

## Enhancement of silicate solubility by use of “green” additives: linking green chemistry and chemical water treatment

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### Abstract

The inhibition performance of three synthetic amine/ammonium-containing cationic polymers in colloidal silica particle growth is reported. The three additives are compared to control (no additives present during silicate polymerization). The three polymers, polyethyleneimine (PEI), polyallylamine hydrochloride (PALAM) and poly(acrylamide-*co*-diallyl-dimethylammonium chloride) (PAMALAM), were screened in two sets of experiments: long term (24–72 h) and short term (0–8 h). Silica inhibition performance is profoundly dependent on the polymeric additive dosage. The most effective dosages were found to be 10 ppm for PEI, 20 ppm for PALAM and 80–100 ppm for PAMALAM. The inhibitory efficiency of PEI (at 10 ppm dosage) reaches 55% at 24 h (inhibitory efficiency is defined as reactive silica in ppm at the time of measurement divided by 500 ppm, times 100). PALAM reaches 65% inhibitory activity at 20 ppm, after 24 h. PAMALAM at 80 ppm dosage shows 60% inhibition. Inhibitory activity drops on longer silicate polymerization times (48 and 72 h). All three inhibitors show activity higher than the control during the first 8 h, exhibiting small variations in performance.

*Keywords:* Colloidal silica; Green additives; Water treatment; Silicate polymerization; Inhibition

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### 1. Introduction

Deposition of amorphous colloidal silica is rare in industrial process water systems [1]. It

only occurs when make-up water is supersaturated with respect to silicate ion. When silicate levels reach ~180 ppm (depending on water chemistry) polymerization takes place, resulting in formation of colloidal silica particles. Eventually, these transform into hard and tenacious

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deposits that cause problematic heat transfer when found on heat exchangers, increased back pressure in clogged pipelines, and underdeposit corrosion on metal surfaces. Certain control strategies can alleviate the situation: (a) removal of silica before “fresh” water enters the system with desilicizers [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]. The first three approaches are preferred preventive options for silica scale control, whereas the latter is a corrective one used only for system recovery. Silica deposit removal by means of chemical cleaning (by dissolution with  $\text{NH}_4\text{F}\cdot\text{HF}$ ) is a challenging task that poses health risks (liberation of HF) and environmental concerns [6]. There is no single approach that can guarantee a system free of silica deposits and the ultimate decision lies 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. Research on chemical inhibitors for silica is ongoing, but actual applications of inhibition chemistries in the field are rather limited [8,9]. The inhibitory additive can only delay silicate polymerization, thus enhancing its solubility.

In the last decade intense efforts have been dedicated to develop additive chemistries that are more environmentally friendly. The “Green Chemistry” approach is gaining acceptance in various technological fields. An important area where green chemistry can potentially find several applications is the use of environmentally acceptable additives for water treatment.

The definition of a “green chemical” has been given by Anastas and Warner [10]. They have given a broad definition of green chemistry based on 12 principles that relate to several steps, from

chemical synthesis to chemical usage. A green chemical should be synthesized in a safe and energy efficient manner, its toxicity should be minimal, whereas its biodegradation should be optimal. Lastly, its impact to the environment should be as low as possible.

The OSPAR Commission (Oslo and Paris Commission [11]) is the international body responsible for harmonization of the strategies and legislation in the North-East Atlantic Region. The Commission has stated that every effort should be made to combat eutrophication and achieve a healthy marine environment where eutrophication does not occur by the year 2010. Chemicals are classified differently depending on the particulars of the geographical area. The guidelines set by OSPAR are:

- Biodegradability (>60% in 28 days. If <20%, the chemical is a candidate for substitution)
- Toxicity (LC50 or EC50 >1 mg/L for inorganic species, LC50 or EC50 >10 mg/L for organic species)
- Bioaccumulation (Logpow <3, pow = partition in octanol/water)

When a chemical fulfils two out of three requirements and its biodegradability is superior to 20% in 28 days, it is eligible to be listed on the PLONOR List (Pose Little Or No Risk). This emphasizes the biodegradability factor and influences usage of water additives.

In this paper we report the inhibitory efficiency of three polymeric additives, polyethyleneimine, polyallylamine hydrochloride and poly(acrylamide-*co*-diallyl-dimethylammonium chloride), for the polymerization of silicate to form colloidal silica.

