptance in recent years. However, membrane treatment is still more expensive than conventional water treatment technologies (e.g., coagulation, flocculation, sedimentation, multi-media filtration). In an effort to reduce the costs of RO and NF treatment, the Metropolitan Water District of Southern California (MWDSC) initiated the Desalination Research and Innovation Partnership to evaluate cost-effective methods to desalinate Colorado River water (CRW), as well as municipal wastewater and brackish groundwater [1]. One option available to lower desalting costs is the use of preexisting conventional treatment prior to RO treatment rather than membrane filtration.

During conventional treatment, aluminum sulfate (alum) coagulation is often employed.

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Conventional treatment alone does not reduce the total dissolved solids (TDS) of the water; in fact, the TDS may increase slightly if coagulant salts are added or the pH is adjusted. In theory, effluent from a conventional treatment plant could serve as the feedwater to any desalting step. Based on alum dosages at MWDSC and aluminum's inherent solubility, as much as 200 μg/L aluminum has been measured at the filter effluent. This aluminum residual may interact with ambient silica within the membrane system to cause unexpected fouling with aluminum silicates. Silica, or silicates, can act as nucleation sites for further fouling by calcium carbonate or barium sulfate and may even increase the rate of biological or organic fouling [2].

This paper presents results using metal chelating agents to prevent aluminum silicate fouling of RO membranes when using conventional treatment as the pretreatment step. Geochemical modeling was conducted to evaluate the aluminum silicate formation potential of CRW treated with alum coagulation, followed by confirmatory testing with a bench-scale RO unit.

2. Background

2.1. Literature survey

Research published on silicate scaling is sparse. Aluminum silicates are frequently found deposited onto plumbing materials in distribution systems [3,4]. This phenomenon may result from the "post-precipitation" of soluble aluminum and silica that pass through a treatment plant or, alternatively, by the deposition of colloidal aluminum silicates that pass through treatment [5]. Amorphous silica scale, rich in aluminum, has also been found deposited in geothermal brines, which usually have temperatures of about 200ºC and pressures of about 116 psi (800 kPa) [6].

Silicates have more recently been found as a foulant in both low-pressure (i.e., microfiltration [MF] and ultrafiltration) and high-pressure (i.e., RO) water treatment processes. Norman et al. [7] described silicate fouling of MF membranes in a demonstration-scale MF plant in Orange County, California. The investigators attributed the silicate fouling of the microfibers to the use of silica-laden water during high-pH cleaning. Additional cleaning of the membrane fibers with ammonium bifluoride was then required; however, the hazardous nature of this cleaning compound precludes its widespread and continuous usage.

Aluminum silicate fouling has been reported in RO applications. Based on previous work at MWDSC, aluminum silicate scaling was observed [8,9]. Byrne [10] documented silicate formation and cleaning with ammonium bifluoride for RO membranes. During a system failure, Butt et al. [11] identified alumino-silicate scale deposition in a hollow-fiber RO unit treating brackish water in Saudi Arabia. The polyacrylate — and hydroxyethylidene diphosphonate — based antiscalant tested was ineffective against aluminum silicate scale.

2.2. Overview of aluminum and silica chemistry

Aluminum undergoes hydration reactions in aqueous systems to form insoluble metal hydroxides (Fig. 1). When alum ($Al_2(SO_4)_3$•14 H_2O) is added to water containing natural alkalinity, the following general reaction occurs [12]:

$$\begin{aligned}&Al_2(SO_4)_3{\bullet}14H_2O + 3Ca(HCO_3)_2\\&\Rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + 6CO_2 + 14H_2O\end{aligned} \quad (1)$$

However, based on solution pH, various aluminum polymers and monomers are possible. At the pH ranges observed at MWDSC's treatment plants (pH 7.5–8.5), aluminum is primarily found in the form $Al(OH)_4^-$; however, other forms of hydrated aluminum seen may include $AlOH^{2+}$, $Al(OH)_2^+$, $Al_3(OH)_4^{5+}$, and $Al_{13}O_4(OH)_{24}^{7+}$ [13]. Aluminum is least soluble from pH 5.7 to 6.2 [14].

In the aluminum system, the most common mineral phase is gibbsite ($Al(OH)_3$). Gibbsite is least soluble at pH 6, and between pH 7 and 9 the major dissolved species is $Al(OH)_4^-$. In natural

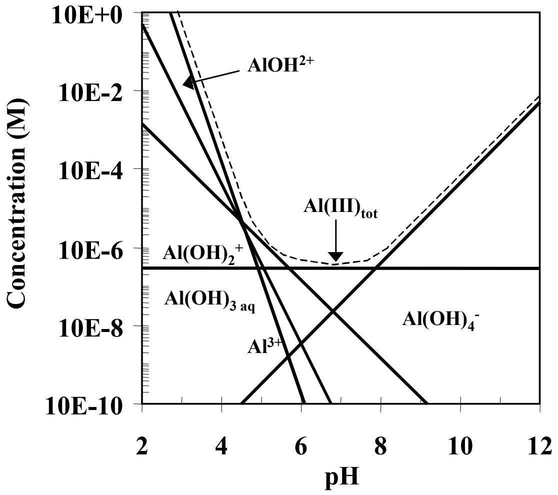


Fig. 1. Solubility of amorphous (a) Al(OH)$_3$. Polynuclear complexes not included. (Adapted from Stumm and Morgan 1996 [13].)

