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AN EVALUATION OF SILICA SCALE CONTROL ADDITIVES FOR INDUSTRIAL WATER SYSTEMS

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ABSTRACT

Deposition of colloidal silica and silicate based salts on equipment surfaces continue to pose serious challenges to industrial water technologists. Currently, a wide variety of non-polymeric and polymeric additives are used to combat the problems of silica scaling. These additives are generally effective as scale inhibitors and dispersants under normal operating conditions. However, polymeric additives may lose some performance activity under thermal stress. This paper investigates the impact of composition and the influence of thermal stress on the performance of polymeric silica polymerization inhibitors.

Keywords: silica scaling, inhibition, polymer thermal stability, industrial water systems

INTRODUCTION

The major cause of industrial water system failures is the deposition of unwanted materials on equipment surfaces. The mineral deposits commonly encountered include carbonates, sulfates, and phosphates salts of alkaline earth metals. The effects of deposits on heat exchangers and reverse osmosis (RO) membrane surfaces result in increased operational costs. The potential for silica scaling occurs when the dissolved silica level in re-circulating water or reject stream in RO system exceeds the solubility limit (~100 mg/L at ambient temperature) for amorphous silica. Colloidal silica formed during silica polymerization can foul RO membrane and heat exchanger surfaces. Additionally, polyvalent metal ions (e.g., iron, aluminum, calcium, magnesium) present in feed water streams can absorb or complex silica and catalyze the precipitation.

The mechanism of silica polymerization is very complex and is believed to occur via the base catalyzed reaction as shown below:

$$Si(OH)_4 + OH^- \longrightarrow (OH)_3SiO^- + H_2O$$

$$Si(OH)_3^- + Si(OH)_4 \longrightarrow (OH)_3Si - \underset{\text{(dimer)}}{O \text{ -- } Si(OH)_3} + OH^-$$

$$\text{Dimer} \longrightarrow \text{Cyclic} \longrightarrow \text{Colloidal} \longrightarrow \text{Amorphous Silica (scale)}$$

The development and application of silica control technology in aqueous systems has been the subject of numerous investigations.[1-3] Several approaches to control silica scaling have been attempted including (a) inhibiting silica polymerization, (b) increasing the silica solubility as it forms, and (c) dispersion of precipitated silica and silicate compounds using polymeric dispersants.

Another type of silica deposit commonly encountered in RO systems is magnesium silicate. The precipitation of magnesium silicate strongly depends on solution pH and temperature. In RO systems operating above pH 9, magnesium silicate is very likely to form due to the presence of magnesium hydroxide and silicate ions. Other hydroxide salts such as calcium, strontium, and sodium can react with silicate ions. However, the resulting products are much more soluble and hence less likely to foul RO membranes.

The influence of additives (i.e., anionic, non-ionic, cationic) as silica polymerization inhibitors has been the subject of numerous investigations. Amjad and Yorke[4] in their evaluation of polymers reported that cationic-based copolymers are effective silica polymerization inhibitors. Similar conclusions were also reported by Harrar, et al.[5] 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 performance in terms of inhibiting silica polymerization, they offered poor silica/silicate dispersancy activity. Gallup and Barcelon[6] investigated the performance of a variety of organic inhibitors as alternatives to strong acids for geothermal application. Results of their study reveal that brine acidification always out-performed the organic inhibitors.

The use of boric acid and/or water soluble salts to control silica based deposits in cooling water systems operating at 250 to 300 mg/L has been reported.[7] 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 performance of a formulated product containing hydroxyl phosphono acetic acid and a copolymer of acrylic acid and allyl hydroxyl propyl sulfonate ether in high hardness water containing high alkalinity, and 250 mg/L silica, has been investigated.[8] The inspection of heat exchangers showed essentially no deposits in the presence of a formulated product compared to heavy silica and silicate deposits in the control (no treatment).