## 2. Experimental

### 2.1. Materials

Polyethyleneimine (PEI, branched, MW 70 kDa, ~25% primary amines, ~50% secondary

amines and ~25% amines) was obtained from Polysciences, polyallylamine hydrochloride (PALAM, MW ~15 kDa) and poly(acrylamide-co-diallyl-dimethylammonium chloride) (PAMALAM, MW ~250 kDa, ~45 wt% diallyl-dimethylammonium chloride and ~55 wt% acrylamide) were obtained from Sigma-Aldrich, Milwaukee, WI. Unfortunately there is incomplete information available for the toxicological and environmental profiles, as well as bioaccumulation and biodegradability of these three additives in the literature. All gathered information from MSDSs (searched through the world wide web) is presented below. PEI has found several uses in biomedical applications proving its compatibility with biological systems. The acute toxicity (LD<sub>50</sub>, oral, rat) was determined to be 2800 mg/L. Its ecotoxicological effects are: LC<sub>50</sub> (fish, *Brachydanio rerio*, 96 h) 7.1 mg/L, EC<sub>50</sub> (fish, *Daphnia Magna*, 48 h) 8.84 mg/L. We were not able to locate any information on PALAM.

## 2.2. Methods

The protocols for all experiments and measurements described herein have been reported in detail elsewhere [12,13]. Soluble silicate was measured using the silicomolybdate spectrophotometric method, which has a ±5% accuracy. Reproducibility was satisfactory.

## 3. Results

### 3.1. Scope of the research

We have been actively exploring chemical technologies for silica scale inhibition that are based on use of chemical additives as inhibitors, with emphasis on environmentally friendly, “green” chemical additives [14]. We recently reported utilization of polyaminoamide-based (PAMAM) dendrimers as silica scale inhibitors, particularly those that are amine-terminated

[12,15,16]. Although these dendrimeric additives are effective silica growth inhibitors they are not likely to be used in actual field applications presently, primarily due to 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<sub>4</sub>N<sup>+</sup> or Et<sub>4</sub>N<sup>+</sup>) are not effective inhibitors at dosages up to 100 ppm. On the other hand, 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 polycationic species and generate precipitates, thus depleting the process fluid from “active” inhibitor by entrapping it within the silica amorphous polymeric matrix. It is apparent that careful balance between the silicate level and the additive cationic charge is necessary for successful application.

### 3.2. Long-term experiments

Three cationic polymeric additives were tested and compared to control samples. These are polyethyleneimine (PEI), polyallylamine hydrochloride (PALAM) and poly(acrylamide-co-diallyl-dimethyl-ammonium chloride) (PAMALAM) (Fig. 1).

PEI carries the cationic charge on primary (~25%), secondary (~50%) and tertiary (~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 (~45 wt.%), while the rest is neutral acrylamide moieties (~55 wt.%). These polymeric additives were screened and repeatedly tested in our laboratories using the well established silica supersaturation test [13,14,16]. This methodology

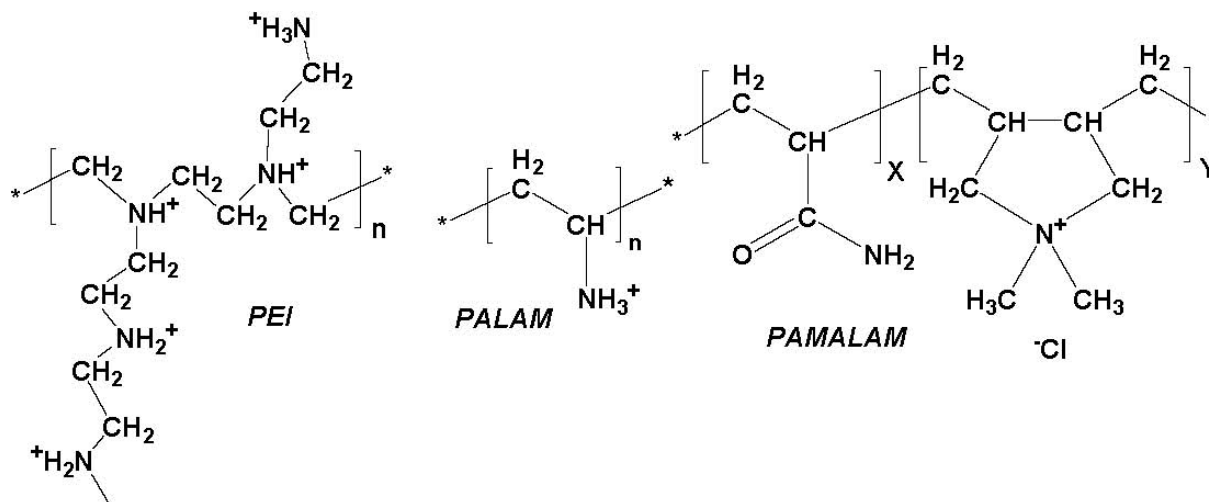


Fig. 1. Schematic structures of the three polymeric additives.

