Maleic acid-based copolymers as silica scale control agents for aqueous systems

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Abstract

The inhibition of silica polymerization by homo- and copolymers containing different functional groups has been studied in aqueous solution. It has been found that silica polymerization reaction is preceded by an induction period that is dependent on silica supersaturation. The investigation in the presence of additives indicates that silica polymerization strongly depends on the additive composition, ionic charge, and molecular weight. This study also presents comparative performance data on bio- and synthetic polymers.
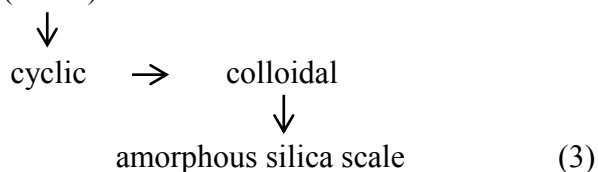
1. Introduction

Silica based scale (*i.e.*, silica, SiO_2; metal silicate) in geothermal brine, high pressure steam generators, and cooling water system has been recognized as a potential impediment in the efficient operation of these systems. In geothermal system, silica-based scale most often occurs when hot brine is cooled during brine handling and energy recovery. Silica in the reservoir is at or near saturation with respect to various forms of crystalline (*i.e.*, quartz) and/or amorphous silica becomes supersaturated with respect to amorphous silica upon flashing and cooling. It has been reported that silica or silicates precipitate typically rapidly due to fast polymerization of silicic acid compared to relatively low crystal growth rate of quartz and/or other crystalline forms of silica [1].

Silica solubility is well known to be dependent on pH, temperature, di- and trivalent metal ions, and total dissolved solids and is generally accepted to be ≈120 mg/L [1]. The potential for silica scaling occurs when the dissolved silica level in a reverse osmosis (RO) system reject stream or recirculating water exceeds the amorphous silica solubility. Exceeding silica solubility can cause silica precipitation and deposition thereby resulting in loss of equipment efficiency, unscheduled shutdown, and in some cases premature equipment replacement. In evaporative cooling systems, plant operators must maintain silica at acceptable levels (usually <160 mg/L) to avoid the formation of silica deposits. This imposes severe limits on water users, leading either to operation at very low cycles of concentration and consuming enormous amounts of water, or to use of chemicals that prevent silica scale formation and deposition.

In brackish water desalination systems, RO membrane surfaces and spacers are particularly susceptible to fouling by polymerized silica. These silica-based deposits are particularly coagulated by small amounts of cations such as Ca, Mg, Al, Fe [2]. The deposition of silica-based deposits on RO membrane surfaces results in poor produced water quality and quantity, increased pumping pressure, and premature membrane replacement. In addition, the potential for silica scale with high calcium and magnesium levels limits the use of polysilicate as a steel and aluminum inhibitor, especially in low-hardness cooling waters. Once formed, silica-silicate deposits are particularly difficult to remove from heat exchanger, RO membrane, and other equipment surfaces. Both mechanical and chemical methods are used to remove silica-based deposits. However, strong chemical cleaners (*i.e.*, ammonium bifluoride, hydrogen fluoride) pose serious environmental challenges and require care to avoid damaging equipment, whereas mechanical cleaning is labor intensive [3].

Silica solution chemistry is very complex and difficult to predict. The formation of silica and metal silicate (*i.e.*, aluminum silicate, iron silicate, calcium silicate, magnesium silicate) in aqueous system depends on several factors including silica solubility, temperature, pH, total dissolved solids, and system operating conditions [1]. The temperature effect of silica solubility depends on the form in which it exists. Unlike metal silicate salts (*e.g.*, magnesium silicate) that shows inverse solubility profile as a function of temperature (*i.e.*, solubility decreases with increasing temperature), amorphous silica exhibits normal solubility behavior *vs.* temperature.

