Factors Impacting Silica-Silicate Control Agent Performance in Industrial Water Systems

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ABSTRACT

The formation and control of silica-silicate based deposits presents enormous operational challenges for industrial water systems including brackish water reverse osmosis, evaporative cooling, and geothermal systems where silica supersaturation levels exceed saturation limits. Water technologists typically maintain silica levels below 180 mg/L in absence of silica inhibitors to avoid silica-based deposition because once formed silica scale is extremely difficult to remove and often requires the use of mechanical and/or chemical cleaning methods.

Water shortages, increasingly poor quality water supplies, and environmental regulations that limit wastewater discharges have resulted in more silica-silicate limited industrial water systems. Consequently, there is a growing need for effective chemical treatments to minimize silica-silicate based fouling. Effective silica-silicate chemical treatments should both (a) function as amorphous silica inhibitors and b) effectively inhibit crystalline scale forming salts. The study herein focuses on the effects of silica supersaturation, water hardness levels, system temperature, and biocide on the performance of a new silica-silicate control agent compared to other commercially available inhibitors. Silica-based deposits formed in both the presence and absence of inhibitors are characterized.

INTRODUCTION

Precipitation and deposition of amorphous silica and metal silicate on heat exchangers, reverse osmosis (RO) membrane, and other equipment surfaces presents an enormous operational challenge to water technologists. Systems affected by silica-silicate based deposits include evaporating cooling,\(^1\) desalination,\(^2\) and geothermal.\(^3\) Silica solubility is well known to be dependent on pH, temperature, trivalent metal ions, and total dissolved solids, and is generally accepted to be <150 mg/L. The potential for silica scaling occurs when the dissolved silica level in re-circulating water or an RO system reject stream exceeds the amorphous silica solubility limit (≈100 mg/L at ambient temperature). Exceeding silica solubility can cause silica precipitation and deposition thereby leading to loss of equipment efficiency, premature shut down, and in some cases irreversible damage. Cleaning silica fouled equipment surfaces is expensive and time consuming. Amorphous silica formation via silica polymerization, colloidal silica suspension, precipitation of metal silicates, and co-precipitation of silica with mineral salts (e.g., calcium carbonate, calcium sulfate) are different processes responsible for the deposition of silica-based deposits. Preventing the formation of silica-silicate based deposits requires control of all these processes simultaneously.\(^4\)

In evaporative cooling systems, water technologists must maintain silica at acceptable levels (usually <180 mg/L in absence of silica-silicate control agents) to avoid the formation of 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, silica-scale formation typically occurs when brine is cooled during brine handling and energy extraction. Factors contributing to silica-based deposits include variable fluid compositions, fluctuating operating conditions, and the complex nature of silica polymerization reaction.

Once formed, silica-silicate based deposits are very difficult to remove from equipment surfaces. Both chemical and mechanical methods are used to remove silica-silicate based deposits.
However, strong chemical cleaners (e.g., ammonium bifluoride, hydrofluoric acid) pose environmental challenges and require care to avoid damaging equipment whereas mechanical cleaning is labor intensive. Figure 1 shows the mechanism of polymerization of amorphous silica which follows a pattern of the breakdown of the soluble silica unit and the growth of the silicate anion into larger macromolecule via hydroxide catalyzed anionic polymerization.

The approaches to prevent silica-silicate fouling in industrial water systems may be grouped into eight (8) categories as follows:

1) Operating systems at low silica-silicate supersaturation.
2) Reducing feedwater silica concentration using precipitation process(es).
3) Preventing silica polymerization using additive(s).
4) Inhibiting metal-silicate precipitation.
5) Incorporating additive(s) into water treatment programs to disperse silica-silicate deposits.
6) Effectively controlling other scales such as CaCO₃ to minimize the incorporation of silica species in crystal matrix.
7) Effective carbon steel corrosion control (<3 MPY).
8) Maintain <pH 8.3 to avoid metal-silicate precipitation.