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 (24–72 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 to 8 [17,18]. Solutions were tested for soluble silica by the silicomolybdate spectrophotometric method [19] after pre-specified polymerization time intervals, and the results are presented in Figs. 2–4. 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

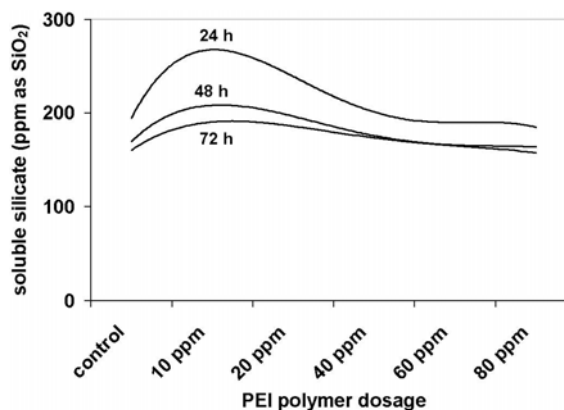


Fig. 2. Solubility enhancement of silicate by PEI in long-term experiments.

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 silica).

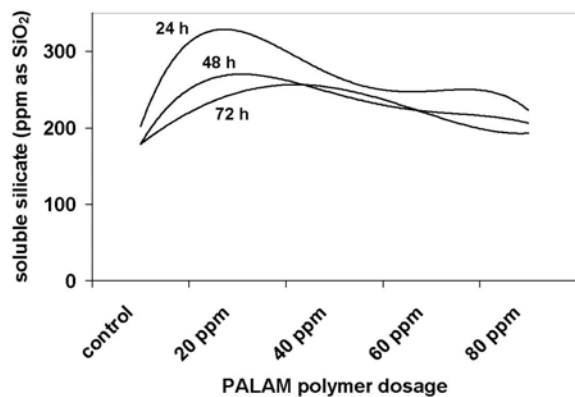


Fig. 3. Solubility enhancement of silicate by PALAM in long-term experiments.

Silicate polymerization continues after 48 h. In control solutions, soluble silicate levels drop to 170 ppm (loss of ~30 ppm). 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 remain soluble. After 72 h of polymerization time, soluble silicate levels drop further and are 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. Dosage increase results in 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<sub>2</sub>-containing polymers (most likely in a -NH<sub>3</sub><sup>+</sup> form at pH = 7) [20,21] associate with negatively charged colloidal silica particles, thus forming

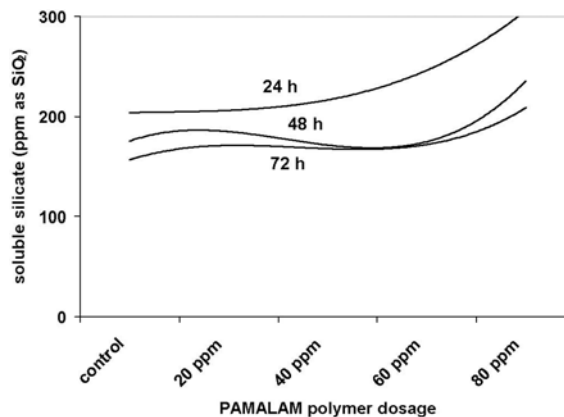


Fig. 4. Solubility enhancement of silicate by PAMALAM in long-term experiments.

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.

### 3.3. Short-term experiments

“Short-term” inhibition experiments were also carried out in order to gain information about the inhibition mechanism 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. Herein, results are presented for 20 ppm dosage for PEI, 20 ppm for PALAM and 80 ppm for PAMALAM and are shown in Figs. 5–7. It appears that in “control” solutions colloidal silica formation in the absence of additives consumes ~250 ppm (~50%) of the initial soluble silicate after 8 h. Addition of 20 ppm PEI enhances silicate solubility up to ~260 ppm at the end of the 8-h experiment. This is because of depletion of inhibitor from solution due to its entrapment in the colloidal silica matrix. PAMALAM at 80 ppm dosage allows ~350 ppm (70%) of silicate to remain soluble, whereas presence of 80 ppm PAMALAM results in ~300 ppm (~60%) silicate to remain soluble.

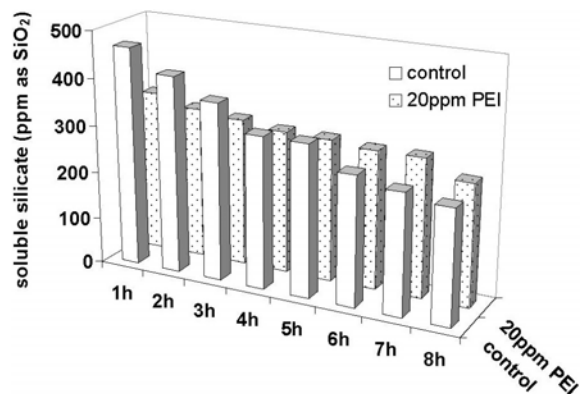


Fig. 5. Solubility enhancement of silicate by PEI in short-term experiments.

