

Solubility Enhancement of Silicate with Polyamine/Polyammonium Cationic Macromolecules: Relevance to Silica-Laden Process Waters[†]

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This paper reports the inhibition efficiency of a family of synthetic amine/ammonium-containing cationic polymers in colloidal silica particle growth. Three polymeric additives were tested and compared to control samples. These are polyethyleneimine (PEI), polyallylamine hydrochloride (PALAM), and poly(acrylamide-*co*-diallyldimethylammonium chloride) (PAMALAM). Two sets of experiments were carried out: long term (0–72 h) and short term (0–8 h). There is a strong dependence of silica inhibition on additive dosage. The optimum dosages are 10 ppm for PEI, 20 ppm for PALAM, and 80–100 ppm for PAMALAM. PEI (at 10 ppm dosage) reaches 55% inhibitory efficiency at 24 h (defined as reactive silica in ppm at the time of measurement divided by 500 ppm, or multiplied by 100 for % efficiency). PALAM shows 65% inhibitory activity at 20 ppm, after 24 h. PAMALAM at 80 ppm dosage exhibits 60% inhibition. Inhibitory activity is reduced upon longer silicate polymerization times (48 and 72 h). Inhibition within the first 8 h is efficient with all three inhibitors exhibiting small differences in performance. There is ~130 ppm silicate stabilization over the control after 72 h of polymerization. These inhibitors present potential for water treatment applications.

Introduction

Formation of amorphous silica deposits is an operational obstacle for industrial process water systems.¹ Silica deposits cause inefficient heat transfer when present on heat exchangers, increased back pressure in clogged pipelines, and underdeposit corrosion phenomena on metal surfaces, and they can act as a matrix for the development of microbiological colonies (biofilms). These problematic issues can be overcome by applying the following control strategies: (a) removal of silica before “fresh” water enters the system,² (b) avoiding supersaturation, (c) use of chemical additives to inhibit colloidal silica formation,^{3,4} and (d) chemical or mechanical cleaning of the silica deposits after their formation.⁵ It is apparent that the first three approaches are preferred preventive measures for silica control, whereas the latter is a corrective one used only for system remediation. Chemical cleaning of silica deposits (usually by dissolution with $\text{NH}_4\text{F}\cdot\text{HF}$) is a difficult task that poses health hazards and environmental concerns.⁶ All four have both advantages and drawbacks, and the ultimate decision on the approach to be used relies on several factors such as cost, ease of application, extent of human involvement, and environmental issues. Amorphous silica deposits are formed by silicate ion polymerization via a condensation polymerization mechanism, at appropriate pH regions.⁷ This polymerization occurs only in supersaturated waters with respect to silica. The resulting silica precipitates form a hard and tenacious scale layer on critical industrial equipment, such as heat exchangers, transfer pipes, reverse osmosis membranes, etc. Silica removal by dissolution is a challenge, and the usual approaches to control it are avoiding supersaturation (leading to water wastage) or pretreatment (with high equipment costs). Research on chemical inhibitors for silica is ongoing, but actual applications of inhibition chemistries in the field are rather limited.^{8,9}

Experimental Section

Materials. Polyethyleneimine (PEI, branched, MW = 70 kDa, ~25% primary amines, ~50% secondary amines, and ~25% amines) was from Polysciences, polyallylamine hydrochloride (PALAM, MW ≈ 15 kDa) and poly(acrylamide-*co*-diallyldimethylammonium chloride) (PAMALAM, MW ≈ 250 kDa, ~45 wt % diallyldimethylammonium chloride, and ~55 wt % acrylamide) were from Sigma-Aldrich, Milwaukee, WI. Sodium silicate $\text{Na}_2\text{SiO}_3\cdot 5\text{H}_2\text{O}$, ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$) were from EM Science (Merck). Sodium hydroxide (NaOH) was from Merck, and hydrochloric acid 37% was from Riedel de Haen. Acrodisc filters (0.45 μm) were from Pall-Gelman Corporation. In-house, deionized water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts.

Methods. The protocols for all experiments and measurements described herein have been reported in detail elsewhere.^{10,11} Soluble silicate was measured using the silicomolybdate spectrophotometric method, which has a $\pm 5\%$ accuracy. Reproducibility was satisfactory. Briefly, the procedures are outlined as follows.