The success of each method and/or combination of methods depends on the feed water chemistry, system design, and operating conditions. The first method or operating systems at low supersaturation levels is a common practice but may not be feasible due to water consumption costs and/or water scarcity. The second approach to minimize silica-based fouling involves reducing system silica concentrations by pre-treating 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 or controlling silica fouling involves the use of additives as discussed herein that effectively inhibit silica polymerization in aqueous solutions. The fourth method or the use of boric acid and/or its water soluble salts to control silica-based deposits in cooling water systems operating at 250 to 300 mg/L silica has been reported. Silica inhibition presumably originates from the ability of borate to condense with silicate to form borate-silicate complexes which are more soluble than silica. The use of borate-based inhibitors to increase silica solubility is limited because of the high use levels for boron-based compounds as well as the associated costs and effluent discharge limitations.

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**Figure 1: Silica Polymerization Process**

<table>
<thead>
<tr>
<th>Si(OH)₄⁻</th>
<th>OH⁻</th>
<th>Reversible reaction</th>
<th>(OH)₂SiO⁻</th>
<th>H₂O</th>
<th>Silicic acid</th>
<th>Hydroxide ion</th>
<th>Silicate ion</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OH)₃⁺</td>
<td>Si(OH)₄⁻</td>
<td>→</td>
<td>(OH)₂Si</td>
<td>– O – Si(OH)₃</td>
<td>+ OH⁻</td>
<td>Silicate ion</td>
<td>Silicic acid</td>
<td>Hydroxide ion</td>
</tr>
</tbody>
</table>

2n (OH)₂Si – O – Si(OH)₃

Polymeric silica scale

Ca, Mg, etc.

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Amjad and Yorke\textsuperscript{7} reported that cationic-based copolymers are effective silica polymerization inhibitors. Similar conclusions were also reported by Harrar, et al.\textsuperscript{8} 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 silica polymerization inhibition, they exhibited poor silica-silicate dispersing activity. Neofotistou and Demadis\textsuperscript{9} in their study on the evaluation of polyaminoamide-based dendrimers as silica inhibitors for cooling water applications reported that polymer performance as silica polymerization inhibitor strongly depends on the branching present in the dendrimer.

Polymeric dispersants that impart negative charge via adsorption onto suspended particles have also been used for minimizing silica-silicate fouling in industrial water systems. Because most silica-based deposits consist of amorphous silica and/or magnesium silicate, the ideal candidate(s) must have two distinct properties: (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{10}

The performance of a formulated product containing hydroxylphosphono acetic acid and a copolymer of acrylic acid:hydroxyl sulfonate ether in high hardness waters containing high alkalinity and 225 mg/L silica, was reported.\textsuperscript{11} 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{12} reported the use of a poly(acrylamide)–based treatment program to control silica in recirculating cooling water. Gill and coworkers,\textsuperscript{13} in a study conducted using high silica water at above 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.

Although, the mechanisms of silica-silicate inhibition, deposition, dispersion, etc., have been studied in great depth, no unified understanding of various processes involved in silica-silicate deposition currently exists. In previous papers, we reported the results of laboratory experiments designed to determine the efficacy of various commercially available polymeric additives touted as silica polymerization inhibitors and metal-silicate dispersants.\textsuperscript{14} It was shown that acrylic acid based homo- and copolymers commonly used as deposit control agents are ineffective as silica polymerization inhibitors. The results of earlier studies also reveal that low level of metal ions (e.g., Al, Fe, cationic polymeric flocculant) exhibit marked adverse effects on silica inhibiting polymer performance.\textsuperscript{15}

It is generally accepted that lowest limit of amorphous silica saturation level in industrial water systems is \(\approx 1.2x\). Based on previously published data, it can be assumed that a conservative maximum treated silica saturation level in cooling water systems is \(\approx 2.2x\). For the purposes of evaluating silica polymerization inhibitors herein, we selected more challenging water chemistry with a silica saturation level extended to \(\approx 3.0x\). We also investigated the impact of various factors affecting the performance of silica polymerization inhibition process including silica supersaturation, temperature, and oxidizing biocide. In addition, silica precipitates formed in the presence and absence of inhibitor were studied by X-ray diffraction and energy dispersive X-ray spectroscopy.
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.

Table 1 summarizes the descriptions, compositions, and acronyms for the commercially available polymers evaluated in the present study. The results herein are reported on an active polymer solids basis.

Silica Polymerization Inhibition Test Method

Reagent grade chemicals and distilled water were used in accordance with Lubrizol’s “Silica Polymerization Inhibition Test Procedure” shown schematically in Figure 2 and discussed below.