The effect of heat treatment on polymer performance as a scale inhibitor and dispersant has been the subject of numerous investigations. Masler[9] investigated the thermal stability of several homo-polymers used for deposit control in boiler water treatment applications. It was demonstrated that under the experimental conditions employed (pH 10.5, 250°C, 18 hr) that poly(acrylic acid), P-AA; poly(maleic acid), P-MA; and poly(methacrylic acid), P-MAA, all underwent some degradation. In terms of molecular weight (MW) loss, P-MAA lost slightly less MW than P-AA which lost considerably less than P-MA. Additionally, P-AA and P-MAA had minimal performance changes whereas P-MA displayed a substantial loss in performance. Amjad[10] in another study using the similar test method showed that polymer performance as dispersants of hydroxyapatite and iron oxide is affected both by temperature level and exposure time. More recently, Amjad and Zuhl[11] in their study reported that heat treatment has a significant effect on a polymer's inhibitory properties. Heat treatment of co- and ter-polymers has been shown to cause (a) a decrease calcium phosphate inhibition and (b) a slight increase calcium carbonate inhibition.

This paper present results of our investigations conducted to determine the role of polymer composition on silica scale inhibition in industrial water systems. We also investigated the influence of thermal stress on inhibitor structure and silica inhibitor performance. Table 1 lists the inhibitors tested.

EXPERIMENTAL

Reagent grade chemicals and distilled water were used in this study. Silicate stock solutions were prepared from sodium metasilicate, standardized spectrophotometrically, and were stored in polyethylene bottles. Calcium chloride and magnesium chloride solutions were prepared from calcium chloride dihydrate and magnesium chloride hexahydrate, and were standardized by EDTA titration. The polymers used in this study were commercial materials. All experimental results are reported on a 100% active inhibitor basis.

Silicate polymerization experiments were performed in polyethylene containers placed in a double-walled glass cell maintained at a required temperature (40°, 55°, or 68°C). The supersaturated solutions were prepared by adding a known volumes of sodium silicate (expressed as SiO_2) solution and water in a polyethylene container. After allowing the temperature to equilibrate, the silicate solution was quickly adjusted to pH 7.0 using the dilute hydrochloric acid. The pH of solution 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 solution. The supersaturated silicate solutions were re-adjusted to pH 7.0 with dilute HCl and/or NaOH and maintained constant throughout the silica polymerization experiment. Experiments involving inhibitors were performed by adding inhibitor solutions to the silicate solutions before adding the calcium chloride and magnesium chloride solutions.

Figure 1 shows experimental set-up. The reaction container is capped and kept at constant temperature and pH during the experiment. Silicate polymerization in these supersaturated solutions was monitored by analyzing the aliquots of the filtrate from 0.22-µm filter paper for soluble silicate using the standard colorimetric method.[12] The polymer performance for silicate polymerization inhibition was calculated according to the following equation:

$$SI = \frac{[SiO_2]_{\text{sample}} - [SiO_2]_{\text{blank}}}{[SiO_2]_{\text{initial}} - [SiO_2]_{\text{blank}}} \times 100\%$$

Where:

SI = Inhibition (%) or %SI

$[SiO_2]_{\text{sample}}$ = Silica concentration in the presence of inhibitor at 22 hr
$[SiO_2]_{\text{blank}}$ = Silica concentration in the absence of inhibitor at 22 hr
$[SiO_2]_{\text{initial}}$ = Silica concentration at the beginning of experiment

Polymer Heat Treatment

A polymer solution was prepared containing 10% polymer (as active solids) at pH 10.5 using sodium hydroxide to neutralize the polymer. Sodium sulfite was added as an oxygen scavenger. A known amount of polymer solution was retained for characterization and performance testing. The balance was charged to a stainless steel tube. The headspace was purged with nitrogen followed by tightening the fittings. The tube was then placed in the oven maintained at the required temperature [either 150ºC (84 psig), 200ºC (241 psig), or 230°C (390 psig)]. After 20 hr, tubes were removed from the oven, cooled to room temperature, and the solutions transferred to vials for characterization and performance testing.

RESULTS AND DISCUSSION

Silicate Polymerization Inhibition by Polymers

Using the experimental protocol described above a series of silicate polymerization experiments were carried out in the presence and absence of polymers. Table 1 shows that the polymers tested in the present study vary significantly in terms of compositions and molecular weights of the polymers tested vary significantly.

