

The interplay between cationic polyethyleneimine and anionic polyelectrolytes for the control of silica scale formation in process waters

A. Spinthaki, A. Stathoulopoulou and K. D. Demadis*

*Crystal Engineering, Growth and Design Laboratory, Department of Chemistry,
University of Crete, Voutes Campus, Crete, GR-71003, Greece
E-mail: demadis@chemistry.uoc.gr*

Abstract

Stabilization of mono- and disilicic acids is accomplished by using a cationic polymeric chemical additive, polyethyleneimine (PEI), in supersaturated silica solutions (the starting solution contained 500 ppm/8.3 mM sodium orthosilicate, $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, expressed as SiO_2) at $\text{pH} = 7$. The PEI polymeric system contains an excess of amine groups (~25% primary amines, ~50% secondary amines and ~25% tertiary amines) that become protonated at circumneutral pH, hence charging the molecules positively. PEI was found to be efficient as a silica scale inhibitor only at the low dosage of 10 ppm. Its inhibitory activity was found to drop as its concentration increased. It was hypothesized that PEI is entrapped into the colloidal silica matrix and deactivated. Thus, one way to maintain its activity was to create blends of PEI and anionic polymers. Anionic polyelectrolytes that were tested included polyacrylic acid (PAA), phosphonated polyacrylic acid ($\text{PAA}(\text{PO}_3\text{H}_2)_2$), carboxymethylinulin (CMI), poly(acrylamide-co-acrylic acid) (PAM-co-AA), phosphonomethylated chitosan (PCH) are also studied for their silica scale inhibition efficiency. It is observed that the silica inhibitory activity of PEI was improved upon its combination with anionic polyelectrolytes.

Key words: *silicic acid stabilization, water systems, inhibitors, polyethyleneimine, PEI, scale, silica deposits, water treatment.*

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Introduction

Due to its notable heat capacity and cost-effectiveness, water is thought to be the most efficient cooling medium used in industry at a global scale [1]. However, its re-use is commonly obligatory, when operations are installed in arid areas, or substantial savings in water utilization are sought [2]. During its re-use, scaling and deposition can develop due to the high content of dissolved species [3]. The identity of the scale deposits depends on the particular water chemistry [4–8]. Among the water-formed deposits colloidal silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$, n is variable and dependent on hydration), a very persistent precipitate, is

especially troublesome, as it can cause serious materials failure and operational shut-downs, Figure 1 [9–13].



Figure 1. Amorphous silica deposits on industrial equipment. Reproduced from <http://www.chemtexlimited.com>.

Silica scale control can be achieved in two ways: (a) by silica species removal before the silica-laden water enters the operation [14], and (b) by use of chemical additives as silica scale inhibitors [15]. Although traditional scale control methods (inhibition and crystal modification) are amply available for crystalline mineral scale salts [16], analogous strategies do not apply to silica because of its amorphous state [17]. Therefore, much more well-designed inhibition approaches have to be applied for controlling silica formation and deposition.

In this paper we report on the inhibitory efficiency of polyethyleneimine (PEI, Figure 2) in preventing silica formation, by stabilizing silicic acid. The branched PEI that was used in our work contains ~25% primary amines, ~50% secondary amines and ~25% tertiary amines. These moieties are protonated at pH ~ 7. Furthermore, because PEI generates silica-PEI composite precipitates and, thus, becomes entrapped within the silica matrix, it was combined with a variety of anionic polyelectrolytes (Figure 3). It was found that its inhibitory efficiency increased as a result of these synergistic mixtures. This research is part of our on-going investigation on the discovery and application of scale inhibitors in industrial process waters [18–32].

