10 Solution Chemistry Impact on Silica Polymerization by Inhibitors

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10.1 INTRODUCTION

Scaling in industrial water systems is caused by the precipitation of sparingly soluble salts dissolved in the feed water. During water system (desalination processes, boilers, cooling loops) operation, the solubility of sparingly soluble salts (or minerals) can be exceeded and may cause precipitation (scaling) and deposition of these salts (or mineral scales) on various substrates. Common mineral scales encountered include calcium carbonate, calcium sulfate, barium sulfate, calcium phosphate, silica, and metal silicates. Other less commonly found scales include calcium fluoride, calcium oxalate, calcium phosphonate, strontium sulfate, and cupric sulfide. 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].

Various approaches can be used to prevent or eliminate mineral scale formation. These methods include (1) operating system at low supersaturation (low recovery or low cycles of concentration, (2) removing hardness ions by ion exchange, (3) decreasing system pH by acid feed, and (4) using scale inhibitor(s). Scale inhibitor addition is generally considered the most effective scale formation prevention method for industrial water systems. Inhibitors are commonly either non-polymeric (e.g., phosphonates, polyphosphates) or polymeric (e.g., acrylic acid- or maleic acid-based homo- and copolymers). These ionic inhibitors effectively control ionic salts such as calcium carbonate, calcium fluoride, and calcium sulfate. However, silica scale (SiO₂) is a covalent amorphous solid that cannot be effectively inhibited by commonly used anionic scale inhibitors. Thus, controlling silica precipitation and deposition on equipment surfaces in industrial water system remains a challenging problem.

10.1.1 SILICA SOLUTION CHEMISTRY

Silica solubility as a function of solution pH and temperature is shown in Figures 10.1 and 10.2, respectively. Silica scaling may occur when the dissolved silica level in an aqueous system exceeds the solubility limit (in the range of 120–150 mg/L at 20°C) for amorphous silica. Exceeding 150 mg/L silica in cold water (<10°C) is
not a serious problem because silica polymerization is a very slow process at lower temperatures. However, silica in excess of 180 mg/L presents a potential problem at any temperature [2].

Silica solution chemistry is very complex and difficult to predict. The formation of silica and metal silicate (i.e., magnesium silicate, iron silicate, aluminum silicate) in aqueous systems depends on several factors including silica solubility, pH, temperature, water chemistry, and system operating conditions [2]. The temperature effect of silica solubility depends on the form in which it exists. Unlike metal silicate salts (e.g., magnesium silicate) that exhibit inverse solubility behavior vs. temperature (i.e., solubility decreases with increasing temperature), amorphous silica solubility increases with increasing temperature [2].

Amorphous silica, based on its reactivity, is generally classified as follows:

- Dissolved (or reactive silica)
- Polymerized silica (reacts slowly)
- Colloidal (or unreactive silica)
- Suspended (or particulate silica)

The term reactive refers to silica that reacts with ammonium molybdate within 2 min to form colored complex. Silica dissolution involves a chemical reaction shown in Equation 10.1:

\[
\text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4
\]  

(10.1)

Measuring silica concentration in aqueous solutions requires an understanding of silica chemistry and attention to analytical detail. Inability to account for all the silica in an aqueous system may be attributable to a combination of limitations with the measurement and/or sampling method(s) as well as silica precipitation in the system. Silica characterization and quantification terminology are discussed as follows:
1. The *total silica* concentration in an aqueous solution is determined by one of the following:
   a. Knowing how much silica was added to the system
   b. Measuring silica by using the induced coupling plasma (ICP) method
   c. Analyzing an unfiltered water sample after addition of NaOH to pH > 13 (which converts all silica to the reactive form) by the standard colorimetric method

2. *Soluble silica* consists of both monomeric silica [Si(OH)₄, a.k.a., reactive silica or silicic acid] and polymerized silica [(OH)₃Si − O−]n. The *total soluble silica* concentration is determined by filtering (typically with 0.22 μm membrane filter) an aqueous solution and measuring (as described earlier) the total silica concentration in the filtrate. The filtrate can also be analyzed using the standard colorimetric method for silica to determine the *monomeric silica* concentration. The amount of polymerized silica in the filtrate can be calculated as the difference between the total and the monomeric silica concentration.

3. Determining the *precipitated silica* concentrations in an aqueous solution requires a filtration (typically with 0.22 μm membrane filter) step. The precipitated silica is the difference between the total silica concentrations (see 1. (b) or (c) earlier) in solution before and after filtering.

4. *Colloidal silica* concentrations must be calculated after determining other silica solutions values including total silica (see 1. above), monomeric silica (see 2. above), and precipitated silica (see 3. above) using the following equation:

   \[
   \text{Colloidal silica} = \text{total silica} - \text{monomeric silica} - \text{precipitated silica}
   \]

10.1.2 **Silica Scaling in Industrial Water Systems**

In many parts of the world including the western United States, Hawaii, Puerto Rico, Mexico, and Southeast Asia, silica solubility limits the efficient use of water in cooling, boiler, geothermal, and reverse osmosis (RO) applications. Water supplies in these geographical areas may have silica levels ranging from 30 to 120 mg/L. Conventional operation of water treatment systems limits the silica concentration to 150 mg/L due to sparing solubility of amorphous silica and silicates.