Silicate Supersaturation Protocol (“control”). A 100 mL portion from the 500 ppm (as SiO_2) sodium silicate stock solution was placed in a plastic beaker which contained a Teflon-covered magnetic stir bar. The pH of this solution was initially ~11.8 and was adjusted to 7.00 ± 0.1 by addition of HCl and NaOH (the change in the resulting volume was ~3%). Then the beaker was covered with plastic membrane and was set aside without stirring. The solutions were checked for soluble silicate by the silicomolybdate method every hour for the first 8 h or after 24, 48, or 72 h time intervals after the pH reduction.

Inhibitor Testing Protocol. 100 mL portions of the 500 ppm (as SiO_2) sodium silicate stock solution were placed in plastic containers charged with Teflon-covered magnetic stir bars. In each container, different volumes of inhibitor (10 000 ppm stock solution) were added to achieve desirable inhibitor concentration. This range included 10, 20, 40, 60, and 80 ppm, and the volumes

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added were 100, 200, 400, 600, and 800 μL for the three inhibitors. After that, the same procedure for the control test was followed.

Determination of “Soluble (Reactive) Silica”. “Soluble or reactive silica” actually denotes soluble silicic acid and was measured using the silicomolybdate spectrophotometric method. According to this method, a 2 mL filtered sample, with 0.45 μm syringe filter, from the test solution is diluted to 25 mL in the cell, with light path 1 cm. Ammonium molybdate stock solution (1 mL) and 0.5 mL of 1 + 1 HCl are added to the sample cell, and the solution is mixed well and left undisturbed for 10 min. Then, 1 mL of oxalic acid solution is added and mixed again. The solution is set aside for 2 min. After the second time period, the photometer is set at zero absorbance with water. Finally, the sample absorbance is measured at 452 nm as “ppm soluble silica”. The detectable concentration range is 0–75.0 ppm. To calculate the concentration in the original solution, a dilution factor is applied. The silicomolybdate method is based on the principle that ammonium molybdate reacts with reactive silica and any phosphate present at low pH (~ 1.2) and yields heteropoly acids, yellow in color. Oxalic acid is added to destroy the molybdophosphoric acid, leaving silicomolybdate intact, and thus eliminating any color interference from phosphates. It must be mentioned that this method measures soluble silica and, in this term, includes not only the monomer silicate acid but also oligomer species such as dimers, trimers, tetramers, etc. It is not stated exactly which are the reactive units. It should be noted that all additives tested in the present paper do not interfere with the silicomolybdate spectrophotometric method.

Results and Discussion

We have been interested in exploiting chemical technologies for silica-scale inhibition that rely on use of chemical additives as inhibitors, with emphasis on environmentally friendly, “green” chemical additives.¹² We recently reported utilization of polyaminoamide-based (PAMAM) dendrimers as silica-scale inhibitors, particularly those that are amine-terminated.^{10,13,14} Although these dendrimeric additives are effective silica growth inhibitors, they are not likely to be used in actual field applications presently, primarily because of high cost. Therefore, alternative, lower-cost chemical approaches need to be sought while maintaining high inhibitory efficiency. During this research effort, we discovered that, in order for an additive to be an effective silica growth inhibitor, it has to possess, to a certain (yet unidentified) degree, some cationic charge. However, it should be noted that “small” cationic species (such as H_4N^+ or Et_4N^+) are not effective inhibitors. On the other hand, the presence of excessive cationic charge is detrimental to the inhibition process because anionic colloidal silica particles (at the experimental pH tested) are agglomerated by these poly-cationic species and generate precipitates, thus depleting the process fluid from an “active” inhibitor by entrapping it within the silica 3D polymeric matrix. It is apparent that careful balance between the silicate level and the additive cationic charge is necessary for successful application.

Three cationic polymeric additives were tested and compared to control samples. These are polyethyleneimine (PEI), polyallylamine hydrochloride (PALAM), and poly(acrylamide-co-diallyldimethylammonium chloride) (PAMALAM); see Figure 1). PEI carries the cationic charge on primary ($\sim 25\%$), secondary ($\sim 50\%$), and tertiary ($\sim 25\%$) amine functionalities. PALAM has the positive charge exclusively on its primary amine groups, whereas PAMALAM possesses the positive charge on a “genuine” alkylammonium group ($\sim 45\%$), while

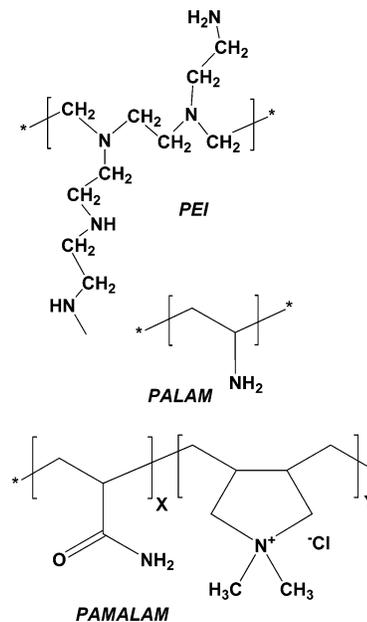


Figure 1. Schematic structures of the three polymeric additives. For PAMALAM, $x = 0.55$ and $y = 0.45$.