Silica scale formation is a very complex process and has been suggested to occur via the base catalyzed reactions as illustrated below:

$$\text{Si(OH)}_4 + \text{OH}^- \quad \rightleftharpoons \quad {}^-\text{O}-\text{Si(OH)}_3 + \text{H}_2\text{O} \tag{1}$$
silicic acid (monomer)   silicate ions

$$\text{Si(OH)}_4 + {}^-\text{O}-\text{Si(OH)}_3 \quad \longrightarrow \quad \text{Si(OH)}_3-\text{O}-\text{Si(OH)}_3 + \text{OH}^- \tag{2}$$
(dimer)

$$\text{cyclic} \quad \rightarrow \quad \text{colloidal}$$
$$\downarrow$$
$$\text{amorphous silica scale} \tag{3}$$

During the last two decades, a number of strategies have been developed and applied to control silica based scales in industrial water systems. These approaches include: *a*) increasing the silica solubility as it forms, *b*) dispersion of precipitated silica and silicate salts with polymeric dispersants, *c*) inhibiting silica polymerization, *d*) operating system at low silica supersaturation, *e*) reducing silica solution concentration by precipitation process in the feed water, and *f*) controlling calcium carbonate scale to reduce silica incorporation in the scale [4]. The success of each approach and/or combination of approaches depends on the feed water chemistry, system design, and operating conditions.
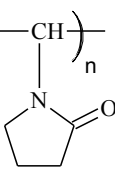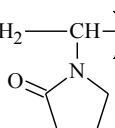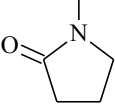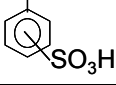
The influence of additives (*i.e.*, cationic, non-ionic, anionic) as silica polymerization inhibitors has attracted the attention of several researchers. The use of boric acid and/or borate to control silica based deposits in cooling water systems operating at 250 to 300 mg/L has been reported [5]. Silica inhibition presumably originates from the ability of borate to condense with silicate to form borosilicate complexes which are more soluble than silica. The efficacy of a formulated product containing hydroxyphosphono acetic acid and a copolymer of acrylic acid/allyl hydroxyl propyl sulfonate either in high hardness water containing high alkalinity, and 250 mg/L silica, has been evaluated [6]. The inspection of heat exchangers showed essentially no deposits in the presence of a formulated product compared to heavy silica/silicate deposits in the control (no treatment).

Amjad and York [7] in their evaluation of polymers reported that cationic-based polymers are effective silica polymerization inhibitors. Similar conclusions were also reported by Harrar *et al.* [8] in their investigation on the use of cationic surfactants and polymers in inhibiting silica polymerization for geothermal application. Although these cationic based additives showed excellent results in terms of inhibiting silica polymerization, they offered poor silica/silicate dispersancy activity. Gallup and Barcelon [9] investigated the performance of a variety of organic inhibitors as alternative to strong acids for geothermal application. Results of their study show that brine acidification always out-performed the organic inhibitors. Neofotistou and Demadis [10] in their study on the evaluation of polyamide-based dendrimers as silica inhibitors for cooling water applications reported that polymers performance as silica polymerization inhibitors strongly depends on the branching present in the dendrimer. Momazaki *et al.* [11] reported the use of a poly(acrylamide)-based treatment program to control silica in recirculating cooling water. In another study by Amjad and Zuhl [12] it was shown that whereas anionic polymers are ineffective as silica polymerization inhibitors, non-ionic polymers under similar experimental conditions show excellent performance in inhibiting silica polymerization reaction. Gill and coworkers [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 : 2-acarylamido-2-methylpropane sulfonic acid can effectively extend the operating limits for silica from 120 to 300 mg/L. In another study, Demadis showed that poly(2-ethyloxazoline), a non-ionic polymer, effectively inhibited silica polymerization reaction [10]. Zhang *et al.* [14] investigated the inhibitory effect of cationic and anionic polymers and polymer blends. The results show that copolymers of adipic acid−amine terminated polyether 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 (polyepoxysuccinic acid) prevents floc formation and also improves the performance of copolymer. However, under similar experimental conditions, PESA shows poor performance as silica polymerization inhibitor.

In our previous paper [15] we studied the performance of maleic acid (MA)-based homo- and co-polymers as scale inhibitors for calcium carbonate and calcium sulfate

dihydrate for aqueous systems. Results of this study show that MA containing polymers exhibit excellent performance as scale inhibitors and moderate performance as iron oxide dispersants. The present paper is focused on the evaluation of homo- and co-copolymers containing anionic and non-ionic functional groups as silica polymerization inhibitors. Table 1 lists the chemical name, structure, functional group, molecular weight, and acronyms of polymers tested.