A. Polymer Dosage. The assessment of polymer effectiveness as a silica inhibitor was done at similar initial silica super-saturation 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 co-polymer blend (P8) and suggests: (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. As illustrated in Figure 2, silica concentration gradually decreases with increasing time and at 22 hr essentially all (>95%) silicate (monomeric) has been converted to polymeric silica. Figure 2 also presents the silica inhibition as a function of P8 concentration. At 22 hr in the presence of 15 mg/L P8, the silica concentration in solution is 190 mg/L compared to 175 mg/L in the absence of P8. Increasing the P8 concentration from 15 to 25 mg/L results in >50% increase (from 190 to 291 mg/L) in silica concentration. Furthermore, in the presence of 75 mg/L P8, >85% of the silicate remains in solution.

Figure 3 presents silica inhibition data for P1 (homo-polymer of acrylic acid) and P8. The data indicate that P1 compared to P8 is an ineffective silica inhibitor; e.g., the %SI values at 22 hr in the presence of 50 mg/L inhibitor are 2% for P1 and 80% for P8. In addition, increasing the P1 concentration seven fold (i.e., from 50 to 350 mg/L) exhibits negligible (from 2 to 4%) performance improvement. It is noteworthy that P1 (a well known polyacrylic acid) that exhibits good to excellent inhibitory properties for both calcium fluoride[13] and calcium sulfate[14] salts is a poor silicate polymerization inhibitor.

B. 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.[15] This 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. Recently, it was also reported[16] that calcium ion tolerance of polymer decreases markedly as solution temperature increases from 25 to 70°C. However, the situation is very different for silica supersaturated system in the sense that silica solubility increases with increasing temperature thus resulting in lower supersaturation.

In order to study the influence of solution temperature on polymer performance, a series of silica polymerization experiment experiments were conducted at similar initial silica concentrations, pH 7.0, and several temperatures (i.e., 40, 55, and 68°C). Figure 4 presents the time-dependent silica concentrations profiles in the absence of polymer. It is evident that solution temperature significantly influences silicate polymerization. There are two competing factors contributing to temperature influence: (a) silicate supersaturation decreases with increasing temperature due to increased silica solubility and (b) silicate polymerization increases with increasing temperature.

The influence of solution temperature on silica inhibition was also studied by conducting a series of polymerization experiments in the presence of varying inhibitor dosages. Figure 5 shows the P8 dosage needed to achieve >80% silicate polymerization inhibition at 22 hr as a function of temperature. The marked influence of solution temperature on silicate polymerization is clearly evident from the data in Figure 5 and summary below:

Solution Temperature	40°C	55°C	68°C
P8 Dosage Required for >80% Silicate Inhibition	50 mg/L	12.5 mg/L	4 mg/L

The data presented in Figure 5 are thus consistent with the effect of temperature on silica supersaturation, i.e., supersaturation decreases with increasing temperature.[17]

C. Polymer Architecture. In recent years, many studies have examined the influence of polymer architecture on the precipitation of scale-forming salts. Studies have shown that polymer performance as scale inhibitors in industrial water systems is strongly affected by polymer MW, composition (monomer types and weight ratios), and polymerization solvent. It has been reported[18] that solvent polymerized polyacrylates are more tolerant to calcium ions than the water polymerized polyacrylates. For carboxylic acid containing polymers, it appears that precipitation inhibition is greatest for MW of below 20,000 (daltons) with the optimum MW dependent on the polymer composition and the salts being inhibited. Regarding calcium phosphate and calcium phosphonates inhibition, acrylic acid and/or maleic acid-based co-polymers have been shown to perform better than homo-polymers of acrylic acid and maleic acid. In the case of particulate matter (i.e., clay, iron oxide) dispersion, polymers that exhibit good dispersion are low MW and generally contain anionic and/or non-ionic monomers. However, for silica inhibition anionic, non-ionic, and cationic additives have been shown to inhibit good to excellent silica inhibition property.[6, 19]

To understand the import of polymer architecture, a series of silica polymerization experiments were conducted in the presence of 350 mg/L polymer and the results appear in Figure 6. For comparative purpose, Figure 6 also includes performance data on non-polymeric additives commonly used in water treatment formulations. It can be seen that even at high inhibitor dosage all non-polymeric additives (i.e., HEDP, PBTC, BA) are ineffective silica inhibitors. HEDP and PBTC are excellent calcium carbonate inhibitors[20] but show poor performance as silica polymerization inhibitors thus suggesting that phosphonate groups do inhibit silica polymerization in aqueous solutions.