In evaporative cooling systems, water technologists must maintain silica at acceptable levels (usually <180 mg/L in the absence of silica polymerization inhibitor) to avoid the formation and deposition of silica-based deposits. This requires (1) operating systems at low cycles of concentration that increases water consumption and/or (2) incorporation of silica polymerization inhibitor in the water treatment formulation. In geothermal applications, silica scale formation typically occurs when brine is cooled in the course of brine handling and energy extraction. Factors contributing to silica scale include variable fluid composition, fluctuating plant operating conditions, and the complex nature of the silica polymerization reaction that collectively contribute to silica scaling problem. The composition
and the amount of silica scale as well as the formation rate depends upon several factors including mineral concentration of feed water, pH, temperature, flow velocity, and system pressure.

In brackish, water RO systems membrane surfaces and spacers are particularly susceptible to fouling by polymerized silica. These silica-based deposits are easily coagulated by small amounts of cations such as Ca, Mg, Fe, and Al [3,4]. The deposition of silica-based deposits on RO membrane surfaces causes decreased produced water quality and quantity, increased pumping pressure, and premature replacement. Table 10.1 presents water system performance targets for silica inhibitors.

Once formed, silica–silicate-based deposits are particularly difficult to remove from heat exchanger, RO membrane, and other equipment surfaces. Both chemical and mechanical methods are used to remove silica–silicate-based deposits. However, strong chemical cleaners (i.e., hydrofluoric acid, ammonium bifluoride) pose serious environmental challenges and require care to avoid damaging equipment, whereas mechanical cleaning is labor intensive.

**10.1.3 Silica Scaling Mechanism**

Amorphous silica polymerization follows a pattern of soluble silica unit breakdown and silicate anion growth into a larger macromolecule via anionic polymerization as shown in the following reactions:

\[
\text{Si(OH)}_4 + \text{OH}^- \rightarrow \text{(OH)}_3 \text{SiO}^- + \text{H}_2\text{O} \quad (10.3)
\]

\[
\text{Si(OH)}_3^- + \text{Si(OH)}_4 \rightarrow \text{(OH)}_3 \text{Si} - \text{O} - \text{Si(OH)}_3 + \text{OH}^- \quad (\text{dimer}) \quad (10.4)
\]

\[
\text{Dimer} \rightarrow \text{Cyclic} \rightarrow \text{Colloidal} \xrightarrow{\text{Ca}^{2+}/\text{Mg}^{2+}} \text{Amorphous silica (scale)} \quad (10.5)
\]
The equations earlier illustrate that the silicic acid (monomer) condensation reaction is catalyzed by hydroxide ions and accelerated by the presence of salts such as CaCl₂ and MgCl₂. It has been suggested [4] that dissolved silica comes out of the supersaturated solution in three forms:

1. Deposits on solid surfaces where monomeric silicic acid [Si(OH)₄] condenses with any solid surface that has an –OH group with which it can react.
2. Colloidal particles after polymerized silica grows to form a 3D polymer. These colloidal particles form large particles (floc) that may deposit on equipment surfaces.
3. Biogenic amorphous silica by living organisms.

It should be mentioned that sessile microorganisms in a biofilm-fouled heat exchanger can entrap colloidal silica. The high affinity of soluble silica toward extracellular biopolymers such as polysaccharides has also been recognized.

The interaction of M–OH with silicic acid is shown in Equation 10.6 [5]:

\[
\begin{align*}
-M\cdot OH + \text{HO} \rightleftharpoons \text{Si} - \text{OH} \rightarrow \text{M} - \text{O} \rightleftharpoons \text{OH} + \text{Si} + 2\text{H}_2\text{O} \\
\end{align*}
\]

(10.6)

10.1.4 Silica-Based Scale Control Approaches

Approaches for combating silica–silicate fouling in industrial water systems are as follows:

1. Operating systems at low silica–silicate supersaturation levels
2. Reducing feed water silica concentration (e.g., by precipitation processes)
3. Additives to inhibit silica polymerization
4. Additives to preferentially form metal–silica compounds with greater solubility
5. Dispersing precipitated silica–silicate compounds
6. Effective control of other scales (e.g., calcium carbonate, calcium phosphate)
7. Effective carbon steel corrosion control (<3 MPY)
8. Maintaining system <pH 8.3 to avoid metal–silicate precipitation

Many different chemical additives have been tested as silica polymerization inhibitors. The use of boric acid and/or its water soluble salts to control silica–based deposits in cooling water systems operating at 250–300 mg/L silica has been reported. Silica inhibition presumably originates from the ability of borate to condense with silicate to form borate–silicate complexes that are more soluble than silica [6]. The use of borate-based inhibitors to increase silica solubility is limited because of the high use levels required for boron-based compounds as well as the associated costs and effluent discharge limitations.
Amjad and Yorke [7] reported that cationic-based copolymers are effective silica polymerization inhibitors. Similar conclusions were also reported by Harrar et al. [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 copolymers showed excellent silica polymerization inhibition, they exhibited poor silica–silicate dispersing activity. Neofotistou and Demadis [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 to minimize 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: (1) disperse both silica and magnesium silicate and (2) disperse scalant particles (e.g., calcium carbonate, calcium sulfate) that can act as nuclei for silica–silicate deposits [10].