Table 1. Additives tested.

Additive	Composition	Functional Group	MW	Acronym
Poly(acrylic acid)	$-(CH_2-CH)_n-$ $\quad\quad\;\; COOH$	Anionic	5k	PAA
Poly(maleic acid)	$-(CH-CH)_n-$ $COOH\;\;COOH$	Anionic	< 1k	PMA
Poly(acrylamide)	$-(CH_2-CH)_n-$ $\quad\quad\;\; CONH_2$	Non-ionic	6k	PAM
Poly(2-ethyloxazoline)	$-(N-CH_2-CH_2)_n-$ $\;\; CO$ $\;\; CH_2CH_3$	Non-ionic	5k	PEOX
Poly(vinyl pyrrolidone)	$-(CH_2-CH)_n-$ with pyrrolidone ring	Non-ionic	15k	PVP
Poly(maleic acid:vinyl pyrrolidone)	$-(CH-CH-CH_2-CH)_n-$ $COO^-\;\;COO^-$ $Na^+\quad Na^+$	Ionic Non-ionic	15k	MVP-1
Poly(maleic acid : sulfonated styrene	$-(CH-CH-CH_2-CH)_n-$ $COO^-\;\;COO^-$ (Na^+, Zn^+)	Ionic Non-ionic	60k	MVP-2
Poly(maleic acid:sulfonated styrene)	$-(CH-CH)_n-(CH_2-CH)_m-$ $COOH\;COOH$ SO_3H	Anionic	<5k	MA:SS
Lignosulfonate	Lignin, sulfonate	Anionic	3.1k	LS
Carboxymethyl inulin	Saccharide, carboxylation	Neutral Anionic	<15k	CMI-25

2. Experimental

Reagent grade chemicals and distilled water were used in this study. Stock solution of sodium chloride was standardized by ion exchange method. Silicate stock solution was prepared from sodium metasilicate, standardized spectrophotometrically, and stored in a polyethylene bottle.

Silica polymerization experiments were performed in polyethylene containers placed in a double-walled glass cell maintained at 40°C. Silica supersaturated solutions were prepared by adding a known volume of sodium silicate (expressed as SiO_2), sodium chloride, inhibitor, and water in a polyethylene container. After allowing the temperature to equilibrate, the silicate solution was quickly adjusted to pH 7.0 using hydrochloric acid. The pH of the solution was monitored using a Brinkmann pH meter equipped with a combination electrode. The pH electrode was calibrated before each experiment with standard buffers.

The progress of silica polymerization reaction was monitored by taking aliquots of silica supersaturated solutions and analyzing the filtrate (0.22 µm membrane filter) spectrophotometrically [12]. The efficacy of the polymer as silica polymerization inhibitor was calculated using the following equation:

$$\text{Percent Silica Polymerization Inhibition } (\%I) = \frac{(SiO_2)_p - (SiO_2)_a}{(SiO_2)_i - (SiO_2)_a} \times 100, \qquad (4)$$

where the terms above are as follows:

$\%I$ = percent silica polymerization inhibition;
$(SiO_2)_i$ = silica concentration at the beginning of experiment;
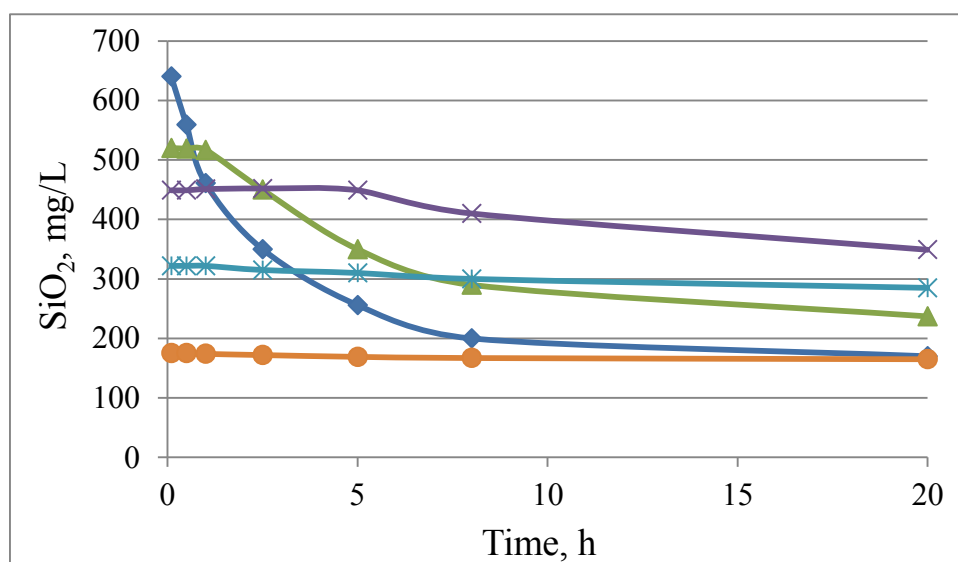$(SiO_2)_p$ = silica concentration in the presence of polymer at 20 hr;
$(SiO_2)_a$ = silica concentration in the absence of polymer at 20 hr.
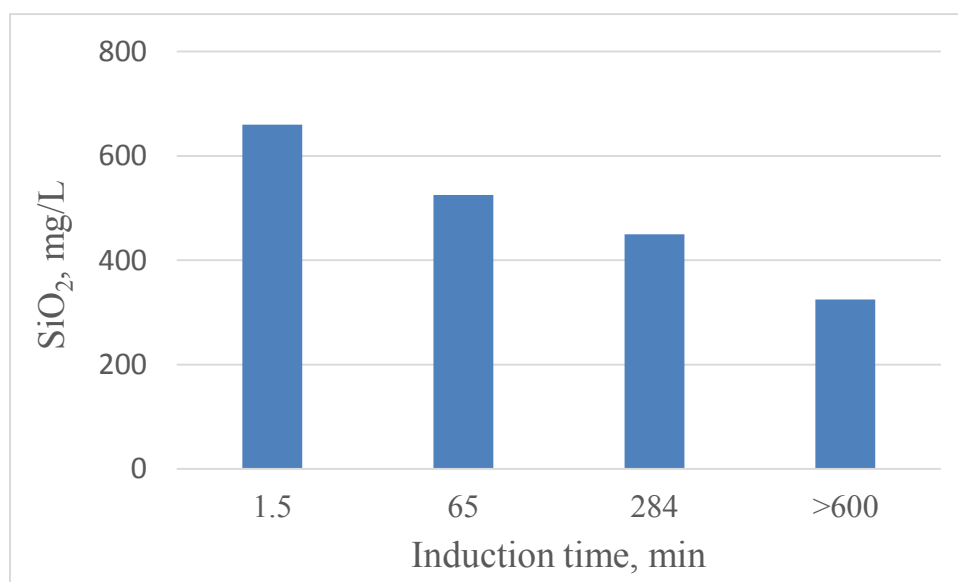
3. Results and Discussion

3.1. Stability of silica supersaturated solutions

Silica supersaturation representing industrial water systems was tested at pH 7.0, 40°C, 0.15 M NaCl, using silica concentrations of 175 mg/L to 660 mg/L. Figure 1 shows soluble silica concentration *vs.* time profile for various silica supersaturated solutions. As illustrated in Figure 1, at higher silica concentration (*i.e.,* 660 mg/L) silica reacts instantaneously, whereas lower silica concentrations react at a much lower rate. It is evident from Figure 1 that at low degrees of supersaturation, a decrease in silica concentration is preceded by a slow polymerization reaction (induction period, I_P). As shown in Figure 1 during this induction period, the concentration of soluble silica does not change significantly. However, once polymerization starts, solution silica begins to decrease. Figure 2 shows the I_P values for various silica supersaturated solutions. It can be seen that I_P values decreases with increasing silica concentration. For example, the I_P

values obtained for 175 mg/L and 325 mg/L are >1,000 min and >600 min, respectively, compared to <2 min observed for the high silica concentration (650 mg/L) solutions. It is worth noting that silica supersaturation *vs.* I_P observed in the present system has been previously reported for other scaling systems *i.e.*, calcium sulfate dihydrate, strontium sulfate, *etc.* [16, 17]. In the present study we have chosen 660 mg/L as a means to evaluate the performance of polymeric additives as silica polymerization inhibitors.

