THE ROLE OF WATER CHEMISTRY ON PREVENTING SILICA FOULING IN INDUSTRIAL WATER SYSTEMS

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ABSTRACT

Deposition of silica and silicate based foulants in industrial water systems (e.g., cooling, desalination, geothermal) and in reverse osmosis systems continues to be one of most difficult challenges for water technologists. The complexity of controlling silica stems from the limited solubility of both amorphous (polymerized) silica and metal silicates in the feed waters. Once formed, silica scale is extremely difficult to remove and often requires the use of mechanical and/or chemical methods; fluoride-based chemicals which present environmental and safety concerns. Therefore, industrial water systems using silica fouling prone feed waters typically employ conservative operating criteria; e.g., cooling systems limit cycles of concentration and desalination systems limit recovery. This paper and results presented herein:

• Compare the performance of polymeric additives as silica polymerization inhibitors.
• Show the impact of impurities (i.e., inorganic and organic coagulant/flocculant) on the performance of silica inhibitors.
• Illustrate the effect of water chemistry (type and concentration of cations) on the performance of silica inhibitors.
• Characterize the composition of silica precipitates formed during the experiments.

Keywords: silica polymerization, inhibitors, iron, aluminum, cationic polymer, water chemistry

INTRODUCTION

Silica and metal silicate-based salts have been described as the most problematic foulants in industrial water systems operating with silica laden feed water.1-3 In desalination of brackish water by reverse osmosis (RO) process, silica-based fouling problems caused reduced permeate production rates (lower recovery rates), increased energy costs, poor permeate quality, and more frequent membrane cleaning. In evaporative cooling systems, water technologists must maintain silica at acceptable levels (usually below 180 mg/L in absence of silica/silicate control agents) to avoid silica-based deposits. This requires (a) operating systems at low cycles of concentration which increases water consumption and/or (b) the incorporation of silica/silicate control agents in the water treatment programs. In geothermal
applications, factors such as variable fluid compositions, fluctuating plant operating conditions, and the complex nature of silica polymerization reaction collectively contribute to silica/silicate fouling problem. The composition and the amount of silica scale as well as the rate at which it forms is dependent on silica supersaturation, pH, temperature, hardness ions concentration, and system impurities. Additionally, silica-based deposits are particularly difficult to remove once they form necessitating the use of strong chemical cleaners such as ammonium bifluoride or even hydrofluoric acid. Clearly, the process of cleaning the systems not only poses environmental challenges but also runs the risk of damaging the heat exchangers and RO membranes.

In silica supersaturated solutions the formation of amorphous silica follows a pattern of the breakdown of the soluble silica unit and the growth of the silicate anion into a larger macromolecule via anionic polymerization as shown in the reaction below:

\[
\text{Si(OH)}_4 + \text{OH}^- \rightleftharpoons (\text{OH})_3\text{SiO}^- + \text{other silicates} \quad (1)
\]

\[
(\text{OH})_3\text{SiO}^- + \text{Si(OH)}_4 \rightarrow \text{colloidal silica} \quad (2)
\]

Over the years, a variety of approaches have been proposed to combat silica/silicate fouling in industrial water systems. These methods fall into five (5) categories: a) operating system at low silica/silicate supersaturation, b) reducing silica concentration by precipitation process in feed water, c) using an additive to prevent silica polymerization, d) creating and inhibiting metal-silicate compound precipitation, and e) incorporating an additive into water treatment formulation to disperse silica/silicate deposits. The success of each method depends on the feed water chemistry, system design, and operating conditions. Although operating systems at low supersaturation levels is a common practice, this approach may become cost prohibitive due to large water consumption cost. The second approach to minimize silica-based fouling involves reduction of silica concentration by pretreating feed water. Commonly used chemicals for silica removal include polyvalent metal hydroxides i.e., Al(OH)₃, Fe(OH)₃, and Mg(OH)₂. It has been reported that these chemicals effectively remove both soluble and colloidal silica. In addition, the amount of hydroxide required for removing silica increases but not in direct proportion with increasing silica concentrations. Various processes involved in silica removal include chemical reaction and/or adsorption.

The third approach to control silica fouling involves the use of additives that effectively inhibit silica polymerization in aqueous solutions. Neofotistou and Demadis in their study on the evaluation of polyaminoamide-based dendrimers as silica inhibitors for cooling water applications reported that a polymer’s performance as silica polymerization inhibitor strongly
depends on the branching present in the dendrimer. Amjad and Yorke\textsuperscript{6} reported that cationic-based copolymers are effective silica polymerization inhibitors. Similar conclusions were also reported by Harrar, et al.\textsuperscript{7} in their investigation on the use of cationic polymers and surfactants in inhibiting silica polymerization under geothermal conditions. Although these cationic-based homo- and co-polymers showed excellent performance in terms of inhibiting silica polymerization, they offered poor silica/silicate dispersing activity.