The performance of a formulated product containing hydroxyphosphono 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 [11]. Heat exchanger inspection showed essentially no deposits in the presence of a formulated product compared to heavy scaling and silicate deposits in the control (no treatment). Momozaki et al. [12] reported the use of a poly(acrylamide)-based treatment program to control silica in recirculating cooling water. Gill [13] in a study 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.

The influence of anionic and nonionic polymers as silica polymerization inhibitors has been reported [14]. This study reveals that anionic polymers containing carboxyl group are ineffective silica polymerization inhibitors. Performance data for nonionic polymers such as poly(2-ethyloxazoline) suggest that polymerization inhibition strongly depends on polymer molecular weight (MW). The results on the evaluation of –NH₂-terminated (polyaminoamide) dendrimer of varying MW suggest that these dendrimers are effective silica scale inhibitors. Experimental results reveal that inhibition efficiency largely depends upon dendrimer structural features such as generation number and nature of end groups as well as dosage levels [9].

Zhang et al. [15] investigated the inhibitory effect of cationic and anionic polymers and polymer blends. The results show that copolymers of adipic acid–amine-terminated polyethers D230–diethylenetriamine (AA:AT:DE) exhibit excellent silica polymerization inhibition. However, a small amount of silica-AA:AT:DE floc appears in the solution. Performance data also show that a blend of AA:AT:DE/PESA (polypeoxysuccinic acid) prevents floc formation and also improves the performance of copolymer. However, under similar experimental conditions, PESA shows poor performance as silica polymerization inhibitor.

Previous papers reported the results of laboratory experiments designed to determine the efficacy of various commercially available polymeric additives touted as silica polymerization inhibitors and meta–silicate dispersants [16,17]. It was shown that acrylic acid-based homo- and copolymers commonly used as deposit control
agents are ineffective as silica polymerization inhibitors. Earlier studies indicate that low levels of metal ions (e.g., Al, Fe, cationic polymeric flocculants) markedly reduce the effectiveness of silica polymerization inhibitors [18].

It is generally accepted that lowest limit of amorphous silica saturation level in industrial water systems is ≈1.2×. Based on previously published data, it can be assumed that a conservative maximum treated silica saturation level in cooling water systems is ≈2.2×. For the purposes of evaluating silica polymerization inhibitors herein, we selected more challenging water chemistry with ≈3.0× silica saturation. This chapter presents results for evaluations of polymers with varying compositions and non-polymeric additives. The additives tested fall into three categories: (1) synthetic polymers, (2) proprietary polymer blends, and (3) non-polymeric materials. The impacts of solution chemistry (i.e., pH, temperature, type, and levels of mono-, di-, and trivalent metal ions), biocides, and thermal stress on silica polymerization inhibitor performance are discussed. X-ray diffraction (XRD) and electromagnetic dispersion spectroscopy (EDS) characterizations of silica precipitates formed in the absence and presence of polymers are also presented.

10.2 EXPERIMENTAL

Reagent-grade chemicals and distilled water were used throughout this study. Silica stock solutions were prepared from sodium metasilicate nonahydrate, standardized spectrophotometrically, and stored in plastic bottles. Calcium chloride and magnesium chloride stock solutions were prepared from calcium chloride dihydrate and magnesium chloride hexahydrate and were standardized by EDTA titration. Standard Fe³⁺ and Al³⁺ solutions were purchased from Fisher Scientific. Table 10.2

<table>
<thead>
<tr>
<th>Additive</th>
<th>Composition</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDP</td>
<td>1-Hydroxyethylidine-1,1-diphosphonic acid</td>
<td>HEDP</td>
</tr>
<tr>
<td>PBTC</td>
<td>2-Phosphonobutane 1,2 4-tricarboxylic acid</td>
<td>PBTC</td>
</tr>
<tr>
<td>BA</td>
<td>Boric acid</td>
<td>BA</td>
</tr>
<tr>
<td>PMA</td>
<td>Poly(maleic acid)</td>
<td>PMA</td>
</tr>
<tr>
<td>K-732</td>
<td>6 k MW solvent polymerized poly(acrylic acid)</td>
<td>PAA</td>
</tr>
<tr>
<td>K-775</td>
<td>Poly(acrylic acid: 2-acrylamido-2-methylpropane sulfonic acid)</td>
<td>CP1</td>
</tr>
<tr>
<td>K-798</td>
<td>Poly(AA:SA: 2-acrylamido-2-methylpropane sulfonic acid–sulfonated styrene)</td>
<td>CP2</td>
</tr>
<tr>
<td>Competitive-1</td>
<td>Poly(AA:SA: 2-acrylamido-2-methylpropane sulfonic acid–nonionic)</td>
<td>CP3</td>
</tr>
<tr>
<td>Competitive-2</td>
<td>Poly(maleic acid–ethyl acrylate–vinyl acetate)</td>
<td>CP4</td>
</tr>
<tr>
<td>Competitive-3</td>
<td>Proprietary acrylic copolymer</td>
<td>CP5</td>
</tr>
<tr>
<td>K-XP212</td>
<td>Proprietary copolymer blend</td>
<td>CP6</td>
</tr>
<tr>
<td>K-XP229</td>
<td>Proprietary copolymer blend</td>
<td>CP7</td>
</tr>
</tbody>
</table>

* Carbosperse™ K-700 polymer supplied by The Lubrizol Corporation.
lists the commercial inhibitors used in this study along with the composition and acronym. Stock inhibitor solutions were prepared on active solids basis.