Figure 1. Silica polymerization as a function of silica concentration and time.

Figure 2. Plots of induction period as a function of silica concentration.

3.2. Effect of Polymeric Inhibitors

The use of polymeric additives in water treatment formulations has increased significantly in the last two decades. The role of additives in these formulations is trifold: *a)* to inhibit
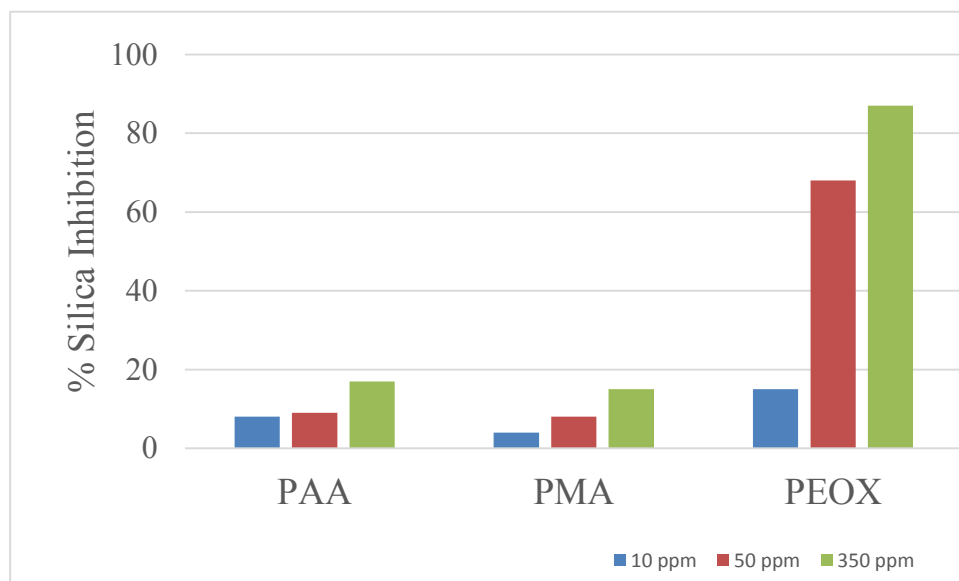
scale formation, *b*) to disperse particulate matter, and *c*) to modify crystal structure. Most of the additives that have demonstrated any efficacy in controlling mineral scale (*i.e.*, $Mg(OH)_2$, $CaSO_4 \cdot 2H_2O$, CaF_2, $BaSO_4$, $CaCO_3$) are either homopolymers containing anionic carboxyl group −COOH (*i.e.*, polyacrylic acid, polymaleic acid), and acrylic acid or maleic acid based copolymers containing anionic and/non-ionic functional groups. Interestingly, homopolymers containing non-ionic and cationic functional groups have been shown to perform poorly as scale inhibitors for carbonate and sulfate salts of alkaline earth metal [18, 19].
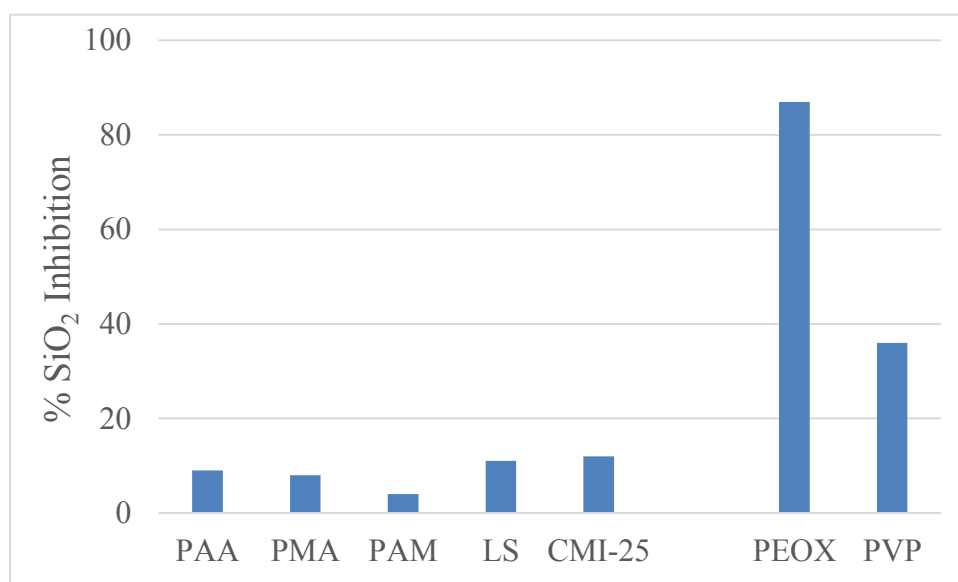
3.2.1. Homopolymers performance

