

Profound “turn-off” effects of anionic polymers on the inhibitory activity of cationic polyallylamine in the prevention of silica scale

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Abstract

Colloidal/amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$, n is variable) is considered as the most undesirable inorganic precipitate that forms during various processes in silica-supersaturated industrial waters. In this paper we present how certain polymeric chemical additives can prevent silicic acid polymerization to form colloidal silica, which may lead to deposition onto industrial equipment. More specifically, stabilization of silicic acid is accomplished by using a cationic polymer, polyallylamine hydrochloride (PALAM), in supersaturated silica solutions (starting silica concentration in the form of silicate 500 ppm, or 8.3 mM sodium orthosilicate, $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, expressed as SiO_2) at $\text{pH} = 7$. PALAM is a linear homopolymer that carries one amine side functional group every two carbon atoms, so it becomes protonated at circumneutral pH, rendering the molecule cationic. Its blends with anionic polymers such as carboxymethylinulin (CMI), poly(acrylamide-*co*-acrylic acid) (PAM-*co*-AA) and phosphonomethylated chitosan (PCH) are also studied for their silica scale inhibition efficiency.

Key words: *silicic acid stabilization, silica, inhibitors, deposits, water systems, inhibitors, polyallylamine, carboxymethylinulin, polymers.*

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Introduction

Water is the global fluid of choice for cooling purposes in industry because of its low cost, and high thermal capacity [1–6]. During its re-use, scaling and deposition can develop due to the high content of dissolved species [7]. The deposits that may appear depend on the specific water chemistry [8]. Among the water-, or steam-formed deposits colloidal silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$, n is variable and depends on hydration), a very persistent precipitate, is thought to be of the toughest to combat, as it can cause serious materials failure and operational shut-downs, Figure 1 [9].



Figure 1. Amorphous silica deposits on steam turbines. Reproduced with permission from <https://tofanhakim.wordpress.com>.

Control of silica polycondensation, in principle, can be achieved by use of chemical additives [10] or capital-intensive water desilicification [11–15]. Unfortunately, traditional scale control methods (inhibition and crystal modification) applied to crystalline mineral salt precipitates [16], do not apply to silica because of its amorphous state [17]. Therefore, carefully designed inhibition approaches have to be implemented for controlling silica deposition. Increasing environmental concerns and discharge limitations have imposed additional challenges in treating process waters. Therefore, the discovery and successful application of chemical additives that have mild environmental impact has been the focus of several researchers [18–22].

In this paper we focus on use of “green” inhibitors silica scale inhibition, plus cost effectiveness, as PALAM is a rather economic additive compared to other “green” ones. This research is part of our on-going investigation on the discovery and application of scale inhibitors in industrial process waters [19–39].

In this work, we present the inhibiting effect of polyallylamine hydrochloride (PALAM), on the formation of amorphous silica starting from water-soluble sodium silicate. PALAM is a linear homopolymer of ~15 KDa molecular weight, which possesses a “tail” of a primary amine functional group (Figure 2). These amine moieties become protonated at circumneutral pH, rendering the polymer cationic, and thus enabling interaction between cationic PALAM with negatively charged silicate. Multifunctional blends of PALAM with anionic polymers (see Figure 3) are also studied for their silica scale inhibition efficiency.

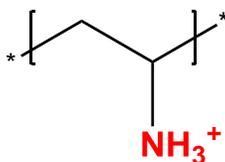


Figure 2. Schematic structure of polyallylamine hydrochloride (PALAM) in its cationic form, highlighted in red.