Another approach that has been attempted for controlling silica/silicate fouling requires the incorporation of a dispersant in the water treatment formulation. Polymeric dispersants used in water treatment are typically low molecular weight and anionic in nature. These dispersants function by imparting negative charge via adsorption onto suspended particles. Because most silica-based deposits consist of amorphous silica and/or magnesium silicate, the ideal candidate must have two distinct properties. It must (a) disperse both silica and magnesium silicate and (b) disperse scalant particles, (e.g., calcium carbonate, calcium sulfate that can act as nuclei for silica/silicate deposits).\textsuperscript{8}

The performance of a formulated product containing hydroxyl phosphono acetic acid and a copolymer of acrylic acid:hydroxyl sulfonate ether in high hardness waters containing high alkalinity and 225 mg/L silica, has been reported.\textsuperscript{9} The inspection of the heat exchanger showed essentially no deposits in the presence of formulated product compared to heavy scaling and silicate deposits in the control (no treatment). Momazaki, et al.\textsuperscript{10} reported the use of poly(acrylamide) – based treatment program to control silica problem in recirculating cooling water systems. Gill and coworkers,\textsuperscript{11} in another study conducted using high silica water at pH>9, documented that a blend of phosphonate and a copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid can effectively extend the operating limits for silica from 120 to 300 mg/L.

The type and extent of impurities such as aluminum, iron, manganese, zinc, suspended matter, etc., present in re-circulating cooling water has been reported to exhibit antagonistic effects on the performance of deposit control polymers used in cooling water treatment formulations.\textsuperscript{12} It has also been shown that the effectiveness of the surface water treatments in reducing suspended solids is dependent on the proper selection and feed rate of coagulants or flocculants, pH, mixing time, and residence time. Chemicals commonly used in a coagulating or flocculating capacity include alum, ferric chloride, and cationic polymer such as diallyldimethyl ammonium chloride. These chemicals are known to “carry over” and have been reported to decrease the performance of calcium phosphate\textsuperscript{13} and calcium phosphonate inhibitors.\textsuperscript{14} In addition, it has also been reported that low levels (0.1 to 1.0 ppm) of flocculants or coagulants exhibit antagonistic influence on the efficacy of iron oxide dispersants.\textsuperscript{15}

In our earlier studies,\textsuperscript{16-18} we reported the results for the performance of a variety of commercial polymers as silica polymerization inhibitors and particulate matter (e.g., iron oxide, clay, silica, magnesium silicate, etc.) dispersants. It was shown that inhibitor architecture plays an important role in preventing the formation of silica scale in industrial water systems. Furthermore, we have also previously reported that low levels of metal ions (e.g., Al, Fe, Mn) exhibit marked antagonistic influence on the efficacy of calcium phosphate\textsuperscript{13} and calcium phosphonate\textsuperscript{14} scale inhibitors, and iron oxide dispersants.\textsuperscript{15} The present work focuses on the impact of various system impurities such as Al(III), Fe(III), and hardness ions on the performance of silica polymerization inhibitors.
EXPERIMENTAL

Reagent grade chemicals and distilled water were used throughout the study. Silica stock solutions were prepared from sodium metasilicate, standardized spectrophotometrically, and stored in polyethylene bottles. Calcium chloride and magnesium chloride solutions were prepared from calcium chloride dihydrate and magnesium chloride hexahydrate, and were standardized by titrating with standard ethylenediammine tetraacetic acid. Standard solutions of Fe(III) and Al(III) were purchased from Fisher Scientific. The inhibitors used in this study were commercial materials† and are listed in Table 1. All experimental results are reported on a 100\% active inhibitor basis for comparative purposes.

Silica polymerization experiments were performed in a polyethylene container placed in a double-walled glass cell maintained at 40°C. The silica supersaturated solutions were prepared by adding a known volume of water in the polyethylene container. After allowing the temperature to equilibrate, the silicate solution was quickly adjusted to pH 7.0 using hydrochloric acid [HCl]. The pH of the solution was monitored using a pH meter equipped with a combination electrode. The electrode was calibrated before each experiment with NIST standard buffers. After pH adjustment, a known volume of a calcium chloride and magnesium chloride stock solution was added to the silicate solution. The silicate supersaturated solution was re-adjusted to pH 7.0 with dilute NaOH and/or HCl and was maintained constant throughout the silica polymerization experiment. Experiments involving inhibitors, Fe(III), Al(III), and cationic polymer were performed by adding inhibitor solutions to the silicate solution before adding the calcium chloride and magnesium chloride solution. The reaction containers were capped and kept at constant temperature and pH during the experiments.