Table 1: Polymers Evaluated

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition &amp; Molecular Weight (M&lt;sub&gt;W&lt;/sub&gt;)</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK732*</td>
<td>Solvent polymerized poly(acrylic acid); 6k M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>P3</td>
</tr>
<tr>
<td>CK798*</td>
<td>Poly(acrylic acid : 2-acrylamido-2-methylpropane sulfonic acid: sulfonated styrene); &lt;15k M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>CP2</td>
</tr>
<tr>
<td>CCP-D**</td>
<td>Poly(acrylic acid : 2-acrylamido-2-methylpropane sulfonic acid : non-ionic); 5k M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>CP3 #</td>
</tr>
<tr>
<td>CCP-A**</td>
<td>Proprietary acrylic copolymer; &lt;20k M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>CP5 #</td>
</tr>
<tr>
<td>CKXP212*</td>
<td>Proprietary copolymer blend; &lt;20k M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>CP6 #</td>
</tr>
<tr>
<td>CKXP229*</td>
<td>Proprietary copolymer blend; &lt;20k M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>CP7 #</td>
</tr>
</tbody>
</table>

Notes:

* Carbosperse™ K-700 polymer supplied by Lubrizol Advanced Materials, Inc.  
** The Lubrizol Corporation.  
# Polymer promoted as silica-silicate deposit control agent.  

Polymer containing >50% carboxylic monomers.

Figure 2: Silica Polymerization Inhibition Experimental Protocol
Silica polymerization experiments were performed in polyethylene containers placed in double-walled glass cells maintained at 40°C. The supersaturated solutions were prepared by adding known volumes of stock solution of sodium silicate (expressed as SiO\textsubscript{2}) solution and water in polyethylene containers. After allowing the temperature to equilibrate, the silicate solutions were quickly adjusted to pH 7.0 using dilute hydrochloric acid [HCl]. The pH of the solutions was monitored using Brinkmann/Metrohm pH meter equipped with a combination electrode. The electrode was calibrated before each experiment with standard buffers. After pH adjustment, a known volume of calcium chloride and magnesium chloride stock solution was added to the silicate solutions. The supersaturated silicate solutions were re-adjusted to pH 7.0 with dilute HCl and/or NaOH and maintained constant throughout the silica polymerization experiments. The experimental set-up used to study silica polymerization is shown in Figure 3.

Experiments involving inhibitors were performed by adding inhibitor solutions to the silicate solutions before adding the calcium chloride and magnesium chloride solution. The reaction containers were capped and kept at constant temperature and pH during the experiments. Silicate polymerization in these supersaturated solutions was monitored by analyzing the aliquots of the filtrate from 0.22-µm filter paper for soluble silica using the standard colorimetric method. The silica polymerization inhibition values were calculated according to the equation below.

% Inhibition = \frac{[\text{SiO}_2]_{\text{sample}} - [\text{SiO}_2]_{\text{control}}}{[\text{SiO}_2]_{\text{initial}} - [\text{SiO}_2]_{\text{control}}} \times 100

Where the terms above are as follows:

- % Inhibition = Percent silica polymerization inhibition or %SI
- [SiO\textsubscript{2}]\text{sample} = Silica concentration in the presence of inhibitor at 22 hr
- [SiO\textsubscript{2}]\text{control} = Silica concentration in the absence of inhibitor at 22 hr
- [SiO\textsubscript{2}]\text{initial} = Silica concentration at the beginning of test
RESULTS AND DISCUSSION

Silica Supersaturation: To understand the effect of supersaturation on silica polymerization process, a series of experiments were carried out under various silica supersaturation (SS) conditions. Figure 4 presents profiles of soluble silica concentration as a function of time for various silica SS solutions. It can be seen that at higher silica concentration (i.e., 550 mg/L) polymerization takes place immediately, as evident from the sharp decrease in soluble silica concentration with time. However, as illustrated in Figure 4, at a lower degree of supersaturation, a decrease in silica concentration is preceded by a slow polymerization reaction (induction time or α). During the induction time, the concentration of soluble silica does not change significantly. However, once polymerization process starts, soluble silica begins decreasing. For example, α values observed for 450 mg/L and 320 mg/L silica concentrations are 5 hr and 8 hr, respectively compared to <5 minutes observed at higher concentration (e.g., 550 mg/L).
**Inhibitor Dosage**: It is generally accepted that lowest limit of amorphous silica supersaturation level in industrial water systems is $\approx 1.2x$. Based on the previously published data, it can be assumed that a conservative maximum silica saturation level for treated cooling water systems is $\approx 2.2x$. Therefore, for the purposes of evaluating silica polymerization inhibitors herein, we selected 3.0x silica saturation (i.e., 550 mg/L) to evaluate polymers as silica polymerization inhibitors.