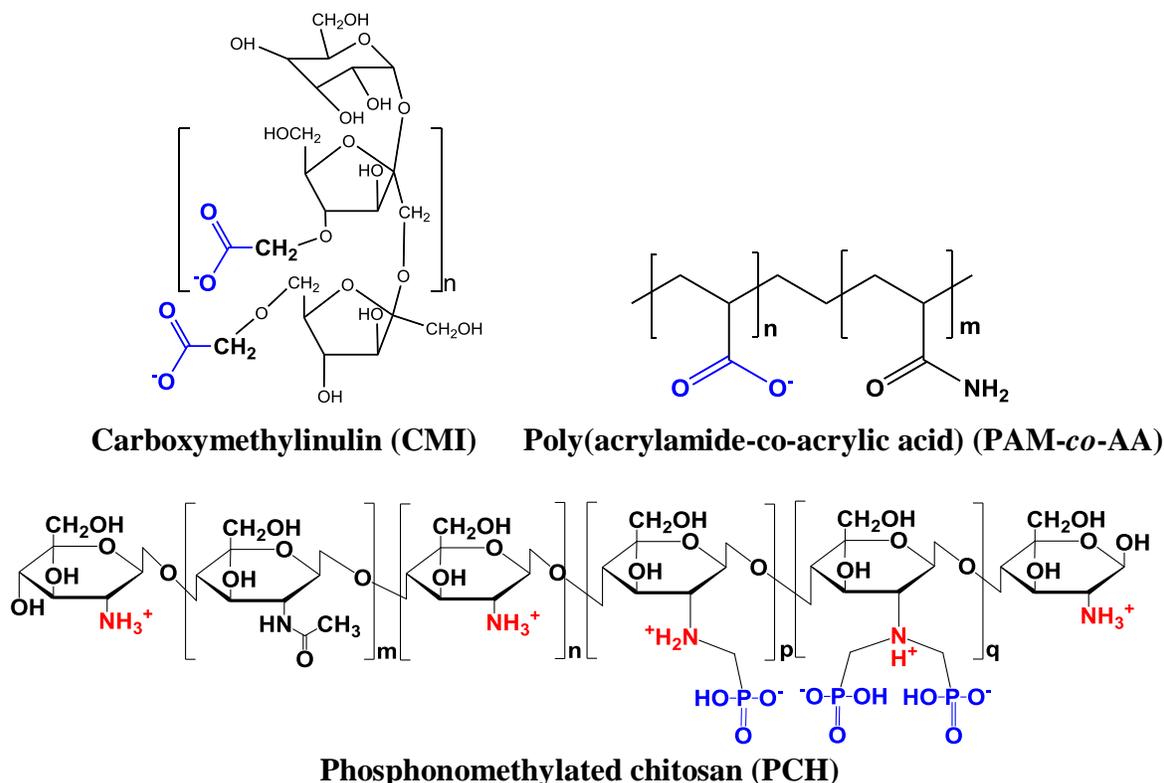


Figure 3. Structures of the silica scale co-inhibitors used in this work. Cationic groups are highlighted in red, anionic ones in blue.

Experimental Section

Instruments

IR spectra were recorded on an FT-IR Perkin–Elmer FT 1760 instrument. The measurements of soluble silicic acid were carried out with a HACH 890 spectrophotometer from the Hach Co., Loveland, CO, U.S.A.

Reagents and Chemicals

Sodium silicate pentahydrate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and PALAM were purchased from Sigma-Aldrich. Ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was obtained from Alfa-Aesar and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) from EM Science (Merck). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) 37% were purchased from Sigma-Aldrich. Deionized water from an ion-exchange resin was used for all experiments and stock preparations. This water was tested for molybdate-reactive silica (interference tests) and was found to contain negligible amounts.

Preparation of Sodium Silicate Solutions ('Stock' Solutions)

A solution containing silicate (500 ppm as SiO_2) was prepared by dissolving 4.08 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in 2 L of deionized water (a non-glass container must be used), followed by

overnight rigorous stirring. Stock solutions of the additives in water (PALAM, CMI, PAM-co-AA, PCH) were 1% w/v (10.000 ppm). The following solutions were prepared for the silicate spectrophotometric detection test: (a) An ammonium molybdate solution: 10 g of ammonium molybdate was dissolved in 100 mL of water, and its pH was adjusted between 7 and 8 with NaOH to avoid precipitation of ammonium molybdate. (b) A hydrochloric acid solution: one volume 37% HCl was mixed with equal volume water. (c) An oxalic acid solution: 8.75 g of oxalic acid was dissolved in 100 mL of water. All solutions were kept in polyethylene containers (glass containers must be avoided to minimize SiO₂ dissolution and silicate leaching into the test solutions). HCl and ammonium molybdate were kept in the fridge, while silica and oxalic acid solution were kept at room temperature.