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 SiO₂) 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 solution pH 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, known volumes of calcium chloride and magnesium chloride stock solution were added to the silicate solutions. The supersaturated silicate solutions were readjusted to pH 7.0 with dilute HCl and/or NaOH and maintained constant throughout the silica polymerization experiments. For experiments involving the effect of solution ionic strength, a known volume of standard NaCl or Na₂SO₄ solution was added to sodium silicate solution. Figure 10.3 schematically illustrates the experimental protocol and Figure 10.4 shows the experimental set-up used to study silica polymerization inhibition.

![Figure 10.3](image1.png)  
**FIGURE 10.3** Silica polymerization inhibition experimental protocol.

![Figure 10.4](image2.png)  
**FIGURE 10.4** Silica polymerization inhibition test equipment setup.
Experiments involving inhibitors were performed by adding inhibitor solutions to the silicate solutions before adding the calcium chloride and magnesium chloride solutions. 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 [16]. Silica polymerization inhibition values were calculated according to the following equation:

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

(10.7)

where the terms earlier are as follows:

- % Inhibition is the percent silica polymerization inhibition or %SI
- \([\text{SiO}_2]_{\text{sample}}\) is the silica concentration in the presence of inhibitor at 22 h
- \([\text{SiO}_2]_{\text{control}}\) is the silica concentration in the absence of inhibitor at 22 h
- \([\text{SiO}_2]_{\text{initial}}\) is the silica concentration at the beginning of test

The membrane filtration residues were analyzed by SEM (Model Zeiss EVO 50) and XRD spectrometry (Model Rigaku Geigerflex).

For studying thermal stability, solutions were prepared containing neutralized 10% polymer (as active solids) at pH 10.5 using sodium hydroxide. Sodium sulfite was used as an oxygen scavenger. Known polymer solution quantities were retained for characterization and performance testing. The balance of the polymer solutions was charged to stainless tubes. The headspace was purged with nitrogen followed by tightening the fittings. The tubes were then placed in the oven maintained at the required temperature (either at 150°C or 200°C). At known times, the tubes were removed from the oven and cooled at room temperature, and the polymer solutions transferred to vials for characterization and performance testing. Nuclear magnetic resonance (NMR) spectra of polymers before and after thermal treatment were obtained on a Brubaker AV-500 NMR.

10.3 RESULTS AND DISCUSSION

Using the experimental protocol described earlier, a series of experiments were conducted to investigate the influence of various factors (i.e., solution supersaturation, pH, temperature, ionic strength, type, and concentrations of metal ions, biocides, polymerization inhibitors). The following sections present results and discussion on these factors on the performance of various inhibitors.

10.3.1 WATER CHEMISTRY EFFECT ON SILICA POLYMERIZATION

10.3.1.1 Silica Supersaturation

Using the experimental setup described earlier, a series of experiments were conducted at various silica supersaturation (SS) conditions and standard test conditions (200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40°C). Figure 10.5 shows soluble silica
concentrations as a function of time for various SS solutions. Figure 10.5 illustrates that a 550 mg/L silica solution reacts instantaneously, whereas lower silica concentrations react at a much slower rate. At low degrees of SS, a decrease in silica concentration is preceded by a slow polymerization reaction (induction time or $\alpha$). Figure 10.5 shows that the soluble silica concentration does not change significantly during the induction period. However, once polymerization is underway, the soluble silica concentration begins decreasing. Figure 10.5 illustrates $\alpha$ values for various SS solutions: 3 h for 525 mg/L, 8 h for 450 mg/L silica, and >20 h for 300 mg/L silica compared to <5 min for high SS solution (550 mg/L silica). The baseline silica saturation (solubility) level appears to be approximately 150 mg/L that is consistent with previously reported silica equilibrium concentrations.

10.3.1.2 Temperature Effect

The solubility of scale-forming salts such as calcium carbonate, calcium sulfate, and calcium phosphates is inversely dependent on solution temperature [19]. 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 [20] that calcium ion tolerance of anionic scale control polymer decreases markedly as solution temperature increases from 25°C to 70°C. However, silica solubility increases with increasing temperature and silica saturation limits go up [2]. The influence of solution temperature on inhibitor performance was determined by conducting a series of experiments using the silica polymerization test conditions (i.e., 550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0) and temperatures ranging from 25°C to 68°C (i.e., 25°C, 40°C, 55°C, and 68°C). The results are shown in Figure 10.6 and illustrate 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: (1) silica saturation limits increase with increasing temperature due to increased silica solubility and (2) the silica polymerization rate increases with increasing temperature. Figure 10.6 data suggest that temperature is the primary driver for changing silica saturation limits impacting silica solubility in these test conditions.