the rest is neutral acrylamide moieties ($\sim 55\%$ wt %). These polymeric additives were screened and repeatedly tested by our laboratory’s well-established silica supersaturation test.¹¹ This methodology is based on soluble silicate measurements in solutions supersaturated in silicate (500 ppm as SiO_2) in the absence and presence of inhibitors at specific time intervals. Two sets of experiments were carried out: long term (0–72 h, with measurements every 24 h) and short term (0–8 h, with measurements every 1 h).

Test solutions of 500 ppm silica (as SiO_2) were utilized in this study. Solubility of silica is strongly dependent on pH, with its lowest values found in the pH regime of 7–8.^{15,16} Solutions were tested for soluble silica by the silicomolybdate spectrophotometric method¹⁷ after prespecified polymerization time intervals, and the results are presented in Figure 2. Under these experimental conditions, all three polymeric inhibitors showed efficacy higher than the control for silica polymerization inhibition. There was a distinct differentiation, however, in the dosage-dependent inhibitory activity.

A general observation is that, during the silica polymerization experiments, silica levels drop even if an inhibitor is present. Therefore, the inhibiting additive can only *retard* silica growth. After 24 h, in control solutions (absence of any additive), silica polymerization proceeds until only 200 ppm SiO_2 remain soluble. The remaining silica forms colloidal particles. PEI at 10 ppm dosage offers 55% inhibition, allowing 275 ppm silica to remain soluble. PALAM shows higher inhibitory activity in controlling silica polymerization, giving 327 ppm of reactive silica (65%). The inhibition efficiency of PAMALAM at 20 ppm dosage appears to be lower and indistinguishable from the control (~ 200 ppm soluble silicate).

Silicate polymerization continues after 48 h. In control solutions, soluble silicate levels drop to 170 ppm (loss of ~ 30 ppm after the 24 h measurement). Inhibition efficiencies of all polymeric additives drop as well. PEI at 10 ppm dosage retains 210 ppm soluble silicate (loss of 65 ppm), 40 ppm above the control. PALAM (20 ppm dosage) retains 270 ppm silicate in solution, whereas in the presence of PAMALAM (20 ppm dosage), ~ 185 ppm of silicate remains soluble. After 72 h of polymerization time, soluble silicate levels drop further and are

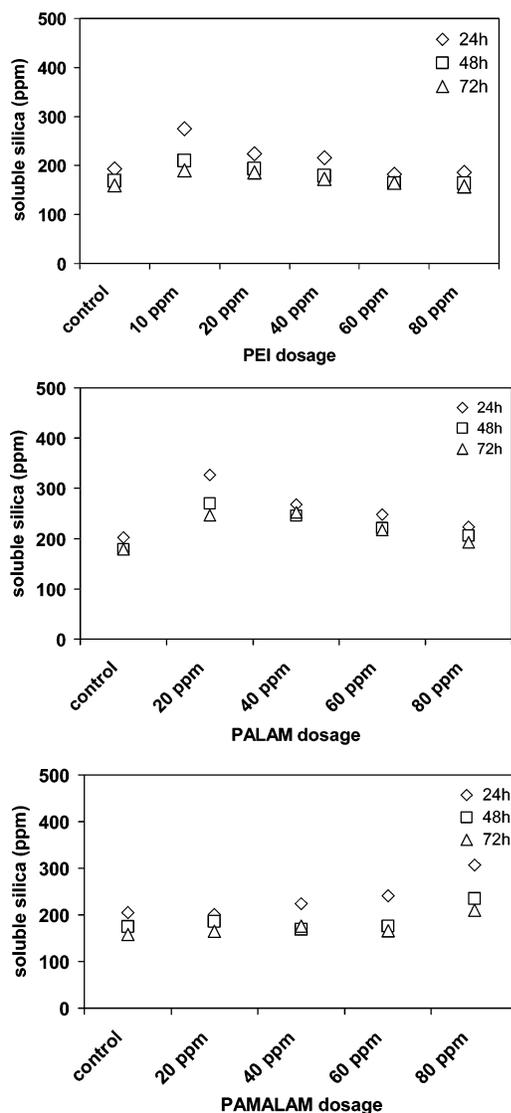


Figure 2. Solubility enhancement of silica in the presence of polymeric additives in long-term experiments.

virtually identical to the control. Therefore, it appears that, after 72 h of polymerization time, all inhibitory activity is lost.