Silicic Acid Polycondensation Protocol (“Control” experiment)

100 mL from the 500 ppm sodium silicate stock solution (see above) was placed in a polyethylene beaker and the initial pH was found to be 11.8. The pH is then adjusted to 7.00±0.1 by addition of HCl and/or NaOH, as needed (the change in the resulting volume was minor and did not affect any of the calculations). Then, the beaker was covered with plastic membrane and set aside without stirring. The solutions were checked for molybdate-reactive silica by the silicomolybdate method every 1 hour for the first 8 hours or after 24, 48, and 72 hours after the pH adjustment (see below). All experiments (control and in the presence of inhibitor and co-inhibitor) were treated in precisely the same way.

Silicic Acid Polycondensation in Presence of PALAM and co-inhibitors

100 mL portions of the 500 ppm sodium silicate stock solution (see above) were placed in polyethylene containers. In each container, different volumes of pure PALAM or PALAM and co-inhibitor (from the prepared 10.000 ppm stock solutions) were added to achieve desirable concentration. After that, the same procedure as the “control” protocol was followed.

Determination of Molybdate-Reactive Silica

Molybdate-reactive silica (mainly mono- and some disilicic acid) was quantified using the well established silicomolybdate spectrophotometric method [40–45]. As in our previous studies [19–39], we used the “yellow molybdate” method (using a HACH DR/890 spectrophotometer) as follows: 2 mL from the working solution is filtered through a 0.45 µm syringe filter and then diluted to 25 mL in a special cylindrical cell of 1 cm path length, made of quartz. Next, 1 mL of ammonium molybdate stock solution and 0.5 mL of HCl (1:1 dilution of the concentrated solution) are added to the sample cell, the solution is shaken well and left standing for 10 min. Afterward 1 mL of oxalic acid solution is added and the cell contents are mixed well. The solution is set aside for 2 min. The photometer is now set to “zero absorbance” using a sample of deionized water (“blank”). Finally, the sample absorbance is measured (at 452 nm) and is expressed as “ppm SiO₂”. The detectable concentration range for this specific protocol is 6–75 ppm. To calculate the concentration in

the original solution, an appropriate dilution factor ($\times 27.5/2$) is applied. The basic working principal of the silicomolybdate test is that ammonium molybdate reacts only with mono- and disilicic acid and any phosphate present and forms yellow-colored complexes. This reaction requires acidic environment in order to take place, and this is why the hydrochloric acid is added to the samples. It should be noted that colloidal silica does not participate in the reaction and thus does not affect the intensity of yellow color, which is proportional to the concentration of the reactive silica present in the sample experiment. Oxalic acid is added to destroy any molybdophosphoric acid formed, leaving the silicomolybdate complex intact, and thus eliminating any color interference from phosphates.

Results and Discussion

Inhibitory activity results of PALAM

Initially, PALAM was tested as silica scale inhibitor in “long term” experiments (up to 3 days). This is an important time frame for scale inhibitors, as it evaluates the ability of a certain inhibitor to prevent scale formation for a prolonged time period. Inhibitory activity results for PALAM (at concentrations 20, 40, 60, and 80 ppm) are presented in Table 1 and plotted in Figure 4.

Table 1. Silica inhibition measurements with PALAM (20, 40, 60 and 80 ppm) in long-term experiments (3 days).