10.3.1.3 Silica Polymerization as a Function of pH
As previously indicated and shown in Figure 10.1, solution pH has a profound effect on silica solubility. A series of experiments was conducted to evaluate the solution pH effect on soluble silica concentration using Lubrizol’s silica polymerization inhibition test procedure. The experiments were conducted at solution pH ranging from 6.5 to 8.75 using 550 mg/L silica and at 40°C. In order to avoid metal–silicate salt precipitation especially at high alkaline pH, these experiments were conducted in the absence of CaCl₂ and MgCl₂. Figure 10.7 presents $T_{1/2}$ (time needed for 50% depletion of soluble silica) as a function of solution pH. It is evident from Figure 10.7 that soluble silica decreases within the pH 6.5–8.3 range but decreases above pH 8.3. The observed $T_{1/2}$ from pH 6.5 to 8.3 is due to the increased amount of hydroxide that catalyzes the silica polymerization reaction. At pH > 8.3, the observed $T_{1/2}$ decrease is caused by the lower driving force resulting from a slight silica solubility increase and a depletion of unionized monomeric silica because of ionization. Figure 10.7 illustrates, above pH 8.5, that $T_{1/2}$ values increase further due to decreased SS.

Figure 10.7 can also be used to help determine the optimum pH range to minimize the rate of silica polymerization and deposition of polymerized silica or fouling.
At pH > 8.5 the potential of Ca and/or Mg silicate formation increases. At pH < 6.5, there is virtually no ionization and no mono-ionized \((\text{H}_3\text{SiO}_4^-)\) that can polymerize with unionized silicic acid \((\text{H}_4\text{SiO}_4)\). Therefore, industrial water systems (e.g., recirculating cooling loops, RO systems) should be operated at pH < 8.3. Figure 10.7 clearly indicates that solution pH dramatically impacts the soluble silica concentration decline with time that agrees with other researchers’ observations [21,22]. Thus, for systems operating at high alkaline pH conditions, the focus should be inhibiting metal silicates because the silica polymerization rate will be comparatively slower than the metal–silicate precipitation rate.

### 10.3.2 Inhibitor Evaluations

#### 10.3.2.1 Inhibitor Concentration Effect

As discussed in previous papers [17–22], it is very important to understand the relationship between polymer dosage and silica polymerization inhibitor performance particularly at the high silica saturation \((3.0\times)\) test conditions. Figure 10.8 shows silica concentration as a function of time at varying CP6 (copolymer blend) dosages. Figure 10.8 data indicate (1) that CP6 dosage strongly affects silica polymerization inhibitor performance and (2) that both 50 and 75 mg/L CP6 dosages provide similar performance.

#### 10.3.2.2 Inhibitor Composition Effect

To evaluate the efficacy of various additives as silica polymerization inhibitors, a series of experiments was conducted in the presence of 25 and 350 mg/L inhibitor dosages. The results that appear in Figure 10.9 clearly show that the performance of copolymer blends (i.e., CP6 and CP7) is superior to the other additives evaluated. The data for the non-polymeric additives (i.e., HEDP, PBTC, BA) tested indicate...
these materials are ineffective silica inhibitors compared to CP6 and CP7. Although HEDP and PBTC are excellent calcium carbonate inhibitors [23], their poor performance as silica polymerization inhibitors suggests that phosphonate groups do not inhibit silica polymerization in aqueous solutions.

It has been reported [24] that solvent polymerized polycrylates are more tolerant to calcium ions than the water polymerized polycrylates. For carboxylic acid-containing polymers, it appears that precipitation inhibition is greatest for MW of below 20,000 (daltons or DA) with the optimum MW dependent on the polymer composition and the salts being inhibited. For calcium phosphate and calcium phosphonates inhibition, acrylic acid- and/or maleic acid-based copolymers have been shown to perform better than homopolymers of either acrylic acid or maleic acid [25].
Solution Chemistry Impact on Silica Polymerization by Inhibitors

Figure 10.9 also presents performance data for polymeric inhibitors containing different functional groups (e.g., carboxylic acid, sulfonic acid). It is evident that the homopolymers (PMA and PAA), copolymer (CP1), and terpolymers (CP2, CP3, CP4, CP5) commonly used for controlling mineral scales and dispersing suspended matter are poor (<20% inhibition) silica inhibitors. The performance data clearly show that carboxylic acid, sulfonic acid, ester, and nonionic groups present in the commonly used polymers exhibit poor interaction with silane groups present in silica.

Figure 10.10 takes a closer look at the silica polymerization inhibition performance of CP2, CP6, and CP7 as a function of polymer dosages in the 10–50 mg/L range. CP2 was selected as being representative of all the other homopolymers (PMA and PAA) and copolymers (CP1, CP3, CP4, and CP5) tested because carboxylic monomer groups dominate (>50%) all these polymer compositions. On the other hand, the CP6 and CP7 copolymer blends (patented and patent pending, respectively) are distinctly different (contain <50% carboxylic acid monomer groups) from the other polymers.

Figure 10.10 indicates that at 12.5 mg/L dosages, CP7 provides 35% SI or more than double the performance of either CP6 or CP2. At ≥15 mg/L dosages, the CP6 performance and dosage response are superior to all other additives tested except CP7 that is dramatically better than all the other materials tested. Table 10.3 summarizes observations about the data in Figures 10.7 and 10.8.