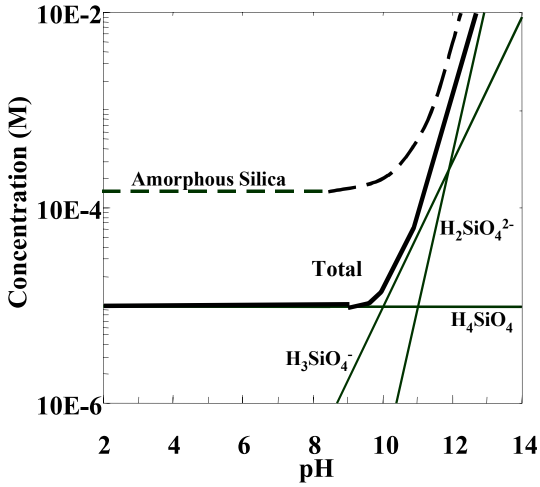


Fig. 2. Activity of dissolved silica species in equilibrium with quartz (the heavy line) and amorphous silica (the dotted line) at 25ºC. (Adapted from Drever 1988 [16].)

water systems, gibbsite formation is complicated by formation of the meta-stable intermediate (polynuclear Al$_{13}$) because of kinetic restraints [15]. However, while experimental evidence confirms the existence of polynuclear Al$_{13}$, there is doubt that "giant" cations such as $Al_{13}O_4(OH)_{24}^{7+}$ are present in coagulated waters [14].

For silica, the major mineral-solution equilibrium would be from the dissolution of quartz. The total dissolved silica concentration is the sum of the ionized and nonionized species (Fig. 2) [16]. At pH 7–9 (the pH range for CRW), mineral quartz forms when dissolved silica exceeds 10^{-4} mol/L (or 6 mg/L). A higher concentration of total dissolved silica — $10^{-2.7}$ mol/L (120 mg/L) — is required for the formation of amorphous silica. The predominant dissolved species in equilibria is silicic acid (H_4SiO_4) at pH 7–9.

2.2.1. Formation tendency of aluminum silicate scales

The presence of multivalent ions such as Al^{3+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, and others affects silica solubility [2,17,18]. Earlier work in the industrial sector developed concentration guidelines to determine silica solubility in the presence of magnesium for cooling-tower waters [18,19]. However, similar relationships for aluminum were not found in the literature.

The formation of aluminum silicates requires the presence of both dissolved aluminum and silica. The mineral equilibrium and pH of the solution regulate the concentration and speciation of dissolved silica and aluminum.

Fig. 3 shows that at the ambient levels of aluminum (10^{-7} mol/L) and silica (~10^{-4} mol/L as H_4SiO_4), CRW is supersaturated with respect to kaolinite and gibbsite [16]. Furthermore, as the solution is concentrated through the RO process, the total aluminum and silica concentrations will continue to increase, thereby further exceeding the solubility of kaolinite. Therefore, the precipitation of kaolinite is thermodynamically possible, however, the kinetics of kaolinite formation within an RO system are unknown.

The general equation for kaolinite formation is:

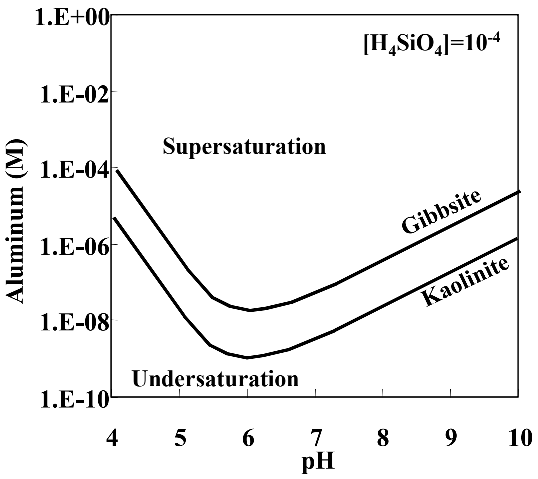


Fig. 3. Solubility diagram of kaolinite and gibbsite at H_4SiO_4 (aqueous) concentration of 10^{-4} mol/L. (Adapted from Drever 1988 [16].)

$$\begin{aligned}&2Al^{3+} + 2H_4SiO_4 + H_2O \\ &= Al_2Si_2O_5(OH)_4 \text{ (kaolinite)} + 6H^+\end{aligned} \tag{2}$$