Figure 1 presents the experimental setup. Silica polymerization in these supersaturated solutions was monitored by analyzing the aliquots of the filtrate from 0.22-µm filter paper for the soluble silica using the standard colorimetric method as described previously.² Unless noted otherwise, all silica polymerization experiments were carried out in the presence of 550 mg/L silica concentration. The silica polymerization inhibition values were calculated according to the following equation:

\[
\%SI = \frac{[\text{SiO}_2]_{\text{sample}} - [\text{SiO}_2]_{\text{blank}}}{[\text{SiO}_2]_{\text{initial}} - [\text{SiO}_2]_{\text{blank}}} \times 100\% \quad (3)
\]

Where:

| SI       |   | Silica Inhibition (%) or %SI |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| [SiO₂]_{sample} | =   | Silica concentration in the presence of inhibitor at 22 hr |
| [SiO₂]_{blank}  | =   | Silica concentration in the absence of inhibitor at 22 hr |
| [SiO₂]_{initial}| =   | Silica concentration at the beginning of experiment |

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† Includes two (2) Carbosperse™ K-700 polymers supplied by Lubrizol Advanced Materials, Inc.

™ Trademark of The Lubrizol Corporation.
RESULTS AND DISCUSSION

Silica Polymerization Inhibition by Polymers

As discussed in the following paragraphs, a series of silica polymerization inhibition experiments were carried out in the presence and absence of polymers using the experimental protocol described above to evaluate the effects of polymer dosage, coagulating/flocculating agents, and hardness ions.

**Effect of Polymer Dosage.** The assessment of polymer effectiveness as a silica inhibitor was done at similar initial silica super-saturation (550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40°C) and in the presence of varying polymer concentrations. Figure 2 details the silica concentrations versus time profiles in the absence and in the presence of varying concentration of copolymer blend (CP5). The results suggest that (a) silica concentration decreases with increasing time indicating the progress in silicate polymerization and (b) silica concentration at a given time increases with increasing polymer dosage. For example, silica concentrations in the absence of polymer at time equal to 0, 1, and 3 hr are 560, 458, and 299 mg/L, respectively. Figure 2 also presents the silica inhibition as a function of CP5 concentration. At 22 hr in the presence of 15 ppm CP5, the silica concentration in solution is 230 mg/L compared to 177 mg/L in the absence of CP5. At 25 and 50 ppm CP5 concentrations the silica concentrations are 370 and 495 mg/L, respectively.

Figure 3 presents silica inhibition data calculated according to equation 3 for CP3, CP4, CP5, and CP6. It can be seen that CP6, compared to CP5, exhibits excellent performance as silica polymerization inhibitor especially at low dosages. For example, %SI value obtained in the presence of 25 ppm of polymers at 22 hr for CP6 is 12% compared to 56% for CP5. Figure 3 also presents performance data for two (2) competitive commercial silica/silicate control polymers (CP3 and CP4). Compared to CP5 and CP6, the competitive polymers (CP3 and CP4) show poor performance (even at 350 ppm dosages; not shown) as silica polymerization inhibitors. Our previous studies have shown that other homo-, co-, and terpolymers that are excellent scale (e.g., calcium sulfate, calcium phosphonates, calcium sulfate) inhibitors and particulate (e.g., iron oxide) dispersants are ineffective silica polymerization inhibitors. The data presented in Figure 3 and earlier studies clearly show that polymer architecture plays an important role in inhibiting scale formation in industrial water systems.