Figure 5 presents 22-hr silica inhibition data for polymeric inhibitors containing different functional groups (e.g., carboxylic acid, non-ionic, sulfonic acid) for up to 50 ppm dosages. The data in Figure 5 indicate the following:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3, CP2, CP3, &amp; CP5</td>
<td>Provide poor (&lt;20%) performance at all dosages tested (including up to 350 ppm).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP6</td>
<td>Performance increases dramatically from poor to excellent with dosages up to 35 ppm and improves incrementally thereafter.</td>
</tr>
<tr>
<td>CP7</td>
<td>Performance increases dramatically as dosage increases from 5 ppm (7% SI) to 25 ppm (85% SI) and improves incrementally thereafter.</td>
</tr>
</tbody>
</table>

It is evident from Figure 5 that the homopolymer (P3) and copolymers (CP2, CP3, CP5) commonly used in water treatment formulations as deposit control agents for controlling mineral scales and dispersing suspended matter are poor (<10% inhibition) silica inhibitors. The performance data for these polymers with the exception of a copolymer blends (CP6 & CP7) show that carboxylic acid, sulfonic acid, and non-ionic groups present in the polymers (i.e., P3, CP2, CP3, and CP5) exhibit poor interaction with silane groups present in silica.
**Hardness Ions:** It is generally known that the presence of metal ions (i.e., Ca, Mg, Al, Fe, Cu) affects both the rate of precipitation and crystal morphology of scale forming salts\(^{17,18,19}\). It has also been reported that hardness ions (Ca, Mg) affects the performance of iron oxide dispersants.\(^{20}\) Metal ions (i.e., Ca, Mg, Fe, Al) are also known to form insoluble salts with silicate ions. The precipitation of metal-silicate salts is known to strongly depend on precipitation conditions (i.e., pH, temperature, silicate, metal concentrations).\(^{21}\)

The influence of varying total hardness (TH) levels (using calcium and magnesium \([Ca^{2+}/Mg^{2+}]\) in a 2:1 ratio and ranging from 0 to 320 mg/L) on silica polymerization in the presence of 50 ppm CP7 has been reported.\(^{15}\) The previous study results indicated that CP7 silica inhibition increases with increasing TH; further research/ investigation is required and underway to explain these results.

To understand whether or not hardness ions are co-precipitated during silica polymerization in the presence of CP7, a series of experiments were conducted. Figure 6 presents silica, calcium, and magnesium concentrations vs. time profile in the presence of 15 ppm CP7. As shown, the initial calcium (200 mg/L) and magnesium (120 mg/L) concentrations remain essentially constant (within the experimental error or ±3\%) during the silica polymerization experiments while silica concentration decreases with time. Figure 6 suggests that neither Ca nor Mg precipitated out of the solutions in the presence of CP7. Although not presented herein, similar results for calcium and magnesium concentrations were also observed with higher silica supersaturated solutions and higher calcium (280 mg/L) and magnesium (168 mg/L) concentrations.

**Solution Temperature:** It is well documented that solubility of scale forming salts such as calcium carbonate, calcium sulfate, and calcium phosphates are inversely dependent on solution temperature.\(^{22}\) The solubility-temperature relationship suggests that the scaling tendency will be higher at the heat exchanger surfaces than in other parts of the recirculating water systems. It was also reported\(^{23}\) that calcium ion tolerance of anionic scale control polymer decreases markedly as solution temperature increases from 25 to 70\(^\circ\)C. However, the situation is very different for silica supersaturated systems because silica solubility increases with increasing temperature thus resulting in lower supersaturation.