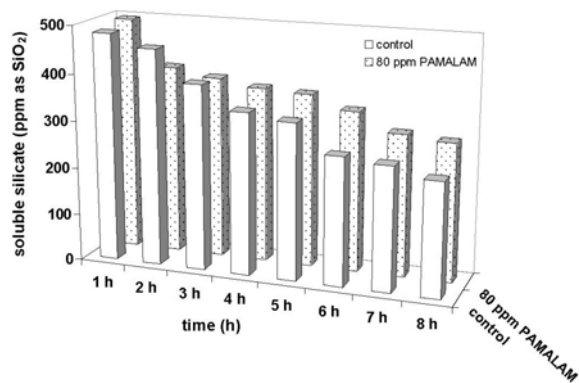


Fig. 7. Solubility enhancement of silicate by PAMALAM in short-term experiments.

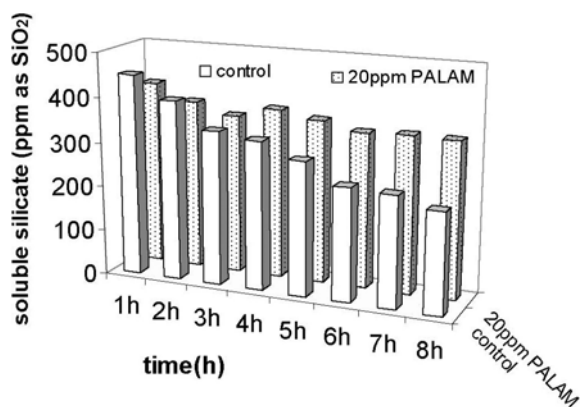


Fig. 6. Solubility enhancement of silicate by PALAM in short-term experiments.

#### 4. Discussion

Charge density in the inhibitor molecule plays a significant role in silica inhibition. Based on previous and the present research, high positive charge density is detrimental to inhibition. As mentioned above, the cationic inhibitor forms insoluble composites with the negatively charged colloidal silica particles (due to incomplete inhibition) and thus becomes deactivated. Depletion of active inhibitor results in uncontrolled silicate polymerization and low soluble silicate levels. PEI has the highest positive charge density (three

bonds between amine groups, Fig. 1) that explains the highest inhibition at only 10 ppm dosage. PALAM possesses lower charge density than PEI (four bonds between amine groups, Fig. 1), a fact that is consistent with the highest inhibitory activity being shown at 20 ppm dosage. Lastly, 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, Fig. 1). Therefore maximum inhibitory activity at 80–100 ppm dosage is consistent with the argument above.

The mechanism of inhibition of silica scale growth is insufficiently understood [22]. The inhibitor interferes with silicate ion polymerization by influencing a nucleophilic attack of silicate ions among themselves (an S<sub>N</sub>2-like mechanism) [23,24]. It is important to note that silicate polymerization inhibition and colloidal silica stabilization (dispersion) are, in principle, two completely different approaches. The latter aims at maintaining small silica colloids dispersed (in suspension) and at avoidance of deposition. In contrast, the former delays (ideally ceases) silicate polymerization, thus maintaining silicate in its soluble forms. Colloidal silica ideally does not

form in that case. This approach is sought in this research.

## 5. Conclusions

In this work novel approaches based on polymer chemical technologies are studied as effective silica scale growth inhibitors in process waters. The most important conclusions are summarized below:

- Cationic polymers enhance silicate solubility at the dosages used.
- PEI (10 ppm), PALAM (20 ppm) and PAMALAM (80–100 ppm) cationic polymers are effective inhibitors of  $\text{SiO}_2$  scale growth at different dosage levels each.
- Their structure and cationic charge density affect inhibitory activity. High positive charge density results in inhibitor co-precipitation with anionic colloidal silica, whereas low charge density renders the inhibitor ineffective at lower dosages.
- These amine/ammonium-containing polymers also act as silica aggregators forming  $\text{SiO}_2$ -polymer composites with subsequent loss of inhibitor efficiency over time due to inhibitor entrapment within the amorphous colloidal silica matrix.

The ultimate decision on which additive is the most appropriate to use is dependent on several factors. Inhibitory activity, potential hazards, ease of application, cost-effectiveness are some of the criteria that dictate such a decision [25]. Based on the data presented herein, it appears that PEI is the additive of choice when the lowest dosage is the criterion. However, if inhibitor performance is the criterion, then PALAM is the additive of choice.

Lastly, it should be emphasized that control of colloidal silica by inhibition is a challenging issue. Colloidal silica is profoundly different than other, crystalline sparingly soluble salts [26], because it is amorphous. An added challenge, is

to develop “green” additives that will be both high performing and environmentally acceptable [27].

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