Figure 6 presents performance data for inhibitors containing different functional groups, i.e., carboxylic acid, sulfonic acid, and non-ionic. It is evident that the homo- (P1 and P2) and co-(P3), and ter-polymers (P4, P5, P6, and P7) commonly used in water treatment formulations as deposit control agents to control mineral scales and disperse suspended matter are poor (<10% inhibition) silica inhibitors. The performance data obtained for these commonly used polymers with the exception of a co-polymer blend (P8) clearly show that acrylic acid, maleic acid, sulfonic acid, and non-ionic groups exhibit poor interaction with silane groups present in silica.

D. Polymer Thermal Stability. Polymer thermal degradation is a well studied 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 pressure environments associated with boiler and thermal desalination processes. McGaugh and Kottle[21] studied the thermal degradation of P-AA and later the thermal degradation of an acrylic acid-ethylene co-polymer. They used infrared and mass spectrographic analysis to examine the degradation processes that occurred in several temperature regions: 25 to 150ºC, 150 to 275ºC, 275 to 350ºC, and above 350ºC. Their results in air (min heating) suggest that dry P-AA decomposes by forming an anhydride, probably a six-member glutaric anhydride-type structure at temperature up to 150ºC. At 350ºC, there is drastic un-measurable change and strong un-saturation absorption. Mass spectrographic analysis showed that carbon dioxide was the major volatile product at 350ºC.

The thermal stability of the deposit control polymers is an important consideration in geothermal systems and in some re-circulating cooling water systems. To understand the impact of thermal treatment (variable temperature [150, 200, and 230ºC], pH 10.5, and 20 hr) on polymer performance, a series of silica polymerization experiments were conducted in the presence of 50 mg/L polymer. Figure 7 presents comparative performance data (before and after thermal treatment) for several additives. It is evident that polyacrylate (P1) and copolymers (P5 and P7) under similar thermal treatment conditions (i.e., 150 and 200ºC) perform poorly (<5% inhibition). Under similar experimental conditions including 150ºC, P8 provides >80% inhibition values. The performance data presented in Figure 7 clearly show that P8 when exposed to thermal stress (150 or 200°C and 20 hr) retains >95% of its inhibitory activity. However, performance is adversely impacted as P8 is exposed to higher temperature (230°C) indicating that the functional groups present in P8 have been degraded but P8 still outperforms all competitive polymers.

SUMMARY

The data presented in this paper suggest that deposit control polymers (homo-, co, and ter-polymers) commonly used as inhibitors for mineral scales (i.e., calcium carbonate, calcium sulfate, calcium phosphate, and barium sulfate) and dispersants for suspended matter perform poorly as silica polymerization inhibitors. It has also been found that under the conditions employed in the present study non-polymeric additives (i.e., HEDP, PBTC, boric acid) are ineffective as silica polymerization inhibitors. The performance data suggest that heat treatment of polymers causes varying effects on the inhibitory power of polymers. However, a co-polymer blend (P8) outperforms all competitive polymers tested with and without heat treatment.

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Table 1. Polymeric and Non-Polymeric Additives Evaluated

Additive	Composition	Acronym
HEDP	1-hydroxythylidene-1,1-diphosphonic acid	A
PBTC	2-phosphonobutane 1,2 4-tricarboxylic acid	B
BA	Boric acid	C
K-732*	Poly(acrylic acid)	P1
P-MA	Poly(maleic acid)	P2
K-775*	Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid)	P3
K-798*	Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid: sulfonated styrene)	P4
Competitive-1	Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid: non-ionic)	P5
Competitive-2	Poly(maleic acid:ethylacrylate:vinyl acetate)	P6
Competitive-3	Proprietary acrylic copolymer	P7
K-XP212*	Proprietary copolymer blend	P8

*Carbosperse™ K-700 polymer supplied by Lubrizol Advanced Materials, Inc.