10.3.3 Hardness Ions Effect

The impact of hardness ions on silica polymerization has been previously investigated. Sheikholeslami et al. [26] studied the impact of Ca$^{2+}$ and Mg$^{2+}$ on silica polymerization at pH 6.5, 20°C, 360 mg/L silica, and as a function of time (0–200 h). Results of their study show that the rate of silica polymerization increases with increase in Ca$^{2+}$ concentrations in the range 100–300 mg/L. Adding high Ca$^{2+}$ concentrations to 200 mg/L silica solutions did not affect the solution metastability. Furthermore,
at 500 mg/L silica concentrations where polymerization was very rapid, Ca²⁺ addition did not seem to show any obvious trend. Sahachaiyunta et al. [27] in their study on the effect of Ba²⁺, Ni²⁺, and Mn²⁺ ions on RO system silica scaling reported that these ions exhibit accelerating effect on silica polymerization but do not show any influence on the structure of precipitated amorphous silica.

To understand the impact of hardness ions on performance of polymers, several silica polymerization experiments were carried out in the presence of 50 mg/L CP7 and varying total hardness (“TH” or Ca²⁺/Mg²⁺ at a 2:1 ratio) concentrations. Figure 10.11 data clearly show that silica polymerization inhibition increases as a function of TH concentration ranging from 0 to 320 mg/L.

A series of experiments was conducted to determine whether or not hardness ions are coprecipitated during silica polymerization in the presence of CP7. Figure 10.12 shows the influence of hardness ions on CP7 performance as a function of dosage and silica concentration.

### TABLE 10.3

<table>
<thead>
<tr>
<th>Additive</th>
<th>Silica Polymerization Inhibition Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Containing &gt;50% carboxylic monomers</td>
<td>Provide poor (&lt;20%) performance at all dosages tested up to 350 mg/L (only up to 50 mg/L dosage shown in Figure 10.8)</td>
</tr>
<tr>
<td>CP6</td>
<td>Performance increases dramatically from poor to excellent with dosage up to 35 mg/L and improves incrementally thereafter</td>
</tr>
<tr>
<td>CP7</td>
<td>Performance increases dramatically as dosage increases from 5 mg/L (7% SI) to 25 mg/L (85% SI) and improves incrementally thereafter</td>
</tr>
</tbody>
</table>

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a See TABLE 10.1 including PMA, PAA, CP1, CP2, CP3, CP4, and CP5.

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![Figure 10.11](image)  
**FIGURE 10.11** Silica concentration vs. time in presence of 50 mg/L CP7 and varying TH levels (550 mg/L silica, pH 7.0, 40°C). (Modified from Paper Number 10048, Presented at CORROSION/2010 Annual Conference and Exhibition, Houston, TX, 2010; Figure 7. Reproduced with permission from NACE International.)
Solution Chemistry Impact on Silica Polymerization by Inhibitors

presents silica, Ca\(^{2+}\), and Mg\(^{2+}\) vs. time profiles in the presence of 15 mg/L CP7. As shown, the initial calcium (200 mg/L) and magnesium (120 mg/L) concentrations remain essentially constant (within the experimental error of \(\pm 3\%\)) during the silica polymerization experiments, while silica concentration decreases with time. Figure 10.12 data suggest 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.

### 10.3.4 Total Dissolved Solids Effect

The influence of total dissolved solids (TDSs) on silica polymerization inhibition in the presence of 50 mg/L CP7 was investigated. Figure 10.13 presents % silica inhibition values at 22 h in the presence of 50 mg/L CP7 and varying TDS concentrations (either Ca\(^{2+}\)/Mg\(^{2+}\) [2:1] as described earlier 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 10.13 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 mg/L CP7 in the presence of similar ionic strength but different TDS levels (i.e., Na\(^{+}\) [1755 mg/L NaCl] and Ca\(^{2+}\)/Mg\(^{2+}\) [320 mg/L TH]) at similar ionic strength are 16% and 92%, respectively. These performance variations caused by TDSs (i.e., Na\(^{+}\) and TH [either Ca\(^{2+}\) or Mg\(^{2+}\)]) on silica polymerization may be attributed to different charge density of these metal ions.

![Figure 10.12 silica, Ca, and Mg concentrations vs. time in the presence of 15 mg/L CP7. (Modified from IWC-11-61, Paper presented at the IWC 2011, Orlando, FL; Figure 6. Reproduced with permission from the International Water Conference®.)](image-url)
10.3.5 **Trivalent Metal Ions Effects**

Aluminum (Al)- and iron (Fe)-based compounds (e.g., alum, sodium aluminate, ferric chloride) have been used for years as flocculating/coagulant aids to clarify municipal and industrial waters [28]. These compounds neutralize the charge of suspended particles in water and they hydrolyze to form insoluble hydroxide precipitates that entrap additional particles. In most cases, these large particles (or flocs) are removed via settling in a clarifier and are collected as sludge. Occasionally, clarifier upsets cause the metal-containing flocs to “carry over.”