Time (hours)	PALAM concentration (in ppm)				
	control	20	40	60	80
24	202	327	268	248	223
48	179	270	245	221	206
72	160	246	252	217	193

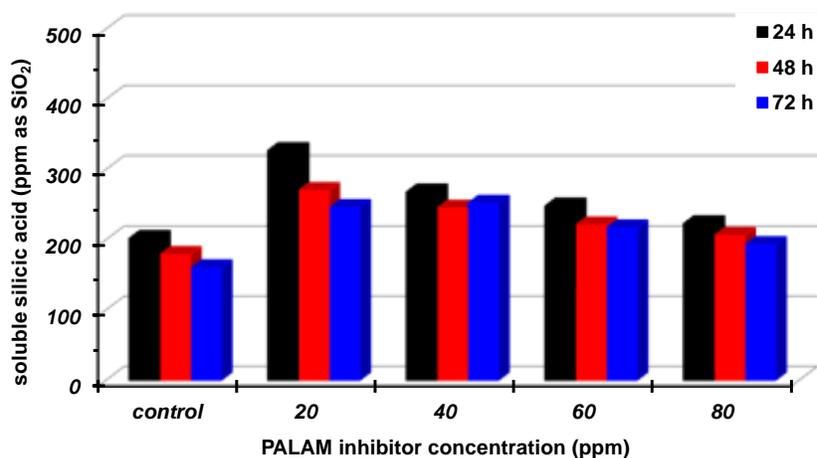


Figure 4. Silica inhibitory activity of PALAM in long-term (3 days) experiments.

Based on these results, it appears that PALAM is active in silicic acid stabilization even at the “low” dosage of 20 ppm. Specifically, it stabilizes 125 ppm (after 24 h) above the control value, when present in the system at 20 ppm. Its inhibitory activity drops over time (as observed with almost all silica inhibitors studied so far), stabilizing 91 ppm (after 48 h) and 86 ppm silicic acid above the control.

An additional point that warrants some attention is that upon PALAM concentration increase, its inhibitory activity is reduced. This is clearly shown in Figure 5, where a virtually linear drop in activity is observed at 24 h, 48 h, and 72 h measurements.

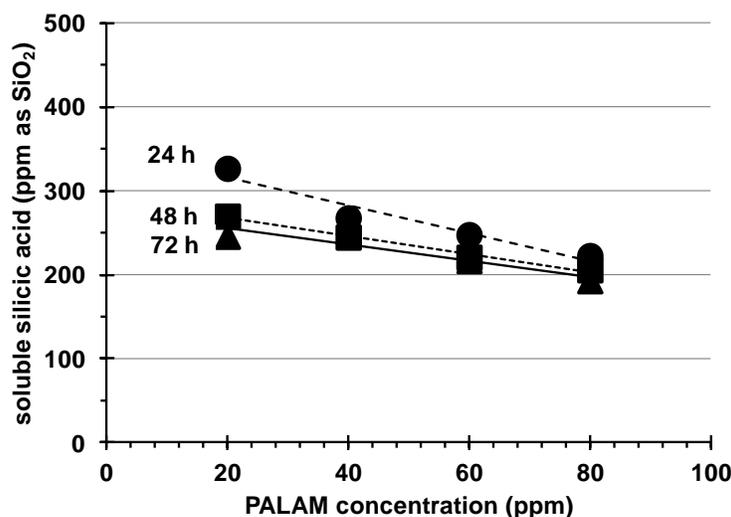


Figure 5. Reduction in inhibitory activity upon PALAM concentration increase.

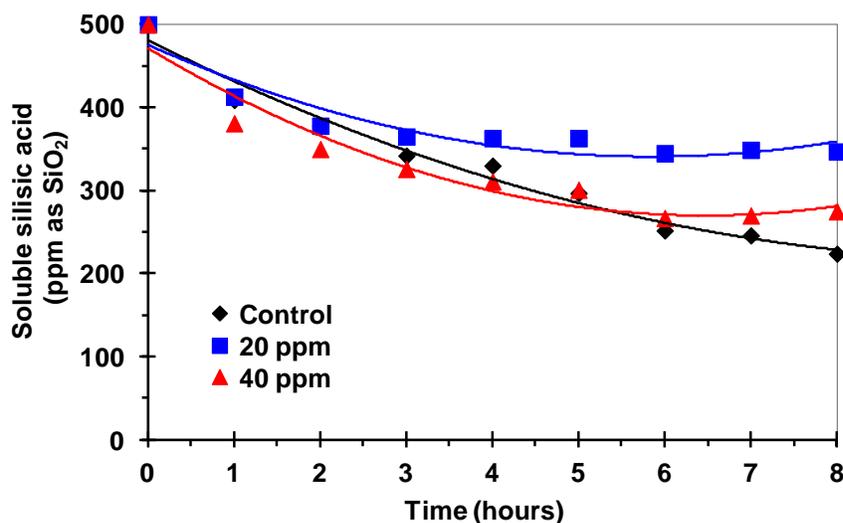
It is important to note, however, that the silicic acid values at all PALAM concentrations and at the three sampling times are consistently higher than those for the control. Moreover, the drop in inhibitory activity as PALAM concentration increases can be explained on the basis of inhibitor entrapment in the forming colloidal silica particles. This has been observed before on several occasions [46, 47] and it is due to the strong hydrogen bonding and ionic interactions between the positively charged PALAM and the negatively charged silica surfaces.