Figure 1: Set-Up for Silica Polymerization Inhibition Experiments

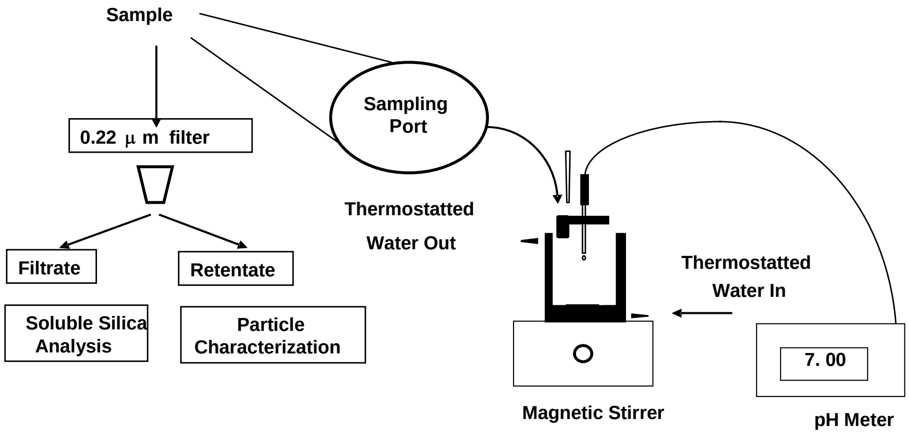


Figure 2: Silica Concentration vs. Time as a Function of P8 Dosage

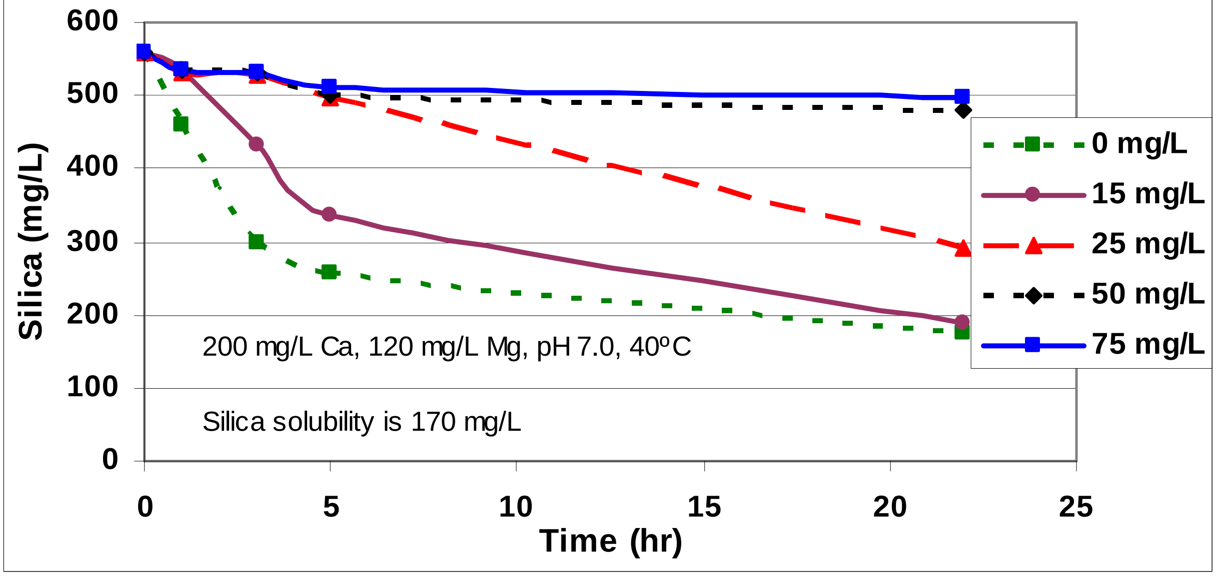