Among the various dissolved impurities present in natural waters, iron-based compounds present the most serious problems in many domestic and industrial applications. In the reduced state, iron (II) or ferrous (Fe\(^{2+}\)) ions are very stable and pose no serious problems, especially at low pH values. However, upon contact with air, ferrous ions are oxidized to higher valence state and readily undergo hydrolysis to form insoluble hydroxides as shown as follows:

\[
\begin{align*}
\text{Fe}^{2+} + \text{air} & \rightarrow \text{Fe}^{3+} \quad (10.8) \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \quad (10.9)
\end{align*}
\]

When ferric or ferrous ions precipitate in water, an amorphous or gelatinous solid is usually formed. At low corrosion rates, the iron hydroxide formed may deposit on the heat exchanger surface as a permeable or impermeable film at the corrosion site. Under these conditions, the iron hydroxides that form are colloidal and form stable suspensions. Other types of iron-based compounds that can potentially deposit on the heat exchanger surfaces include iron carbonate, iron silicate, and iron sulfide.
The presence of iron in recirculating waters and/or brine in RO system, whether originating from the feed water, as a result of iron-based metal corrosion in the system, or the carryover from a clarifier using iron-based flocculating agents, can have profound effects on the performance of polymers used as scale inhibitors and dispersants. It has been previously reported that polymer performance as a calcium phosphate inhibitor is negatively impacted by Fe(III) [29].

10.3.5.1 Fe(III) Effect

It is well established that low levels of coagulating/flocculating additives present in recirculating waters are antagonistic to scale inhibitor and dispersant performance. To understand the impact of inorganic and organic coagulants/flocculants on silica polymerization inhibitor performance, several experiments were carried out in the presence of varying Fe(III) concentrations. As shown in Figure 10.14, low Fe(III) levels (e.g., 0.25 mg/L) exhibit a negative or antagonistic influence on the silica polymerization inhibition by CP6 and CP7. Increasing Fe(III) levels to the 0.50–1.0 mg/L range further decreases silica inhibition (%Si) values. It is evident from Figure 10.14 that CP7 is more tolerant to Fe(III) than is CP6. Similar antagonistic effects caused by Fe(III) have been reported [30,31] in studies involving calcium phosphate inhibition by anionic polymers.

10.3.5.2 Al(III) Effect

The influence of low Al^{3+} levels was also investigated by carrying out a series of silica polymerization experiments in the presence of 50 mg/L copolymer blend dosages. Results presented in Figure 10.15 clearly show that silica polymerization inhibitor performance is strongly impacted by the presence of Al^{3+}. As illustrated, silica polymerization inhibition values for both CP6 and CP7 decreased ≥20% by adding 0.1 mg/L Al^{3+} and more pronounced antagonistic effects occurred when adding 0.25 mg/L Al^{3+}. By comparing the CP6 and CP7 silica polymerization inhibition

![Figure 10.14](image_url) Effect of Fe(III) concentration on silica polymerization inhibition by polymers (550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, 50 mg/L polymer, pH 7.0, 40°C, 22 h). (Modified from Paper Number 10048, Presented at CORROSION/2010 Annual Conference and Exhibition, Houston, TX, 2010; Figure 4. Reproduced with permission from NACE International.)
in the presence of metal ions (see Figures 10.14 and 10.15), it is evident that Al\(^{3+}\) exhibits a more antagonistic effect than Fe\(^{3+}\). The markedly greater silica polymerization inhibition antagonism caused by Al\(^{3+}\) compared to Fe\(^{3+}\) may be attributed to the different cationic charge density present on metal salts hydroxides.

### 10.3.6 CATIONIC POLYMER EFFECT

As previously discussed, the use of flocculating agents (inorganic and organic types) to remove suspended matter from feed water and wastewater streams is well known. Commonly used inorganic salts (e.g., aluminum chloride, aluminum sulfate, and ferric chloride) while very effective are corrosive and generate large sludge volumes. These metal salts treatments can be augmented by the use of cationic polymers such as diallyldimethylammonium chloride (DADMAC).

Figure 10.16 presents silica polymerization inhibition data for CP6 and CP7 in the presence of varying DADMAC concentrations. Figure 10.16 data indicate that DADMAC dosages up to 3.0 mg/L cause slightly antagonistic effects on CP6 and CP7 silica polymerization inhibition performance. 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 [32] and calcium phosphonate [33] inhibitors. The silica polymerization inhibition performance differences observed in Figure 10.16 may be attributed to different ionic charges.

### 10.3.7 SOLUTION TEMPERATURE EFFECT

The impact of solution temperature on silica polymerization inhibition was investigated as a function of inhibitor dosage. For example, Figure 10.17 compares silica inhibition (%SI) as a function of CP7 dosage at 40°C and 55°C and clearly shows that...
increasing solution temperature (or reducing SS) 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 10.18. Table 10.4 summarizes the observations from Figure 10.18 data and the CP6 and CP7 polymer dosages needed for >80% silica inhibition are functions of both temperature (decrease as temperature increases) and time (increase with time).
10.3.8 Impact of Biocides on Polymer Efficacy

Microbial growth on heat exchanger and RO membrane surfaces is a major concern in industrial water systems that causes operational problems including microbiologically influenced corrosion, reduced heat transfer rates, decreased flow rates, reduced system cleanliness, and potential health concerns [30]. 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.