The use of −COOH containing homopolymers such as poly(acrylic acid), PAA; poly(maleic acid), PMA; poly(aspartic acid), PAS; poly(itaconic acid) as scale inhibitors and dispersants for various scale forming salts and particulate matter has been well documented [20, 21]. Results of these studies suggest that performance of these polymers depends on various factors including molecular weight (MW), polymerization solvent, and end group. To check the impact of ionic charge of functional group present in homopolymers, a series of silica polymerization experiments were carried in the presence of 10, 50 and 350 ppm of a variety of homopolymers containing different functional groups (*i.e.*, −COOH, −SO_3H, −CONH_2, $-\text{N}-$, *etc.*).

Results presented in Figure 3 clearly show that polymers containing anionic groups (*i.e.*, −COOH, −SO_3H, *etc.*) are ineffective silica polymerization inhibitors. For example, %SI (silica inhibition) values calculated according to Equation 2, obtained in the presence of 10 and 50 ppm of two commonly used scale inhibitors (*i.e.*, PAA, PMA), are <10%. As shown in Figure 3, increasing the polymer concentration by seven folds, *i.e.*, from 50 to 350 ppm, results in only marginal increase in silica inhibition values from <10 to <20%). Figure 3 also presents performance data on poly(2-ethyloxazoline), PEOX, an additive containing non-ionic group. It can be seen that whereas PAA and PMA are ineffective silica polymerization inhibitors, PEOX under similar experimental conditions exhibits excellent performance in inhibiting silica polymerization. For example, %SI values obtained in the presence of 50 ppm of PEOX are 68% compared to <10% obtained for PAA and PMA respectively.

Figure 4 presents performance data collected in the presence of 350 ppm of bio- and synthetic polymers. The biopolymers tested include lignosulfonate (LS) and carboxymethyl inulin (CMI-25, with 25% degree of carboxylation). It is evident that under the conditions used, all polymers containing anionic functional group showed poor performance as silica polymerization inhibitors suggesting poor interactions of −COOH and −SO_3H group with Si−OH present in silicic acid. It is interesting to note that whereas −SO_3H containing polymers (PSA, LS) exhibit poor performance as silica polymerization inhibitors, these polymers have shown good to excellent performance as dispersants for particulate matter [22].

Figure 3. Silica inhibition in the presence of varying dosages of various polymers.
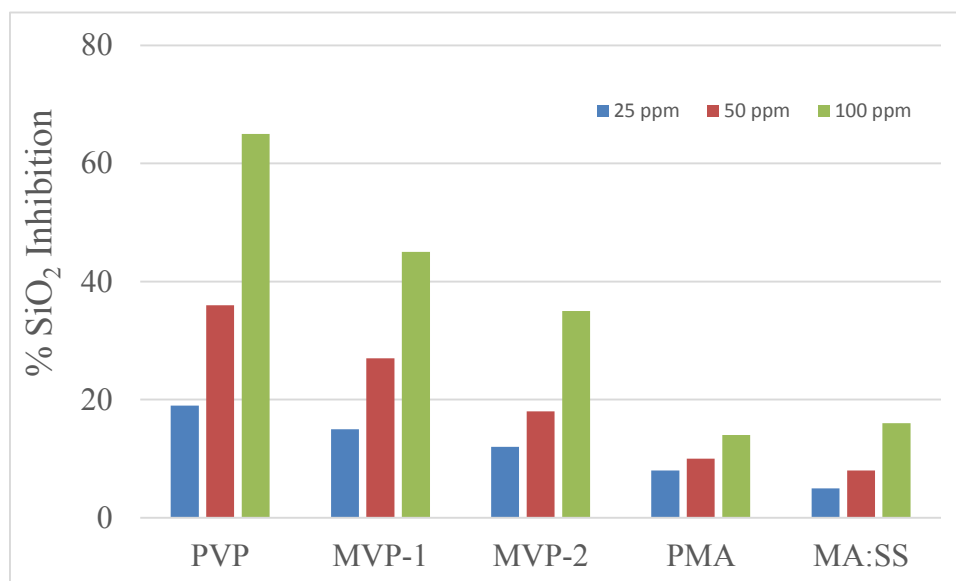