Additive dosage appears to play an important role in silica inhibition. For PEI and PALAM, there appears to be an optimum dosage, 10 ppm for the former and 20 ppm for the latter for optimum inhibition. A dosage increase results in a drop in performance. This decrease in inhibitory activity is accompanied by the presence of a “fluffy” precipitate after ~24 h of polymerization. This can be rationalized on the basis of the positive charge on the inhibitor molecules. In the case of PEI and PALAM, it is apparent that these NH_2 -containing polymers (most likely in a $-\text{NH}_3^+$ form in the pH ranges examined)^{18,19} associate with negatively charged colloidal silica particles, thus forming silica-polymer composites that are insoluble. In the case of PAMALAM, the performance maximum is in the 80–100 ppm range. Higher dosages up to 150 ppm were also tested that revealed that reduction of inhibitory activity occurs above 100 ppm.

Charge density also plays a role in silica inhibition. On the basis of previous and present research, a high positive charge density is detrimental to inhibition. As mentioned above, the cationic inhibitor forms insoluble composites with the negatively charged colloidal silica particles and, thus, becomes deactivated. Depletion of active inhibitor results in uncontrolled silicate

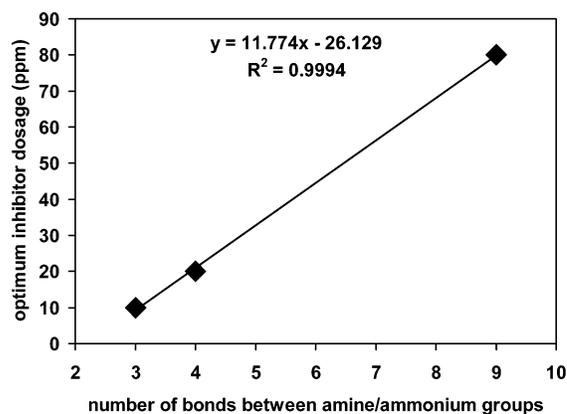


Figure 3. Dependence of optimum inhibitor dosage on structural features of the polymeric inhibitors.

polymerization and low soluble silicate levels. PEI has the highest positive charge density (three bonds between amine groups, Figure 1), which explains the highest inhibition at only 10 ppm dosage.

PALAM possesses a lower charge density than PEI (four bonds between amine groups, Figure 1), a fact that is consistent with the highest inhibitory activity being shown at 20 ppm dosage. Last, PAMALAM has the lowest charge density of all three polymers, because the neutral amide groups “dilute” the positively charged diallyldimethylammonium groups (nine bonds *on average* between quaternary ammonium groups, Figure 1). Therefore, maximum inhibitory activity at 80–100 ppm dosage is consistent with the argument above.

There is an excellent correlation between the number of bonds separating two positive $-\text{NH}_3^+$ (or $-\text{NR}_4^+$) groups and the optimum dosage of the polymeric inhibitors. This is appropriately shown in Figure 3. On the basis of this relationship, the optimum inhibitor dosage is directly proportional to the distance separating the cationic groups in the polymer backbone. On the basis of the present results, it is not clear whether ammonium ($-\text{NH}_3^+$) or quaternary ammonium (NR_4^+) groups show distinct differences in inhibition performance. Both groups are capable of participating in electrostatic interactions with the anionic colloidal silica particles, but the former has the additional ability of forming hydrogen bonds with silica or silicate monomers or oligomers, whereas the latter cannot. To investigate this hypothesis, careful polymer synthetic design is necessary, and this is underway in our laboratory.

“Short-term” inhibition experiments were also performed in order to examine inhibition properties within the first 8 h of silicate polymerization. Various dosages of the three inhibitors were again tested. Results based on the optimum dosage of each inhibitor (10 ppm for PEI, 20 ppm for PALAM, and 80 ppm for PAMALAM) are shown in Figure 4. It appears that, in “control” solutions, colloidal silica formation in the absence of additives consumes ~250 ppm (~50%) of the initial soluble silicate. Addition of 20 ppm PALAM enhances silicate solubility up to ~350 ppm (~70%) at the end of the 8-h experiment. PAMALAM at 80 ppm dosage allows 385 ppm (77%) of silicate to remain soluble, whereas the presence of 10 ppm PEI results in ~350 ppm (~70%) silicate remaining soluble.