The influence of hypochlorite, a widely used oxidizing biocide on the performance of deposit control polymers, has been the subject of numerous investigations [34–36]. Results of these studies reveal that acrylic acid, maleic acid, and aspartic acid homo- and copolymers are resistant to degradation by hypochlorite. To study hypochlorite’s impact on CP2, CP6, and CP7 silica polymerization inhibition performance, a series of experiments were conducted in the presence of 4 mg/L Cl₂.
Experiment results include 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.

10.3.9 IMPACT OF THERMAL STRESS ON POLYMER EFFICIENCY

Polymer thermal degradation is a well-investigated area. However, there is little practical information available to water treatment technologists pertaining to the thermal stability of low MW polymers used in high-temperature applications. Polymers used in high-temperature applications should be able to sustain performance where exposed to high-temperature and high-pressure environments associated with boiler and thermal desalination processes. McGaugh and Kottle [37] studied the thermal degradation of PAA and later the thermal degradation of an acrylic acid–ethylene copolymer. They used infrared and mass spectrographic analysis to examine the degradation processes that occurred in several temperature regions: 25°C–150°C, 150°C–275°C, 275°C–350°C, and >350°C. Their results in air (min. heating) suggest that dry PAA decomposes by forming an anhydride, probably a six-membered glutaric anhydride-type structure up to 150°C. At 350°C, there is drastic unmeasurable change and strong unsaturation absorption. Mass spectrographic analysis showed that carbon dioxide was the major volatile product at 350°C.

In an earlier paper [38], we reported the effects of thermal treatment (i.e., a variable temperature [150°C, 200°C, and 230°C], pH 10.5, and 20 h) on the silica polymerization inhibition performance of the polymers herein designated as PAA, CP3, CP5, and CP6. The results of that study clearly show that the PAA and copolymers CP3 and CP5 (promoted as silica–silicate deposit control agents) performed poorly (<5% inhibition) as silica polymerization inhibitors when exposed to 150°C and 200°C, whereas CP6 retained >95% of its performance (vs. no thermal stress).

To understand the impact of thermal treatment on the performance of CP7 as well as the other polymers discussed herein, we conducted a series of experiments exposing the polymer to thermal stress (variable temperature [200°C, 230°C, 250°C, and 300°C], pH 10.5, and 20 h) before evaluating the silica polymerization inhibitor performance [39]. Figure 10.19 presents comparative silica polymerization inhibition data before and after thermal stress at 50 mg/L polymer dosages.

Figure 10.19 silica polymerization inhibition data in the absence of thermal stress show that the copolymer blends (i.e., CP6 and CP7) are effective but the other polymers evaluated are ineffective inhibitors under the high silica saturation level (3.0×) test conditions. More specifically the %SI values obtained for the homo- (i.e., PMA and PAA) and copolymers (i.e., CP2, CP3, and CP5) are <20% compared to >80% obtained for the copolymer blends (CP6 and CP7). The data clearly show that the deposit control polymers containing >50% carboxylic acid monomer groups (i.e., PMA, PAA, CP2, CP3, and CP5) exhibit poor performance as silica polymerization inhibitors. By contrast, the copolymer blends (CP6 and CP7) that contain <50% carboxylic acid monomer groups are significantly better silica polymerization inhibitors and a significant improvement over current silica inhibitor technology.
Silica inhibition data for polymers after thermal stress presented in Figure 10.19 indicate the following:

1. The homopolymers (PAA and PMA) and copolymers (CP2, CP3, and CP5) are ineffective (<10%) silica polymerization inhibitors.
2. The copolymer blends (CP6 and CP7) are very effective (≈80%) silica polymerization inhibitors after thermal stress at 200°C.
3. Thermal stress above 230°C for CP6 causes a significant reduction in performance.
4. Thermal stress above 250°C for CP7 causes a reduction in performance. However, the CP7 silica polymerization inhibitions after thermal stress at 250°C and 300°C were >70% and >60%, respectively.

Figure 10.20 takes a closer look at the silica polymerization inhibition performance of CP6 and CP7 after thermal stress as a function of polymer dosages in the 10–50 mg/L range. The post-thermal stress results shown in Figure 10.20 indicate that (a) both CP6 and CP7 experience a modest (<15%) performance reduction (suggesting some degradation of the polymer functional groups) and (b) CP7 is a more effective silica polymerization inhibitor than CP6 at lower dosages both before and after thermal stress. Collectively, the results discussed earlier as well as Figures 10.19 and 10.20 clearly show that CP7 is a superior silica polymerization inhibitor over a wide range of dosages and after thermal stress. Thus, CP7 because of its superior thermal stability at high temperature may be a suitable candidate for high-temperature silica control applications.

10.3.10 Silica Precipitate Characterization

The silica precipitates formed during the silica polymerization experiments were investigated using XRD and EDS. Figure 10.21 shows the XRD spectra of the
FIGURE 10.20  Silica polymerization inhibition as a function of polymer thermal stress and dosage (550 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40°C).

FIGURE 10.21  XRD spectra of amorphous silica formed in the absence and presence of CP6 and CP7.
precipitates formed in the absence of polymer and in the presence of 15 mg/L polymer (CP6 and CP7). The spectra suggest that the silica precipitates formed during polymerization process are amorphous.

Figure 10.22 presents EDS 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 spectra may be due to surface adsorption of Ca and Mg on the unwashed precipitated silica.

REFERENCES