**Effect of Coagulating/Flocculating Agents.** The use of flocculating agents (inorganic and organic types) to flocculate/coagulate suspended matter in feed water and wastewater streams is well known. The purpose of this treatment is to remove suspended colloidal solids that are responsible for color, odor, taste, etc. The suspended solids commonly present in feed waters include metal oxides, clays, microorganisms, organic debris, etc. Bulk water treatment is facilitated by adding inorganic metal salts to destabilize the colloidal particles and induce coagulation and flocculation. Commonly used inorganic salts include aluminum chloride, aluminum sulfate, and ferric chloride. Although these chemicals are effective in coagulating/flocculating colloidal particles, they are corrosive and generate large sludge volumes. However, the metal salts treatment can be augmented by the use of cationic polymer such as diallyldimethyl ammonium chloride.
• **Inorganic Metal Salts.** It is well established that low levels of coagulating/flocculating additives present in recirculating waters are antagonistic to the performance of scale inhibitors and dispersants. To understand the role of both inorganic and organic coagulants/flocculants on the performance of silica polymerization inhibitors (i.e., CP5 & CP6), a series of experiments were carried out in the presence of varying Fe(III) concentrations. As shown in Figure 4, low Fe(III) levels (e.g., 0.25 ppm) exhibits a negative or antagonistic influence on the silica polymerization inhibition by CP5 and CP6. Increasing Fe(III) levels to 0.50 to 1.0 ppm further decreases silica inhibition (%Si) values. For example, the %Si values obtained in the presence of 0.50 ppm Fe(III) are 59% for CP5 and 70% for CP6. It is evident from Figure 5 that CP6 is more tolerant to Fe(III) than is CP5. Similar antagonistic effects by Fe(III) have been reported\(^{12}\) in studies involving calcium phosphate inhibition by anionic polymers.

The influence of low Al(III) levels was also investigated by carrying out a series of silica polymerization experiments in the presence of 50 ppm of CP5 and CP6. Results presented in Figure 5 clearly show that silica polymerization inhibitor performance is strongly impacted by the presence of Al(III). As illustrated in Figure 5, silica polymerization inhibition values for both polymers decreased 20 to 30% by adding 0.10 ppm Al(III) and more pronounced antagonistic effects occurred when adding 0.25 ppm Al(III). By comparing the silica polymerization inhibition of CP5 and CP6 in the presence of metal ions (see Figures 4 and 5), it is evident that Al(III) exhibits a more antagonistic effect than Fe(III). The markedly greater antagonism on silica inhibition values caused by of Al(III) compared to Fe(III) may be attributed to the different cationic charge density present on metal salts hydroxides.

• **Cationic Polymer:** Figure 6 presents silica polymerization inhibition data for CP5 and CP6 in the presence of varying concentrations of a cationic polymer (diallyldimethyl ammonium chloride or DADMAC). The data presented in Figure 6 indicate that DADMAC dosages up to 3.0 ppm cause a slightly antagonistic effect on the silica polymerization inhibition performance of CP5 and CP6. This is very interesting, because cationic polymers such as DADMAC have previously been shown to exhibit strong antagonistic effects on the performance of calcium phosphate\(^{12}\) and calcium phosphonate\(^{14}\) inhibitors. The silica polymerization inhibition performance differences observed in Figure 6 may be attributed to different ionic charges.

**Effect of Hardness Ions.** It is generally known that the presence of metal ions affects both the rate of precipitation and crystal morphology of scale forming salts. Metal ions are also known to form insoluble salts with silicate ions in aqueous solution. To understand the role of metal ions (i.e., Ca\(^{2+}\), Mg\(^{2+}\)) on silica polymerization inhibition in the presence of CP6, a series of experiments were carried out at similar initial silica concentration and varying concentrations of calcium/magnesium chloride solution.

Figure 7 presents silica concentrations as a function of time for experiments carried out in the presence of 50 ppm CP6 and varying total hardness (“TH” or Ca\(^{2+}/\)Mg\(^{2+}\)) concentrations. The data indicate that silica polymerization inhibition increases as a function TH concentration. A comparison of data in Figures 2 and 7 suggests that Ca\(^{2+}/\)Mg\(^{2+}\) addition exhibits an opposite effect on silica polymerization inhibition, i.e., silica polymerization inhibition is greater in the presence than in the absence of Ca\(^{2+}/\)Mg\(^{2+}\).

The influence of total dissolved solids (TDS) on silica polymerization inhibition in the presence of 50 ppm CP6 was investigated. Figure 8 presents % silica inhibition values at 22 hr in the presence of 50 ppm CP6 and varying TDS concentrations (either Ca\(^{2+}/\)Mg\(^{2+}\) [2:1] as described above or sodium chloride [NaCl]). As indicated, silica polymerization inhibition strongly depends on the Ca\(^{2+}/\)Mg\(^{2+}\) concentration present in the silica supersaturated solutions.
Figure 8 also shows that divalent metal ions (i.e., Ca$^{2+}$, Mg$^{2+}$) in the presence of constant ionic strength exhibit a greater effect on silica polymerization inhibition than monovalent cations (i.e., Na$^+\). Specifically, % silica inhibition values obtained using 50 ppm CP6 in the presence of similar ionic strength but different total dissolved solids levels (i.e., Na$^+$ [1,755 mg/L NaCl] and Ca$^{2+}$/Mg$^{2+}$ [320 mg/L TH or total hardness]) at similar ionic strength are 16% and 92%, respectively. The performance variations caused by total dissolved solids (i.e., Na$^+$ and total hardness [either Ca$^{2+}$ or Mg$^{2+}$]) on silica polymerization may be attributed to different charge density of these metal ions.