2.2.2. Potential mitigation strategies

Strategies for avoiding precipitative scaling often include ways of reducing the concentration of either the anion or the cation portion of the ion pair of concern [20–22]. For example, by adding acid [H^+], magnesium hydroxide solubility can be increased by shifting Eq. (3) to the right:

$$Mg(OH)_{2(s)} \Leftrightarrow Mg^{2+} + 2OH^- \tag{3}$$

However, at the pH levels typically encountered at MWDSC's drinking-water filtration plants, aluminum solubility is fairly insensitive to pH adjustment (Fig. 1), though the speciation changes from $Al(OH)_4^-$ (pH 8.5) to Al^{3+} (pH 6.0). It should be noted that at lower pH (pH 5.7–6.2), improved coagulation occurs that will result in lower soluble aluminum. Silica solubility is also insensitive to pH over the same pH range (Fig. 2). For aluminum silicate scale in the geothermal brine fields, Gallup [6] showed that lowering the brine pH to below 5 or increasing it above 9 retarded the kinetics of silica polymerization and the formation of aluminum-rich silica. However, for municipal water treatment applications, these pH levels would not be feasible because adjustment to pH 5 would be too expensive, and raising the pH would lead to severe calcium carbonate scaling. Therefore, pH control may not be a practical solution to prevent aluminum silicate fouling.

Many antiscalants designed to control for silica scaling are ineffective against aluminum silicates [2,23]. During the aluminum silicate fouling episodes using MF, Norman et al. [7] suggested that ethylenediaminetetraacetic acid (EDTA) or other chelating agents may sequester dissolved metals and avoid silicate fouling. However, no further studies were reported. Gallup [6] demonstrated that sequestering agents such as citric acid, acetic acid, and EDTA may inhibit aluminum silicate scale formation in geothermal brines. In a follow-up pilot-scale study, Gallup [24] indicated that complexing and/or sequestering agents with carboxylate functional groups showed promise in achieving metal-silicate scale inhibition by complexation with aluminum or iron in brine to form anionic species that are less prone to precipitation reactions with silicic acid oligomers. The potential aluminum complexing or sequestering agents included glycolic acid, formic acid, sodium formate, tartaric acid, and glyoxal. While dispersant agents containing phosphonic acid and/or phosphonate functional groups may inhibit pure amorphous silica, they potentially precipitate aluminum as phosphates or phosphonates; thus, they may act as foulant themselves. Treatment of brine with potassium tetrafluoroborate (KBF_4) yielded good inhibition results [24]. However, KBF_4 is highly corrosive.

Results from Metropolitan's in-house studies indicated that early silicate-fouling problems might have been exacerbated by low cross-flow across the membrane surface of the last element in the system. Under these conditions, colloidal silica may have deposited onto the membrane surface [25]. However, as water recoveries increase past 85%, maintaining adequate cross-flow velocity may not be possible. Therefore, a new silica-control alternative is desirable.

3. Experimental methods

3.1. Modeling methods

Geochemical modeling (WATEQ4F, US Geological Survey, Denver, Colo.) was conducted to compute major and trace element speciation and mineral saturation for RO influent water [26]. Predominance area diagrams were used to evaluate the formation tendency of silicate scales on RO membrane surfaces. The assumption was that there was sufficient time to reach equilibrium at the membrane surface. Historical unfiltered raw-water data from Lake Mathews, California, for major ions (data taken between June 1976 and September 2000) and trace metals (data taken between October 1993 and April 1999) were used to model CRW influent and effluent. The RO concentrate data were calculated based on experimental data taken at 85% water recovery.

3.2. Bench-scale testing

3.2.1. Source water

For bench-scale testing, CRW (550 mg/L TDS) at pH 6.7 was used, and aluminum nitrate (Fluka Chemical Corp., Milwaukee, Wis.) ($Al(NO_3)_3 \cdot 9H_2O$) was added to raise the aluminum concentration to 200 μg/L. For inorganic analysis of the test water (Table 1). The source water was pretreated prior to the RO unit by a 0.2 μm nominal pore size microfiltration membrane (Aqua Pro Membranes, Gardena, Calif.). No chloramine residual was maintained in the influent water. A 20-gal (76 L) reservoir was used to store the MF effluent prior to RO treatment. Combinations of citrate (34 mg/L), EDTA (16 mg/L), and antiscalant (Pretreat 191 (1.6 mg/L), Permacare, Fountain Valley, Calif.) were added to the RO influent to sequester the aluminum via chelation.