Figure 4. Silica inhibition in the presence of 50 ppm of polymers containing different functional groups.

3.2.2. Copolymers performance

Recently, the use of acrylic acid and maleic acid copolymers containing different functional groups (*i.e.*, $-SO_3H$, $-CONR_1R_2$, $-COOR$, $-OH$) as calcium phosphate and calcium phosphonates and iron oxide dispersants has increased significantly [23, 24, 25]. Results of these studies reveal that various factors including type and amount of co-monomer, ionic charge, hydrophobicity of co-monomer, and MW contribute to the performance of copolymers as scale inhibitors and/or dispersants. In our earlier study [15] it was shown that copolymers of maleic acid : vinyl pyrrolidone (MVP) exhibit good to mediocre performance as $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ inhibitors and iron oxide dispersants.

To investigate the performance of MVP, a series of silica polymerization experiments were conducted in the presence of varying dosages. Results are presented in Figure 5. It is evident that homopolymer of vinyl pyrrolidone (PVP) compared to homopolymer of maleic acid show excellent performance in inhibiting silica polymerization. For example, %Si values obtained in the presence of 100 ppm of PVP and PMA are 65 and 14%, respectively. As indicated, replacing maleic acid (MA) with vinyl pyrrolidone, VP, the resulting copolymers (*i.e.*, MVP-1, MVP-2) show mediocre performance as silica polymerization inhibitors. The observed difference in copolymers performance may be attributed to MW and/or counter ions (Zn^{2+} or Na^+) present in MVP-1 and MVP-2, respectively. It is worth noting that whereas PMA shows poor performance as calcium phosphate inhibitor, incorporation of a bulkier and hydrophobic monomer (*i.e.*, sulfonated styrene, SS) markedly improves the performance of copolymer in inhibiting calcium phosphate precipitation in aqueous system [20]. It is interesting to note that whereas MA : SS copolymer has been shown to exhibit excellent performance as calcium phosphate inhibitor, this copolymer is an ineffective inhibitor for silica polymerization, as illustrated in Figure 5. These observations clearly show that copolymers performance depends on the scaling system being inhibited.

Figure 5. Silica inhibition in the presence of varying dosages of homo- and copolymers.

Summary

The potential for silica scaling occurs when the dissolved silica in re-circulating water or reject stream in RO system exceeds the solubility limit at ambient temperature for amorphous silica. To avoid the formation of silica-based deposits, which are very difficult to remove safely and economically, water technologists typically employ conservative operating criteria; *e.g.*, cooling system limit cycles of concentration and desalination systems limit recovery. These approaches result in either large water consumption (which

increases water costs) and/or water treatment chemical program modification to incorporate silica/silicate control agent.

The results presented in this paper show that bio- (*e.g.*, lignosulfonate, carboxymethyl inulin) and synthetic additives (*e.g.*, polyacrylic acid, polymaleic acid) containing anionic functional groups (*i.e.*, $-COOH$, $-SO_3H$), are ineffective silica polymerization inhibitors. The performance data on poly(2-ethyloxazoline) and poly(vinylpyrrolidone) containing non-ionic functional group show that these polymers exhibit good to excellent performance as silica polymerization inhibitors. Additionally, vinyl pyrrolidone-maleic acid based copolymers show mediocre performance in inhibiting silica polymerization reaction.

Acknowledgement

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