![Figure 6: Silica, Ca, & Mg Concentrations vs. Time in the Presence of 15 ppm CP7](image)
To investigate the influence of solution temperature on inhibitor performance, several experiments were conducted using the silica polymerization test conditions and temperatures ranging from 25 to 68°C (i.e., 25, 40, 55, and 68°C). Figure 7 illustrates the time-dependent silica concentration profiles in the absence of inhibitor indicating that solution temperature significantly influences silica polymerization. There are two competing factors contributing to temperature influence: (a) silica supersaturation decreases with increasing temperature due to increased silica solubility and (b) silica polymerization rate increases with increasing temperature. Figure 7 data suggests that temperature is the primary driver for silica supersaturation impacting silica solubility in these test conditions.

The impact of solution temperature on silica polymerization inhibition was also investigated in the presence of various inhibitor dosages. For example, Figure 8 compares silica inhibition (%SI) as a function of CP7 dosage at 40 and 55°C and clearly shows that increasing solution temperature (or reducing silica supersaturation) reduces the CP7 dosage necessary to inhibit silica polymerization.
Similarly, the influence of solution temperature on silica polymerization is clearly evident from the data in Figure 9. As shown, the CP6 and CP7 polymer dosages needed for >80% silica inhibition is a function of both temperature (decrease as temperature increases) and time (increase with time) which can be summarized as follows:

<table>
<thead>
<tr>
<th>Temperature impact on polymer dosage</th>
<th>Time impact on polymer dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;3x higher @ 25°C than @ 40°C</td>
<td>≈2x higher at 24 hr vs. 5 hr</td>
</tr>
</tbody>
</table>

**Oxidizing Biocide:** Microbial growth on heat exchanger and RO membrane surfaces is a major concern in industrial water systems affecting a variety of operational problems including microbially influenced corrosion, reduction in heat transfer, decreased permeate rate in RO process, system’s cleanliness, and potential health concerns. To overcome these operational challenges, microbiocides are often incorporated into the water treatment programs. The principles of applications, mechanisms of action, monitoring techniques, and response to system contamination differ significantly between biocide types. Biocides are often classified as either oxidizing or non-oxidizing as summarized below:

<table>
<thead>
<tr>
<th>Biocide Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizing</td>
<td>Chlorine, chlorine dioxide, stabilized bromine chloride, dibromodimethylhydantoin, ozone, and peracetic acid</td>
</tr>
<tr>
<td>Non-Oxidizing</td>
<td>Aldehyde, dithiocarbamates, isothiazolin, and quaternary compounds</td>
</tr>
</tbody>
</table>

The influence of hypochlorite on the performance of deposit control polymers have been the subject of numerous investigations. Results of these studies reveal that acrylic acid, maleic acid, aspartic acid homo- and copolymers are tolerant to degradation by hypochlorite.

To study the impact of hypochlorite on the performance of CP2, CP6, and CP7, a series of silica polymerization inhibition experiments were carried out in the presence of 4 ppm Cl₂. Results of these experiments indicate that there is negligible polymer performance change (<2% loss) and residual chlorine loss (<3%) thus indicating that these polymers are not adversely impacted by chlorine nor consume chlorine.
Silica Precipitate Characterization: The silica precipitates formed during the silica polymerization experiments were investigated using X-Ray Diffraction (XRD) and Electromagnetic Dispersion Spectroscopy (EDX). Figure 10 shows the XRD spectra of the precipitates formed in the presence of 0 ppm, 15 ppm CP6, and 15 ppm CP7. The spectra suggest that the silica precipitates formed during polymerization process are amorphous.

Figure 10: XRD Spectra of Amorphous Silica Formed in the Absence & Presence of CP6 & CP7

Figure 11 presents EDX spectrum of precipitated amorphous silica. From the spectrum, it is apparent that the precipitates consist essentially of silicon and oxygen with only trace amounts of calcium and magnesium present in the silica precipitates. 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 un-washed precipitated silica.

Figure 11: EDS Spectra of Amorphous Silica
SUMMARY

Silica polymerization is complex process impacted by several competing factors including water chemistry, temperature, and time. Silica-silicate scale control in an industrial system must take into consider these competing factors as well as system operating conditions. The study herein indicates the following:

1. Silica polymerization inhibitor dosage requirements:
   a. Decrease with increasing hardness ions.
   b. Decrease with increasing temperature
   c. Increase with time.

2. CP7 is a very effective silica polymerization inhibitor that is superior to other commercially available silica-silicate deposit control polymers.

3. The silica polymerization inhibition performance of CP7 is not adversely impacted by the presence of chlorine and CP7 does not consume chlorine.

REFERENCES


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