Table 1
Mean influent water quality data for bench-scale testing

Parameter	Bench-scale testing*
Total dissolved solids, mg/L	609 (2, 2.8)
Total hardness as $CaCO_3$, mg/L	290 (2, 4.9)
Total alkalinity as $CaCO_3$, mg/L	73 (2, 0.7)
Total organic carbon, mg/L	2.98 (2, 0.13)
Hydrogen concentration (pH)	6.8 (2, 0.2)
Calcium, mg/L	69.5 (2, 0.7)
Magnesium, mg/L	26 (2, 0)
Potassium, mg/L	4.25 (2, 0.07)
Sodium, mg/L	82 (2, 1.4)
Sulfate, mg/L	272 (2, 0.7)
Chloride, mg/L	70 (2, 0)
Fluoride, mg/L	0.28 (2, 0.01)
Nitrate, mg/L	2.00 (2, 0)
Silica, mg/L	9.13 (2, 0.27)
Aluminum, μg/L	171 (2, 15)
Barium, μg/L	95 (2, 6)
Iron, μg/L	39 (2, 13)
Strontium, μg/L	931 (2, 35)

*CRW after pH adjustment and aluminum addition.
Data in parentheses indicate number of samples and standard deviation, respectively.

3.2.2. Bench-scale RO unit

Three identical, closed-loop, bench-scale RO units were used during this phase of testing. The bench-scale RO testing used spiral-wound, thin-film-composite, polyamide membranes (Energy Saving Polyamide ESPA1-2012, Hydranautics, San Diego, Calif.). The dimensions of each element were 1.8 in. (4.6 cm) diameter by 12 in. (30 cm) long, with 4.8 ft^2 (4,500 cm^2) of membrane surface area per element. Prior to testing, each RO element was soaked in deionized water for 3 h. The RO elements were then placed in the RO unit and flushed with 10 gal (39 L) of deionized water for 1 h, followed by a second flush with deionized water for an additional 3 h in order to equilibrate the permeate flux and salt rejection of the RO membranes under normal operating pressure (80 psi [550 kPa]) and constant concentrate flow (0.85 gpm [3.2 L/min]).

For each experiment, the final water recovery was set at 95% in order to accelerate the scale formation. Throughout the experiment, the operating pressure and concentrate flow rate were maintained at 80 psi and 0.85 gpm, respectively. The RO unit recycled the concentrate flow and discarded the permeate flow. Water recovery of 95% (from 20 gal [76 L] to 1 gal [3.8 L]) was typically reached within 9 h. Permeate flow rate was recorded every hour. The feed, permeate, and concentrate temperature and conductivity were also measured hourly. Once 95% water recovery was reached, the RO unit was shut down and the RO elements and final concentrate were collected for analysis. All samples taken were refrigerated for further analyses. The unit was then flushed with tapwater to remove any residual solution.

3.3. Analytical methods

Alkalinity, hardness, major cations and anions, TDS, trace metals, turbidity, temperature, and pH were measured per Standard Methods [27]. Membrane flux and salt rejection were normalized to 25°C per ASTM method D 4516-85 [28].

Upon fouling, the RO membranes were autopsied to evaluate the level of fouling, if any. Swatches of membrane material were collected and sent to independent laboratories for microscopic analysis. Scanning electron microscopy (SEM) (Cambridge Instruments model 360, Leo Electron Microscopy, Thornwood, NY) was conducted by the Scripps Oceanographic Institute in La Jolla, Calif. Membrane samples were prepared for top surface views by cutting a small piece of membrane and then attaching it to an aluminum mount with double-stick tape. Cross-sections were prepared by fracturing a small strip of the membrane in a liquid nitrogen bath; this was also attached to an aluminum mount. The mounted sample was sputter-coated with a 30 nm layer of gold and palladium. Energy-dispersive spectroscopy (EDS) (Model QX2000, Oxford Instruments, Concord, Mass.) was conducted in concert with the SEM by the Scripps Oceanographic Institute. The membrane sample for EDS analysis was attached to a graphite mount with graphite tape; there was no coating on the sample. This technique was used because graphite is not detected by EDS and does not interfere with atoms being measured in the sample.

4. Results and discussion

4.1. Geochemical modeling

Given that the RO scaling involves precipitation-dissolution reactions of metals and inorganic constituents in water, geochemical modeling was used to calculate the mineral scaling potentials of the RO influent water at equilibrium. A potential limitation of this modeling is that all the model results assume that equilibrium has been reached and reaction kinetics do not control the process. The geochemical modeling also calculated the concentrations of different species of various elements in the system, based on the total concentration of that element and all possible equilibrium mineral reactions that may be involved. The element speciation calculation predicted the prevalent element forms and may help identify the major reactions leading to scaling. Modeling results showed that the total dissolved aluminum was 99% in the form of $Al(OH)_4^-$ at pH 8.2. Because $Al(OH)_4^-$ at pH 8.2 would be converted to Al^{3+} at pH 7.0, Al^{3+} was the sole important ion in aluminum silicate formation in CRW.