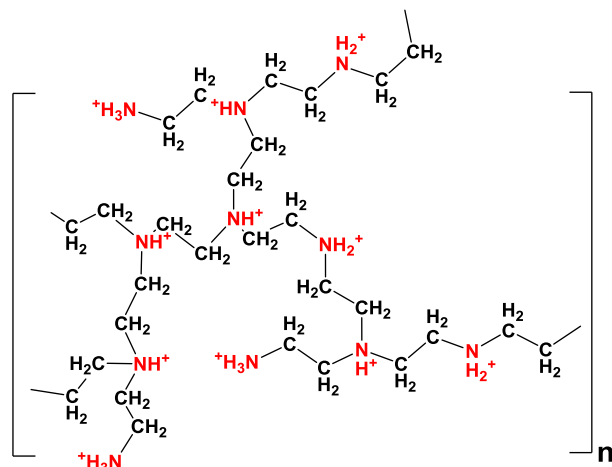
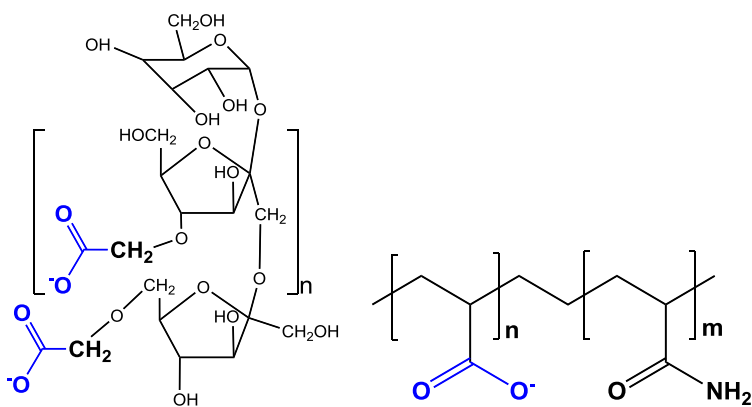
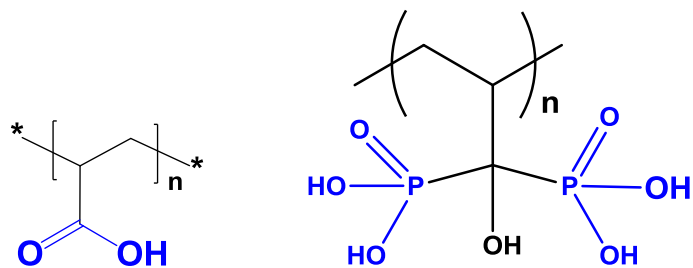


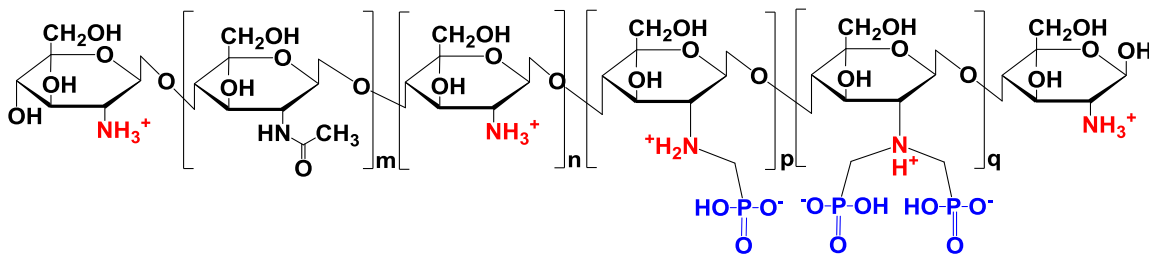
Figure 2. Structure of polyethyleneimine (PEI) in its cationic form, highlighted in red.



Carboxymethylinulin (CMI) Poly(acrylamide-co-acrylic acid) (PAM-co-AA)



Polyacrylic acid (PAA) Phosphonated polyacrylic acid (PAA(PO₃H₂)₂)



Phosphonomethylated chitosan (PCH)

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

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

Reagents and chemicals

Polyethyleneimine (PEI, branched, MW 70 kDa, ~25% primary amines, ~50% secondary amines and ~25% amines) was from Polysciences, USA. PAA and PAM-co-AA was from Aldrich. CMI was a commercial product from ThermPhos, Switzerland. PAA(PO₃H₂)₂ was synthesized by a reaction of PAA with PCl₃/H₃PO₃ in water, as published before [33]. PCH was synthesized according to literature procedures [34]. Sodium silicate pentahydrate, Na₂SiO₃·5H₂O, was purchased from Sigma Aldrich. Ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was obtained from Alfa Aesar and oxalic acid (H₂C₂O₄·2H₂O) 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 and were found to contain negligible amounts.