Based on these “long-term” results, we decided to further study the silica inhibition event at its early stages, during the first 8 hours. For this, we selected the PALAM dosages 20 and 40 ppm. These results are presented in Table 2 and plotted in Figure 6.

Silicic acid polymerizes to yield amorphous silica at pH = 7 at a fairly fast rate. For example, in the absence of inhibitors 409 ppm silicic acid remain soluble after the first hour. The effect of inhibitors is not significant during the first hours of silicification, however, it becomes visible after the 4th hour. After 8 hours, the difference in silicic acid levels between the control and the PALAM-containing solutions is obvious. Specifically, at 20 ppm PALAM 123 ppm silicic acid remain soluble, whereas at 40 ppm PALAM 51 ppm silicic acid remain soluble.

Table 2. Silica inhibition measurements with PALAM at concentrations 20 and 40 ppm in short-term experiments (8 hours).

Time (hours)	PALAM concentration (in ppm)		
	Control	20	40
1	409	413	381
2	378	378	330
3	342	355	326
4	330	378	311
5	297	363	301
6	252	345	267
7	246	349	270
8	224	347	275

**Figure 6.** Silica inhibitory activity of PALAM in short-term experiments (8 hours).

Inhibitory activity results of PALAM with co-inhibitors

In the presence of PALAM amorphous “fluffy” silica precipitates are observed. As mentioned above, these are formed due to the ability of the cationic PALAM to coagulate the formed anionic silica particles that is unable to inhibit. In order to “relieve” the excessive polycationic charge that may induce silica flocculation, we thought of using a second anionic polymer, mentioned as the *co-inhibitor*, in hope that it will partially neutralize the positively charged primary amine groups. We evaluated three co-inhibitors,

namely CMI, PAM-*co*-AA, and PCH (their structures are shown in Figure 3). The “long-term” results (3 days) are shown in Table 3 and plotted in Figure 7.

Table 3. Silica inhibition measurements with 20 ppm PALAM and its blend with CMI (20 ppm), PAM-*co*-AA (20 ppm), and PCH (40 ppm).

Time (hours)	Inhibitor Blend Composition				
	control	20 ppm PALAM	20 ppm PALAM + 20 ppm CMI	20 ppm PALAM + 20 ppm PAM- <i>co</i> -AA	20 ppm PALAM + 40 ppm PCH
24	202	336	274	281	326
48	179	286	195	193	254
72	160	246	184	179	238