Figure 3: Silica Inhibition for P1 and P8 as a Function of Polymer Dosage

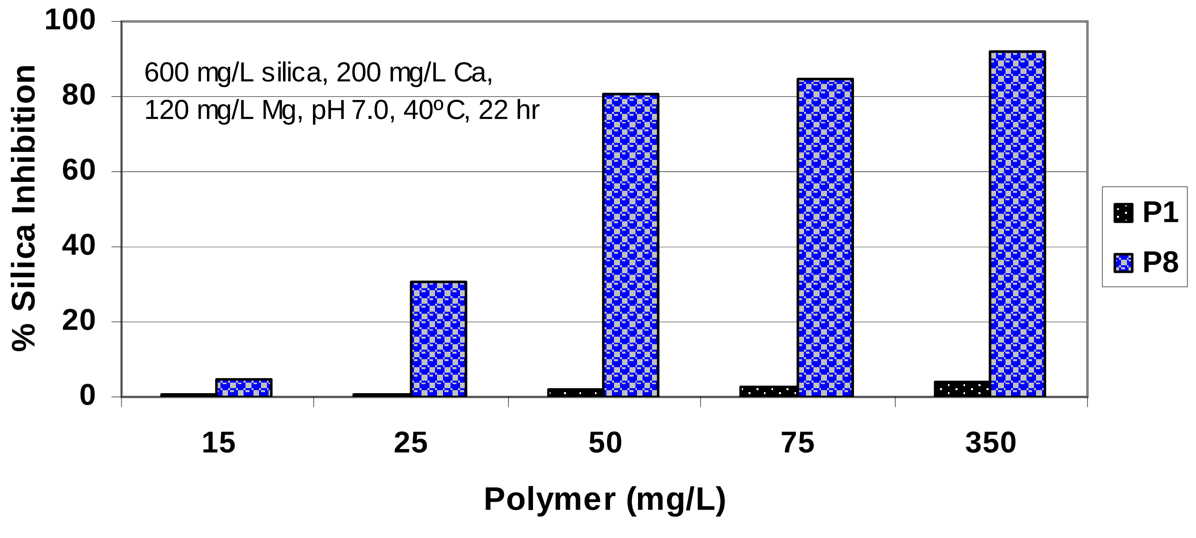


Figure 4: Silicate Polymerization as a Function of Time and Temperature

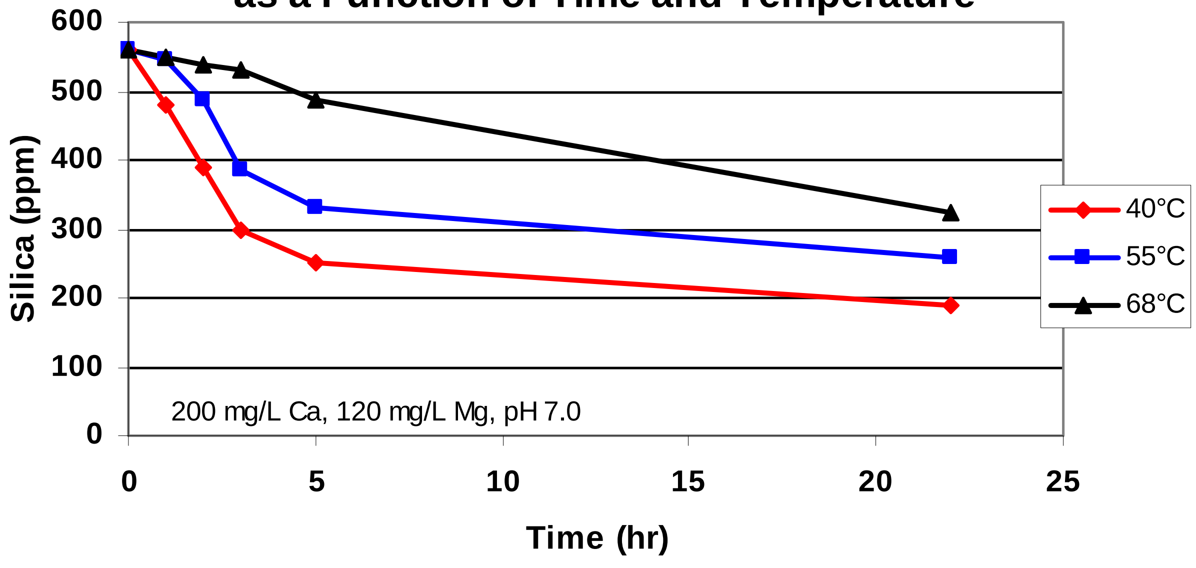