From Figs. 4–6, the potential aluminum silicates that could be precipitated in the influent and effluent of an RO system at 85% water recovery were kaolinite and muscovite. For CRW, the concentrations for major cations exhibited the following pattern in both the RO influent and effluent: Na > Ca > K (Table 1). Therefore, theoretically, kaolinite would precipitate before muscovite in the presence of either calcium or potassium. The

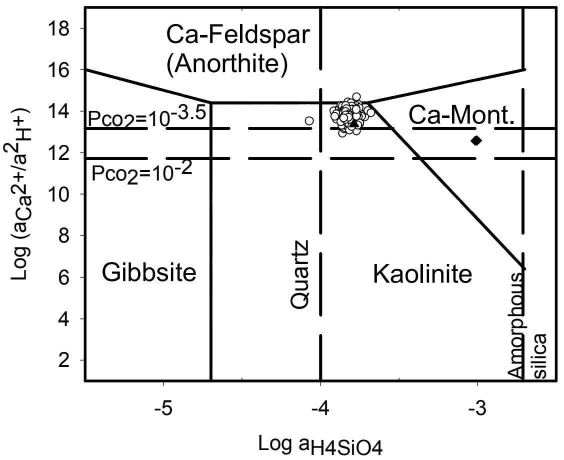


Fig. 4. Predominance area diagram of CaO–Al_2O_3–SiO_2–H_2O system at 25°C. Symbols indicate modeling results using historical water quality data (O = influent data; ◆ = RO brine).

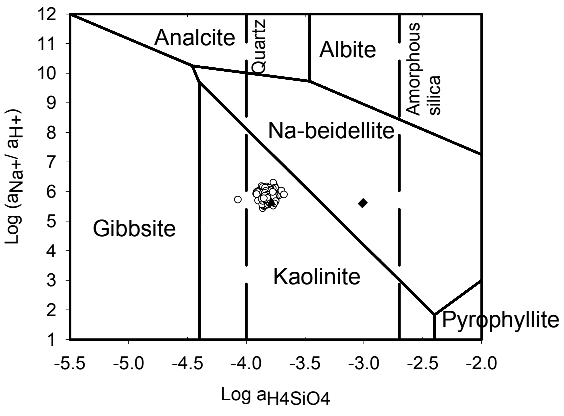


Fig. 5. Predominance area diagram of Na_2O–Al_2O_3–SiO_2–H_2O system at 25°C. Symbols indicate modeling results using historical water quality data (O = influent data; ◆ = RO brine).

modeling of the concentrate also showed that Ca–montmorillonite ($Ca_3(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$), Na–beidellite ($NaAl_2(Si,Al)_4O_{10}(OH)_2{\cdot}nH_2O$) and K–feldspar ($KAlSi_3O_8$) might also be formed when the solution reached saturation.

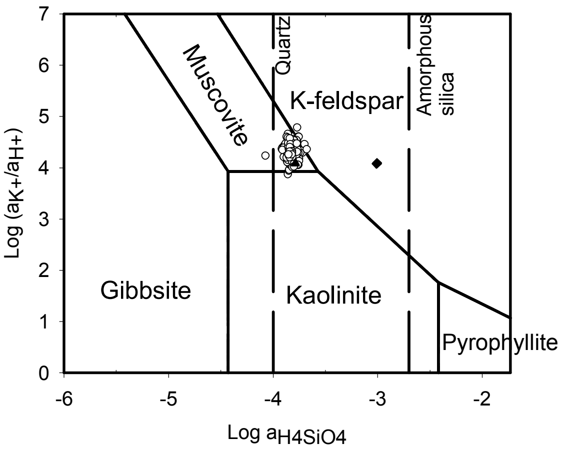


Fig. 6. Predominance area diagram of K_2O–Al_2O_3–SiO_2–H_2O system at 25°C. Symbols indicate modeling results using historical water quality data (O = influent data; ◆ = RO brine).

4.2. Bench-scale testing

Preliminary testing with CRW at ambient (58 µg/L) aluminum levels (i.e., prior to alum coagulation) showed no fouling of the membrane surface by aluminum silicates or other aluminum-containing species upon concentration of the water by 20 x using a variety of antiscalants. These data indicate that when the amount of aluminum is insufficient, aluminum silicates are not formed.

To mimic the aluminum level often encountered at MWDSC's treatment plants, excess aluminum (as $Al(NO_3)_3{\cdot}9H_2O$) was added to the microfiltered source water to yield 200 µg/L dissolved aluminum. In addition, the pH of the feedwater was reduced to pH 6.7 (using H_2SO_4) to avoid calcium carbonate scaling, which can complicate data interpretation. The measured dissolved aluminum in the source water was 170 µg/L, which agreed closely with the theoretical yield. Therefore, prior to RO treatment a majority of the aluminum remained in solution. Combinations of a commercial antiscalant (CA1) and two generic antiscalants (citrate and EDTA) were used in this test. Note: Citrate and citric acid are essentially the same chemical; only the counter-ion differs between the two. Since CA1 had demonstrated its ability to prevent calcium and barium scales [29], and EDTA and citrate/citric acid were good potential aluminum sequestering agents, combinations of these antiscalants may provide protection against both traditional (e.g., barium sulfate and calcium carbonate) and nontraditional (i.e., aluminum silicates) scales.