Preparation of sodium silicate solutions (“stock” solutions)

A solution containing silicate (500 ppm as SiO₂) was prepared by dissolving 4.08 g of Na₂SiO₃·5H₂O 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 (PEI, CMI, PAM-co-AA, PCH) were 1% w/v (10.000 ppm). The following solutions were prepared for the silicomolybdate 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 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 PEI 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 PEI or PEI 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 [35-40]. As in our previous studies [18–32], we used the “yellow molybdate” method (using Spectrophotometer *HACH DR/890*) 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 SiO_2 ”. 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 principle 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

We previously reported some preliminary results on the inhibitory activity of PEI for silica control [26, 28]. PEI showed a peculiar inhibition behavior. Specifically, its inhibitory

activity dropped as its concentration increased. This phenomenon was very intriguing and deserved further study. Hence, the concentration dependence of the inhibition of PEI is presented in Table 1 (3-day experiment duration) and plotted in Figure 4.

Table 1. Silica inhibition measurements with PEI (10, 20, 40, 60 and 80 ppm) in long-term experiments (3 days).

Time (hours)	Control	PEI concentration (in ppm)				
		10	20	40	60	80
24	193	275	224	216	182	186
48	169	210	193	179	164	164
72	160	190	186	173	165	157

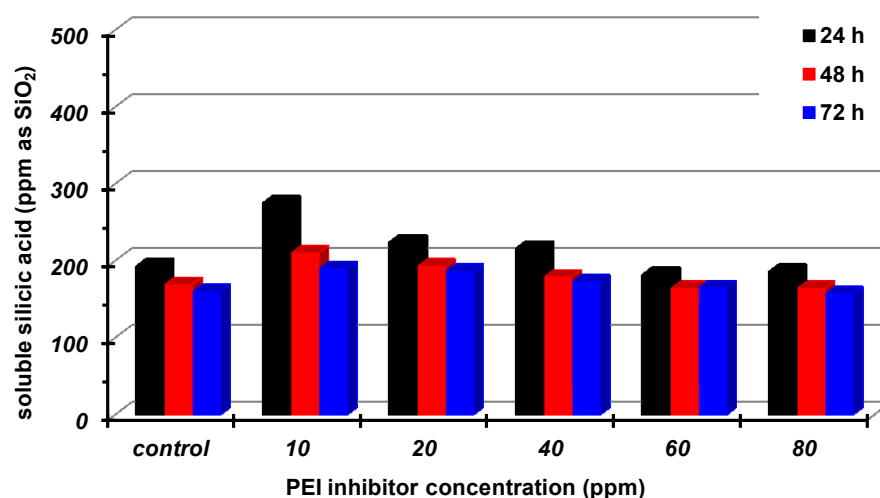


Figure 4. Silica inhibitory activity of PEI in long-term experiments (3 days).

A general observation is that PEI is a “mediocre” silica inhibitor, with its optimum concentration being 10 ppm. As PEI concentration increases, its inhibitory activity is reduced. This confirms our earlier observations [26, 28] and is reminiscent of the behavior of polyallylamine (PALAM) [41]. Silicic acid polymerizes to yield amorphous silica at pH = 7 at a fairly fast rate. In the absence of inhibitors, 193 ppm remain soluble after 24 hours, 169 ppm after 48 h, and 160 ppm after 72 h. PEI was tested at various dosages (at pH = 7) ranging from 10 ppm up to 80 ppm, and it was discovered that the dosage of 10 ppm was the optimum. At this dosage it substantially increases the levels of soluble silicic acid: 275 ppm (after 24 h), 210 ppm (after 48 h) and 190 ppm (after 72 h), see Figure 4.

The optimum concentration of 10 ppm was further studied in “short-term” (8 h) experiments in order to gain further insight into the inhibition event during the first stages. The results are presented in Table 2 (8-hour experiment duration) and plotted in Figure 5. Silicic acid polymerization proceeds gradually in the presence of 10 ppm PEI, however, the drop in soluble silicic acid is consistently above the “control”. It is also important to mention that almost 100 ppm of silica remain soluble above the control after the first 8 hours (Figure 5).