Silica Precipitates Characterization and Composition

The silica precipitates formed during the silica polymerization experiments were studied using X-Ray Diffraction (XRD) and Electromagnetic Dispersion Spectroscopy (EDS). Figure 9 shows the XRD spectra of the precipitates formed in the presence of 0 and 50 ppm of CP5 and CP6. The spectra suggest that the silica precipitates are amorphous in nature. The Figure 10 silica precipitate XRD spectra show that the precipitates consist essentially of silicon and oxygen with only trace amounts of calcium and magnesium present in the filtered solid. This observation was confirmed by analyzing calcium and magnesium ions before and after filtration wherein there was no significant concentration difference. The trace levels of Ca and Mg shown in the EDS spectrum may be due to surface adsorption of Ca and Mg on the unwashed precipitated silica.

SUMMARY

The silica polymerization process that may lead to silica scaling in industrial water systems is complex and primarily governed by system operating conditions (e.g., pH, temperature, impurities). Unfortunately, unlike other scales (i.e., calcium carbonate, calcium phosphate) silica scaling is not easily controlled by simply adjusting pH of the re-circulating waters. Operating cooling water and RO systems under alkaline pH may lead to the formation of undesirable magnesium silicate scale. The proprietary inhibitors and/or formulated products developed and touted for silica control over the last three decades have achieved limited commercial success primarily due to either inhibitor inefficiency under the system operating conditions and/or poor cost/benefit ratios.

Results presented herein indicate that silica polymerization strongly depends on water chemistry, i.e., type and concentration of mono, di- and triavlant ions. It has been found that low levels ($\leq$1 ppm) of inorganic flocculants such as Al(III) and Fe(III) exhibit antagonistic effects on the performance of silica polymerization inhibitors. However, the presence of up to 3 ppm of cationic flocculant (DADMAC) has insignificant (<5%) antagonistic effects on the performance of both CP5 and CP6.

The data presented in this paper show that Ca$^{2+}$ and Mg$^{2+}$ present in the silica supersaturated solution exhibits a synergistic effect on the performance of CP6 whereas the presence of Na$^+$ has an insignificant influence on silica polymerization. In addition, XRD and EDS spectra of silica samples collected in the presence and absence of CP5 or CP6 show that the silica precipitates formed are amorphous in nature with essentially no incorporation of hardness ions.
REFERENCES


Table 1: Polymeric Additives Evaluated

<table>
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<tr>
<th>Additive</th>
<th>Composition</th>
<th>Acronym</th>
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<tr>
<td>Comp-1</td>
<td>Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:non-ionic)</td>
<td>CP3</td>
</tr>
<tr>
<td>Comp-3</td>
<td>Proprietary acrylic copolymer</td>
<td>CP4</td>
</tr>
<tr>
<td>K-XP212</td>
<td>Proprietary copolymer blend</td>
<td>CP5</td>
</tr>
<tr>
<td>K-XP229</td>
<td>New proprietary copolymer blend</td>
<td>CP6</td>
</tr>
</tbody>
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Figure 1: Set-Up for Silica Polymerization Inhibition Experiments
Figure 2: Silica Polymerization Inhibition as a Function of CP5 Dosage
(550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40 deg C)

Figure 3: Silica Polymerization Inhibition as a Function of Polymer Dosage
(550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40ºC, 22 hr)
Figure 4: Effect of Fe(III) Concentration on Silica Polymerization Inhibition by Polymers (50 ppm)
(550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40°C, 22 hr)

Figure 5: Effect of Al(III) Concentration on Silica Polymerization Inhibition by Polymers (50 ppm)
(550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40°C, 22 hr)
Figure 6: Effect of Cationic Polymer on Silica Polymerization Inhibition by Polymers (50 ppm)
(550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40°C, 22 hr)

Figure 7: Silica Concentration vs. Time in Presence of 50 ppm CP6 and Varying Total Hardness (TH) Levels
(550 mg/L silica, pH 7.0, 40°C)
Figure 8: Influence of Total Dissolved Solids Levels on Silica Polymerization Inhibition by 50 ppm CP6
(550 mg/L silica, pH 7.0, 40°C, 22 hr)

Total Dissolved Solids (TH = Total Hardness)

Figure 9: XRD Spectra of Amorphous Silica Formed in the Absence and Presence of CP5 and CP6
Figure 10: EDS Spectra of Amorphous Silica