Fig. 7 shows the percentage of dissolved aluminum and silica that remained in solution after concentration by 20 ×. Citrate and EDTA appeared to perform better as aluminum complexation agents than did the commercial antiscalant (CA1) alone. Citrate and EDTA increased the dissolved percentage of aluminum by 40 and 10%, respectively, which amounted to more than a 200% improvement in aluminum solubilization relative to the control. In terms of silica solubilization, EDTA showed the greatest percentage of increase (52% compared to 23% for the control), with citrate demonstrating an 80% increase in silica solubilization (42% dissolved silica) (Fig. 7). Adding a commercial antiscalant (CA1) did not improve the aluminum binding potential of either citrate or EDTA. These data may indicate that for antiscalant CA1, a majority of the aluminum was deposited on the membrane surface (further discussion to follow). The silica data for two of the experiments (CA1 and CA1/Citrate) are unavailable, although previous testing using both CA1 and citric acid showed no effect on silica solubility [29].

As a result of aluminum addition, both aluminum and silica were detected by EDS of the colloidal material collected by filtering the brine through a 0.45 μm filter for the control sample (Table 2), indicating the formation of aluminum silicates. Furthermore, the filtered colloidal

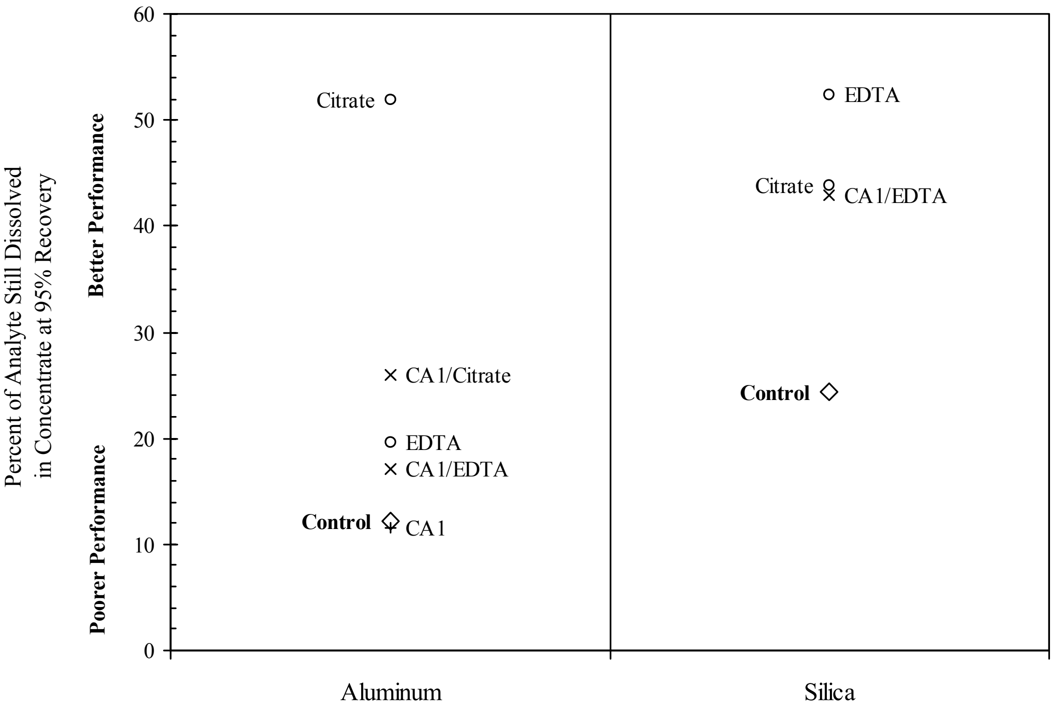


Fig. 7. Dissolved analytes in RO concentrate for commercial, generic, and blends of commercial and generic antiscalants in bench-scale testing with 170 μg/L aluminum added. (CA1 = commercial antiscalant, Permacare Pretreat 191).