However, in the presence of PEI as inhibitor, turbid solutions are noted. This means that amorphous silica precipitates are present, mixed, perhaps, with PEI polymer. These precipitates form due to the ability of the cationic PEI polymer to coagulate the uninhibited colloidal silica particles. In order to “relieve” the excessive cationic charge, we thought of using a second anionic polymer “add-on”, *co-inhibitor*, in hope that it will partially neutralize the positively charged amine groups of PEI, and thus reduce its excessive cationic charge.

Table 2. Silica inhibition measurements with PEI (10 ppm) in short-term experiments (8 hours).

Time (hours)	PEI concentration (in ppm)	
	control	10
1	466	400
2	419	392
3	377	380
4	323	380
5	323	369
6	275	362
7	257	363
8	243	340

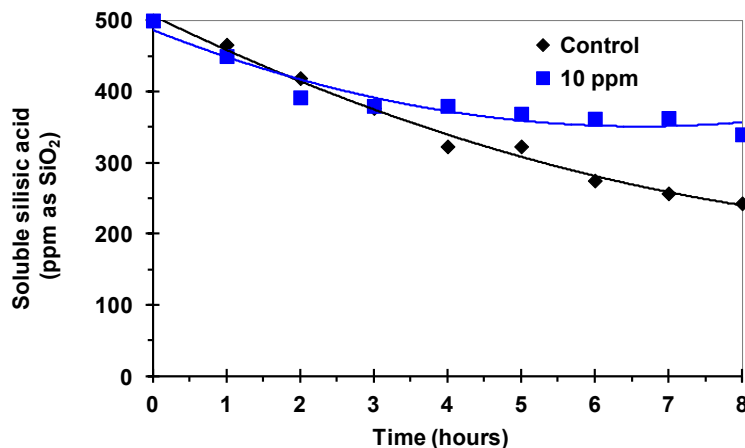


Figure 5. Silica inhibitory activity of PEI (10 ppm) in short-term experiments (8 hours).

The first co-inhibitor that was evaluated was CMI. Inhibitory activity results with PEI (10 ppm) and its blend with CMI (10 ppm) are presented in Table 3 and Figure 6 in long-term experiments (24 h).

Table 3. Silica inhibition measurements in the presence of a synergistic blend of PEI (10 ppm) and CMI (10 ppm).

Time (hours)	Control	Inhibitor Blend Composition	
		10 ppm PEI	10 ppm PEI + 10 ppm CMI
24	182	232	396
48	139	183	235
72	147	149	191

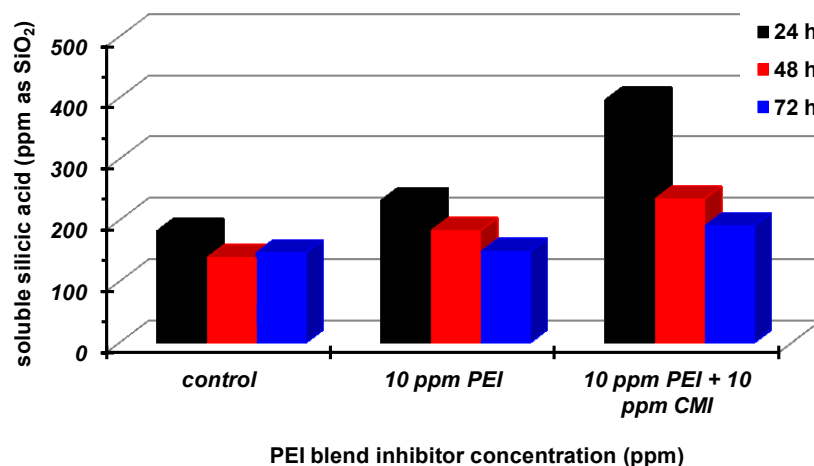


Figure 6. Silica inhibitory activity of 10 ppm PEI and its blend with CMI (10 ppm).

Based on the measurements of Table 3 and Figure 6, it is apparent that CMI exerts an enhancing effect on PEI. Specifically, in the presence of 10 ppm PEI (alone) 50 ppm silicic acid above the “control” are measured after 24 h. Importantly, when 10 ppm CMI are added, 164 ppm silicic acid above that with PEI are recorded (and 214 ppm above the control), after 24 h. This is significant proof that CMI causes solubilization of PEI, and thus, there is no polymer entrapment into the silica matrix. This is corroborated by the absence of silica precipitates.