Figure 5: P8 Dosage Required to Achieve >80% Silica Polymerization Inhibition as a Function of Solution Temperature

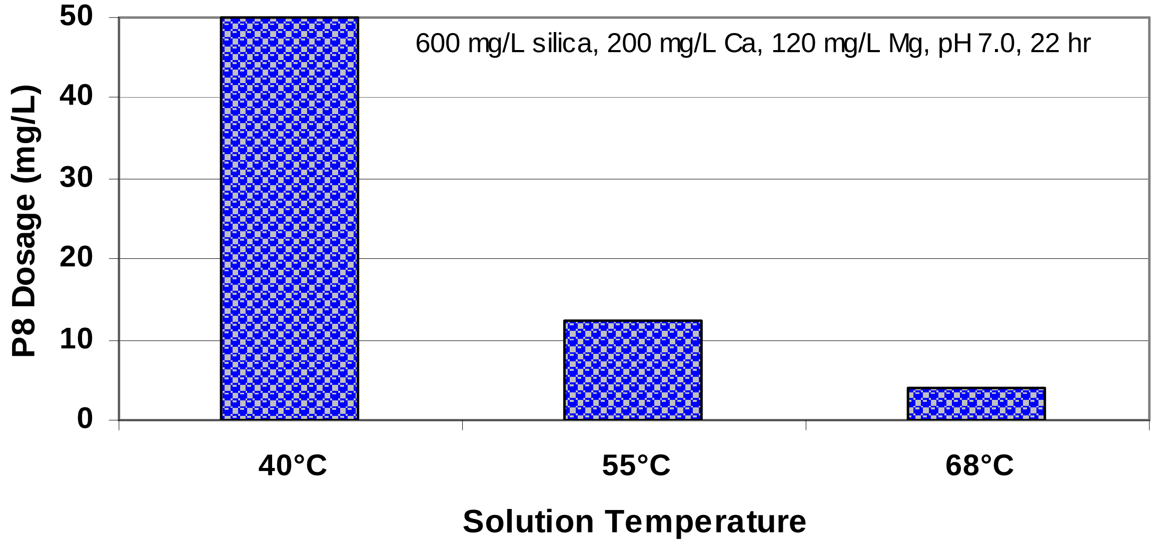
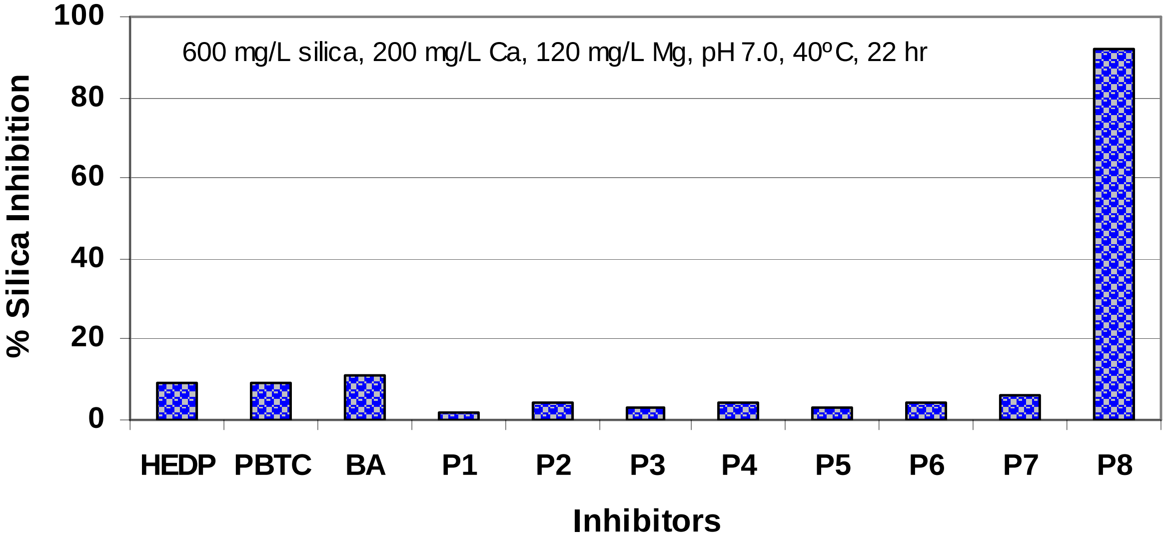