Table 2
EDS data for colloidal material from brine stream using CRW with 170 µg/L aluminum*

Element	Antiscalant					
	Control	CA1	EDTA	Citrate	CA1/EDTA	CA1/Citrate
Aluminum	21	—	—	16	26	19
Arsenic	—	—	—	—	—	—
Bromine	—	4.5	—	—	—	—
Calcium	12	82	94	16	17	44
Chlorine	2.8	—	—	2.0	3.1	3.1
Copper	14	4.3	—	—	—	—
Iron	—	—	—	3.3	2.3	—
Magnesium	4.2	—	1.1	6.4	4.7	4.1
Phosphorus	—	—	—	6.3	12	4.9
Potassium	—	—	—	2.3	—	—
Silica	41	6.7	—	36	24	16
Sodium	—	—	1.0	6.7	4.5	4.3
Sulfur	4.4	2.8	3.5	5.3	6.0	5.4

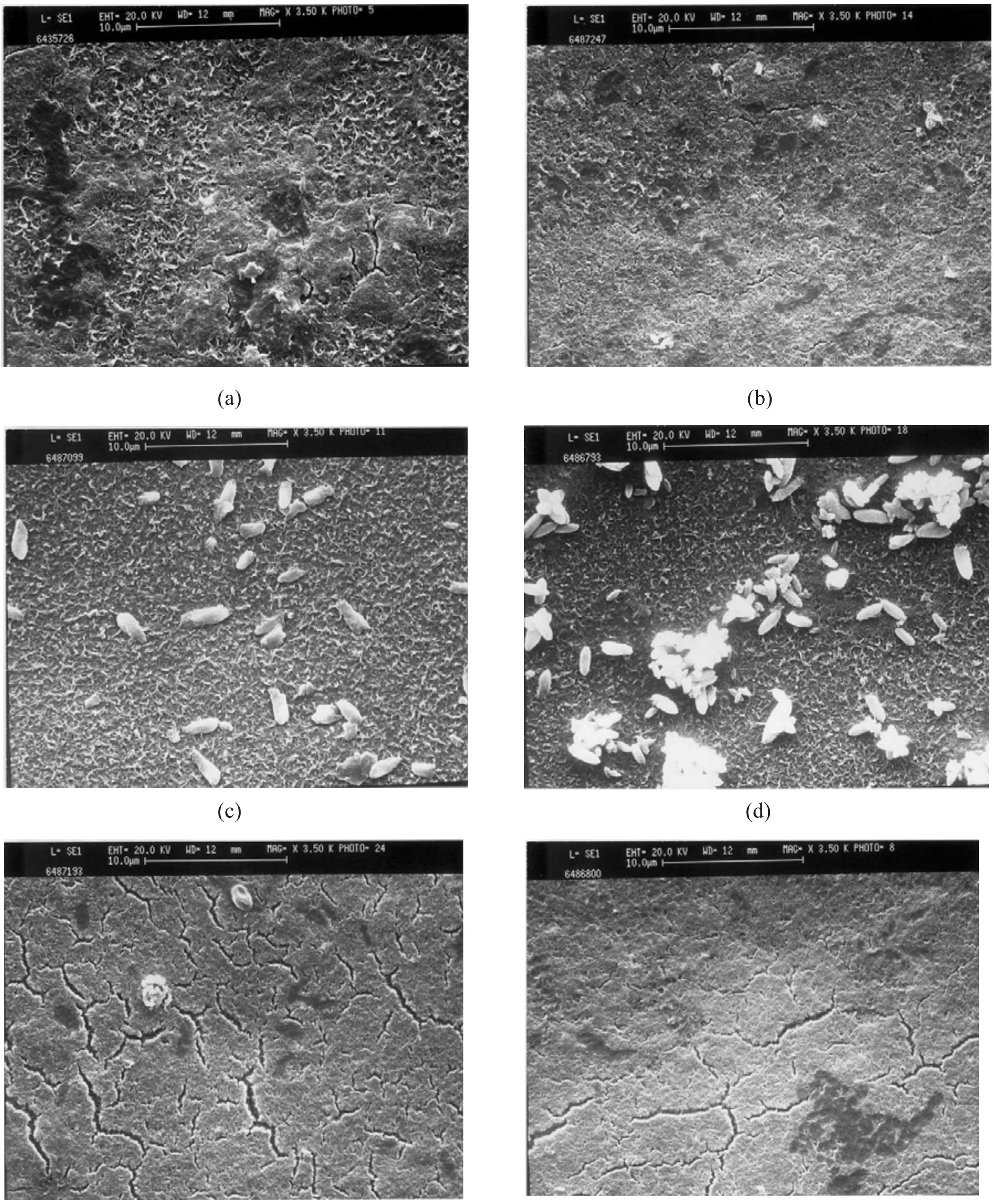
*All data given as % w/w
— Not detected

material contained gray material that cracked upon drying, which was a typical characteristic of clay-containing scales found previously at Metropolitan [9]. When the gray precipitate was exposed to 0.1 N HCl, the material did not dissolve or effervesce, which indicated a lack of calcium carbonate scaling. Additionally, the acid test provided a key indication that the gray precipitate material was aluminum silicate rather than aluminum hydroxide in nature. Below pH 5.7, freshly precipitated aluminum hydroxides are quite soluble [14]. These results demonstrated that aluminum played a vital role in the formation of aluminum silicate scales in CRW.