Information on inhibition of silica-scale growth is insufficient at present, and thus, details on the inhibitory mechanism are poorly understood. The inhibitor disrupts silicate polymerization by influencing nucleophilic attack of silicate ions among themselves (an $\text{S}_\text{N}2$ -like mechanism).²⁰ The inhibition pathway of other inhibitors tested by other authors is entirely different. Orthoborate ion, for example, inhibits silica growth by forming

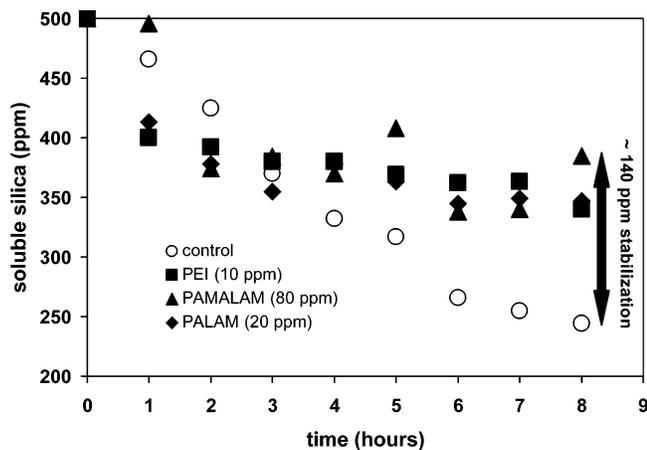


Figure 4. Solubility enhancement of silica in the presence of polymeric additives during short-term experiments (8 h).

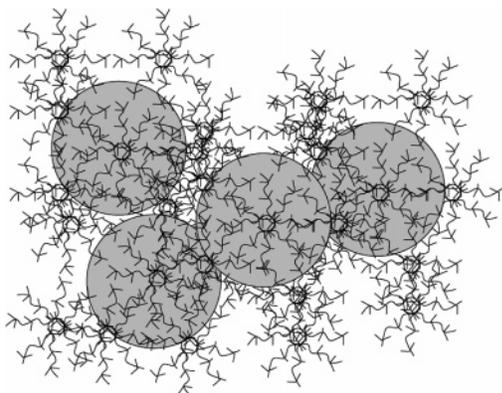


Figure 5. Schematic structure of the silica-polymer composites formed by polyanion-polycation association (see text).

borosilicates that possess much higher supersaturation indices than colloidal silica.^{21,22} Neutral polymers such as polyethyl-oxazoline, containing amide groups, have been shown to control silica growth in simulated industrial waters.^{11,23} Inhibition of growth of *crystalline* scale deposits, on the other hand, is achieved by use of additives, such as phosphonates (most notably PBTC, HEDP, and AMP) or polyacrylate-based polymers and derivatives,^{24,25} or other biopolymers, such as carboxymethyl inulin.²⁶ These scale inhibitors achieve inhibition by stereospecific adsorption onto crystallographic planes of a growing nucleus after a nucleation event, resulting in “poisoning” further growth and crystallite agglomeration.²⁷ The aforementioned “classical” mineral-scale inhibitors have virtually no effect on silicate polymerization.¹⁰ The unique nature of colloidal silica requires “nonclassical” inhibition approaches and, perhaps, more “exotic” inhibitor molecular structures.

Conclusions

The purpose of this work is to identify and exploit novel polymer chemical technologies as effective silica-scale growth inhibitors in process waters. The principle findings are summarized as follows: (1) Cationic polymers enhance silicate solubility. (2) PEI (10 ppm), PALAM (20 ppm), and PAMALAM (80–100 ppm) cationic polymers are effective inhibitors of SiO₂-scale growth at different dosage levels for each. (3) Their structure and cationic charge density affects inhibitory activity. High positive charge density results in inhibitor coprecipitation with anionic colloidal silica, whereas low charge density renders the inhibitor ineffective at lower dosages. (4) These amine/ammonium-containing polymers also act as silica

aggregators forming SiO₂-polymer composites with a subsequent loss of inhibitor efficiency over time due to inhibitor entrapment within the amorphous 3D silica matrix. These composites could be envisioned as colloidal silica particles “glued” together with cationic polymers and are shown schematically in Figure 5. Inhibition-performance dependence on particular structural features of the inhibitor molecule is of great importance. Structure/activity relationships may help in the rational design of inhibitors with precise structures and topologies that may show, ideally, predictable inhibition performance. Inhibition of silica growth most probably occurs at the early stages of silicate polymerization. Unfortunately, there is little information available at the molecular level on the silicate oligomers formed. Such data would be of great importance, because they would greatly facilitate inhibitor design and improvement.

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