Figure 6: Silica Polymerization in the Presence of 350 mg/L of Various Inhibitors



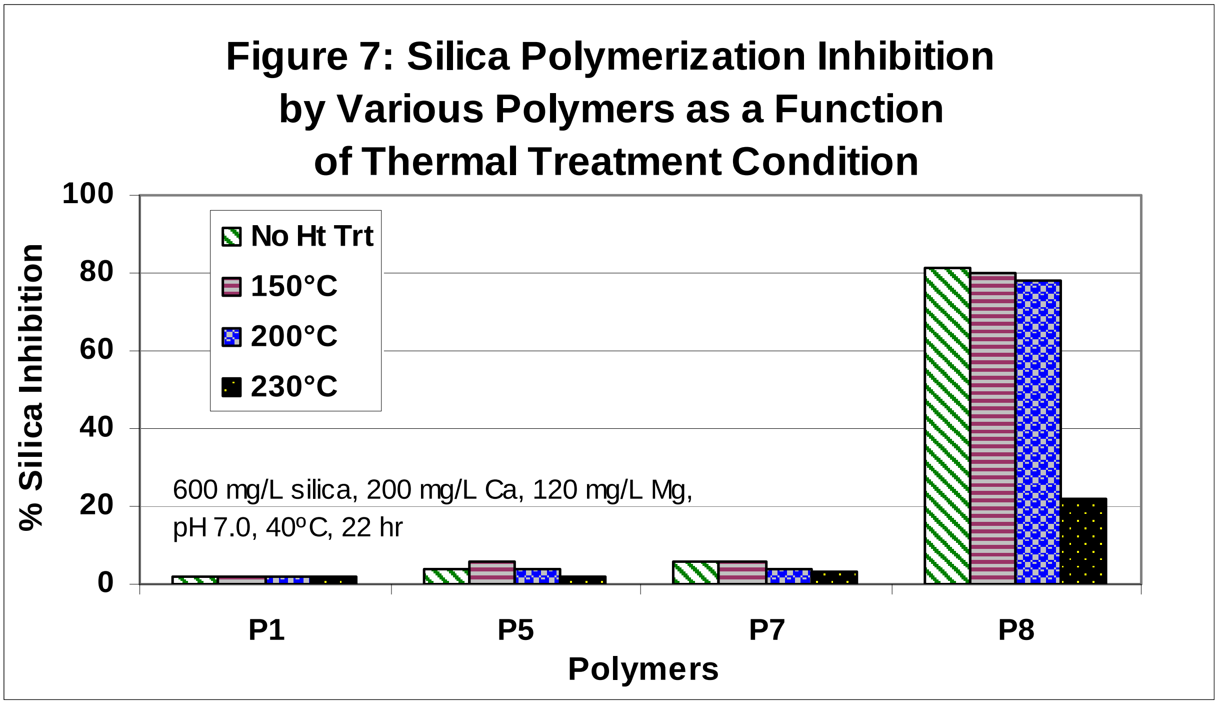


Figure 7: Silica Polymerization Inhibition by Various Polymers as a Function of Thermal Treatment Condition

600 mg/L silica, 200 mg/L Ca, 120 mg/L Mg, pH 7.0, 40ºC, 22 hr