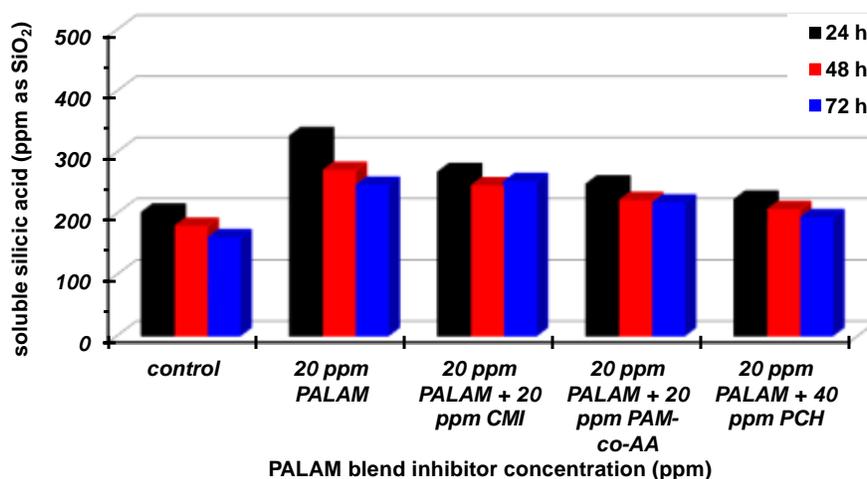


Figure 7. Silica inhibition measurements with 20 ppm PALAM and its blend with CMI (20 ppm), PAM-*co*-AA (20 ppm), and PCH (40 ppm).

Upon testing blends of PALAM in “long-term” experiments (at a constant concentration of 20 ppm) and a variety of anionic co-inhibitors, we observed that the inhibitory activity of PALAM is dramatically affected, but it still is slightly above the “control”. These results prove unequivocally that the amine cationic groups on the PALAM backbone are essential for silica scale inhibition.

As before, we also studied the silica inhibition event during its early stages (8 hours) in the presence of two blends: 20 ppm PALAM + 20 ppm CMI, and 20 ppm PALAM + 60 ppm PCH. These results are given in Table 4 and Figure 8.

These “short-term” results confirm those obtained during the 3-day period (Table 3, Figure 7). CMI (20 ppm) shows a minor effect for the first 4 hours, but this is statistically

insignificant. PCH (60 ppm) induces a profound effect on the inhibitory activity of PALAM, essentially reducing it to the control levels.

Table 4. “Short-term” silica inhibition measurements at a constant PALAM concentration (20 ppm) and its blends with CMI (20 ppm) and PCH (60 ppm).

Time (hours)	Inhibitor Blend Composition			
	control	20 ppm PALAM	20 ppm PALAM + 20 ppm CMI	20 ppm PALAM + 60 ppm PCH
1	409	413	435	413
2	378	378	410	404
3	342	355	393	388
4	330	378	403	370
5	297	363	397	355
6	252	345	378	358
7	246	349	347	356
8	224	347	333	345

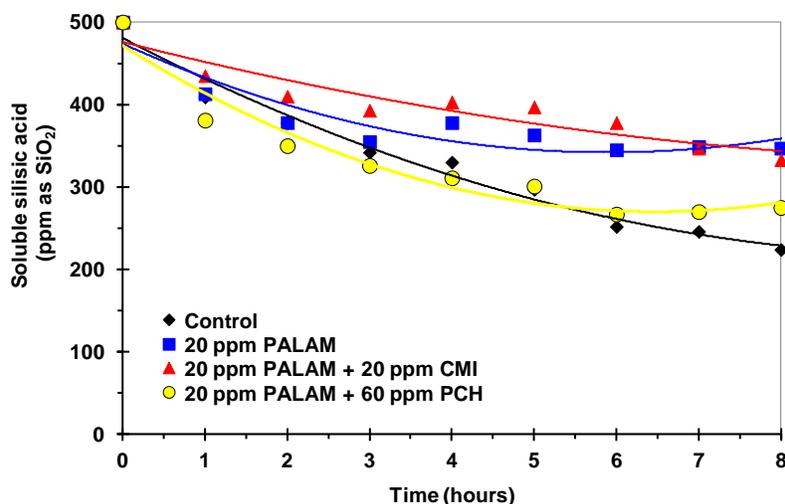


Figure 8. Silica inhibition measurements (8 hours) with PALAM (20 ppm) and blends with CMI (20 ppm) and PCH (60 ppm).

Conclusions

In this paper we reported the inhibitory efficiency of polyallylamine hydrochloride (PALAM) and its multifunctional synergistic mixtures on silica scale formation. The cationic charge on the PALAM backbone appears to be detrimental to its inhibitory activity. In an effort to “relieve” the excessive cationic charge on the PALAM backbone we used

secondary, anionic polymer add-ons (co-inhibitors), such as PAM-co-AA, PCH and CMI. However, it was observed that all these co-inhibitors caused reduction in PALAM inhibitory activity.

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