SEM data showed a clay-like coating on the membrane surfaces for most experiments using excess aluminum (Fig. 8). Notable exceptions are experiments using citrate and EDTA alone, in which both samples showed white grains on the membrane surface, with little other foulant present. These grains may have been calcium carbonate or calcium sulfate scales, as no protection against these foulants (i.e., a commercial antiscalant) was present. EDS data indicated the presence of calcium for the EDTA-treated sample (Table 3). The EDS method uses a small sample area and may not include the grains in the analysis; therefore, calcium may have been present, but not detected, in the citrate-treated sample.

EDS detected aluminum on the membrane surface for all but the citrate-treated sample. For this sample, the visual evidence supports the lack of aluminum silicate fouling (Fig. 8) based on the absence of semi-porous, clay-like material on the membrane surface. In addition, citrate demonstrated superior performance in keeping aluminum in solution (Fig. 7), which may have prevented aluminum from precipitating as either a silicate or hydroxide material. While no visual evidence of aluminum silicate was observed on the EDTA-treated sample, EDS data detected the presence of both aluminum and silica on the membrane surface. Therefore, both citrate and EDTA demonstrated good aluminum silicate preventive properties, citrate more so than EDTA.

The combination of CA1 and citrate showed the strong presence of aluminum and silica on the membrane surface (Table 3) despite this



(a) (b)

(c) (d)

(e) (f)

Fig. 8. SEM micrographs (3,500 x magnification) of fouled RO membranes from the aluminum addition study: (a) control, (b) CA1, (c) citrate, (d) EDTA, (e) CA1/citrate, (f) CA1/EDTA. (CA1 = commercial antiscalant, Permacare Pretreat 191).

Table 3
EDS data from RO membranes using CRW and 170 µg/L aluminum*

Element	Antiscalant					
	Control	CA1	EDTA	Citrate	CA1/EDTA	CA1/Citrate
Aluminum	19	19	18	—	25	26
Arsenic	—	—	—	—	—	14
Calcium	—	4.3	30	—	—	—
Chlorine	—	6.4	—	8.9	—	7.3
Magnesium	—	8.1	5.3	—	—	—
Silica	10	5.6	6.9	6.8	—	5.5
Sodium	23	21	8.4	31	19	22
Sulfur	48	35	32	53	56	27

*All data given as % w/w
— Not detected

combination's ability to keep aluminum in the soluble form (Fig. 7). The CA1/EDTA combination also showed the presence of aluminum in excess of the generic antiscalant alone, though no silica was detected (Table 3). These data suggest that the commercial antiscalant component of the mixture may have reacted with the aluminum to form a precipitate. Phosphorous, a key inorganic component of the CA1 antiscalant, was detected in the colloidal phase for both of the antiscalant combination experiments (Table 2), which supports the theory that the aluminum reacted with the commercial antiscalant. Multivalent ions (e.g., Al^{3+}) have been shown to form precipitates with soluble phosphates [30]. The basic reaction involved in the precipitation of phosphorus and aluminum follows:

$$Al^{3+} + H_nPO_4^{n-3} \Leftrightarrow AlPO_4 + nH^+ \tag{4}$$

While phosphorous was not detected via EDS on any of the membrane samples during this study, other research conducted at the MWDSC Water Quality Laboratory has positively identified phosphorus on the membrane surface under similar test conditions [29].

Alternatively, the aluminum may have deposited as a hydroxide salt; the hydroxide ion is not detected by EDS analysis. Given EDTA's ability to sequester silica (Fig. 7), the precipitate may be in the form of an aluminum hydroxide; this possibility is supported by the lack of silica detected on the membrane surface (Table 3). In addition, both silica and aluminum were detected in the CA1/citrate sample, indicating fouling caused by aluminum silicates and/or aluminum hydroxides. A potential fouling pathway is through the creation of an aluminum hydroxide or other bound-aluminum foulant that originally precipitates onto the membrane surface, with these foulants then serving as nucleation sites for subsequent aluminum silicate formation.

5. Conclusions

Geochemical data developed through this project showed that aluminum silicate scale formation is thermodynamically plausible, with kaolinite and muscovite being the most likely silicate end products. Based on the limited experimental data, citrate and EDTA may effectively act as aluminum sequestering agents that may lead to the prevention of aluminum silicate or hydroxide scaling. Adding a commercial antiscalant did not improve the generic chemicals' ability to control for aluminum silicate fouling, and may be a contributing factor in aluminum-based scalant formation. Three different forms of aluminum-based foulants were potentially identified during this project: (1) aluminum silicates, (2) aluminum hydroxides, and (3) aluminum phosphates. Further research is needed to confirm the presence of any one of these compounds preferably through crystallography or X-ray diffraction spectroscopy. Finally, alternative methods of controlling aluminum, such as alum coagulation at reduced pH or ferric-based coagulation, need to be explored.

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