The inhibitory activity of 10 ppm PEI in combination with CMI (10 ppm) or PCH (40 ppm) was evaluated in short-term experiments (8 h). These results are presented in Table 4 and Figure 7.

Table 4. Silica inhibition measurements in the presence of a synergistic blend of PEI (10 ppm) and CMI (10 ppm), or PCH (40 ppm) in short-term experiments (8 h).

Time (hours)	Control	Inhibitor Blend Composition		
		10 ppm PEI	10 ppm PEI + 10 ppm CMI	10 ppm PEI + 40 ppm PCH
1	448	400	429	408
2	395	392	399	381
3	363	380	424	363
4	318	380	404	362
5	283	369	407	366
6	263	362	378	369
7	243	363	366	363
8	219	340	327	337

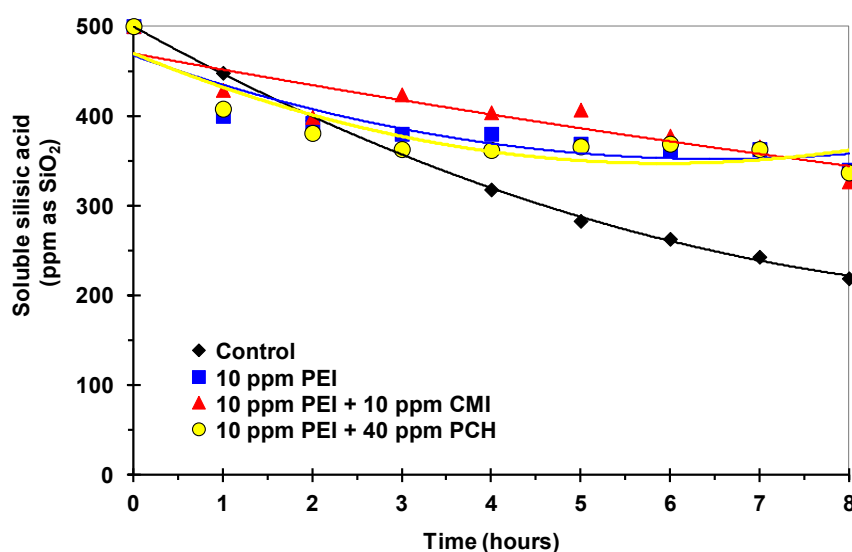


Figure 7. Silica inhibition measurements with 10 ppm PEI and its blends with CMI (10 ppm) or PCH (40 ppm).

Based on these results it is evident that during the first 8 h of the silica inhibition event the inhibitor blends do not offer additional inhibitory enhancement beyond that of PEI alone. Hence, the influence of these co-inhibitors on the activity of PEI takes effect after 8 hours and before 24 hours.

PEI is marginally effective in silica inhibition at 20 ppm concentration, stabilizing only 30 ppm silicic acid beyond the “control”, after 24 h (see Table 1 and Figure 4). Hence, the blends of PEI (at 20 ppm) with various co-inhibitors would be worth-studying. Long-term (3 days) inhibitory activity results of PEI (at 20 ppm) and its synergistic blends with the co-inhibitor “add-ons” PAA(PO_3H_2)₂, PAA (2 kDa), PAM-co-AA, and PCH (all in 20 ppm concentration) additions, are presented in Table 5 and Figure 8. To assist the reader, we have added the silicic acid values on the 24 h bars.

Table 5. Long-term silica inhibition measurements with 20 ppm PEI and its synergistic blends with the co-inhibitors PAA(PO_3H_2)₂, PAA (2 kDa), PAM-co-AA, and PCH.

Time (hours)	Control	Inhibitor Blend Composition				
		20 ppm PEI	20 ppm PEI + 20 ppm PAA(PO_3H_2) ₂	20 ppm PEI + 20 ppm PAA (2 KDa)	20 ppm PEI + 20 ppm PAA-co-AA	20 ppm PEI + 20 ppm PCH
24	193	224	337	452	404	322
48	169	193	243	286	381	246
72	160	186	191	216	329	224

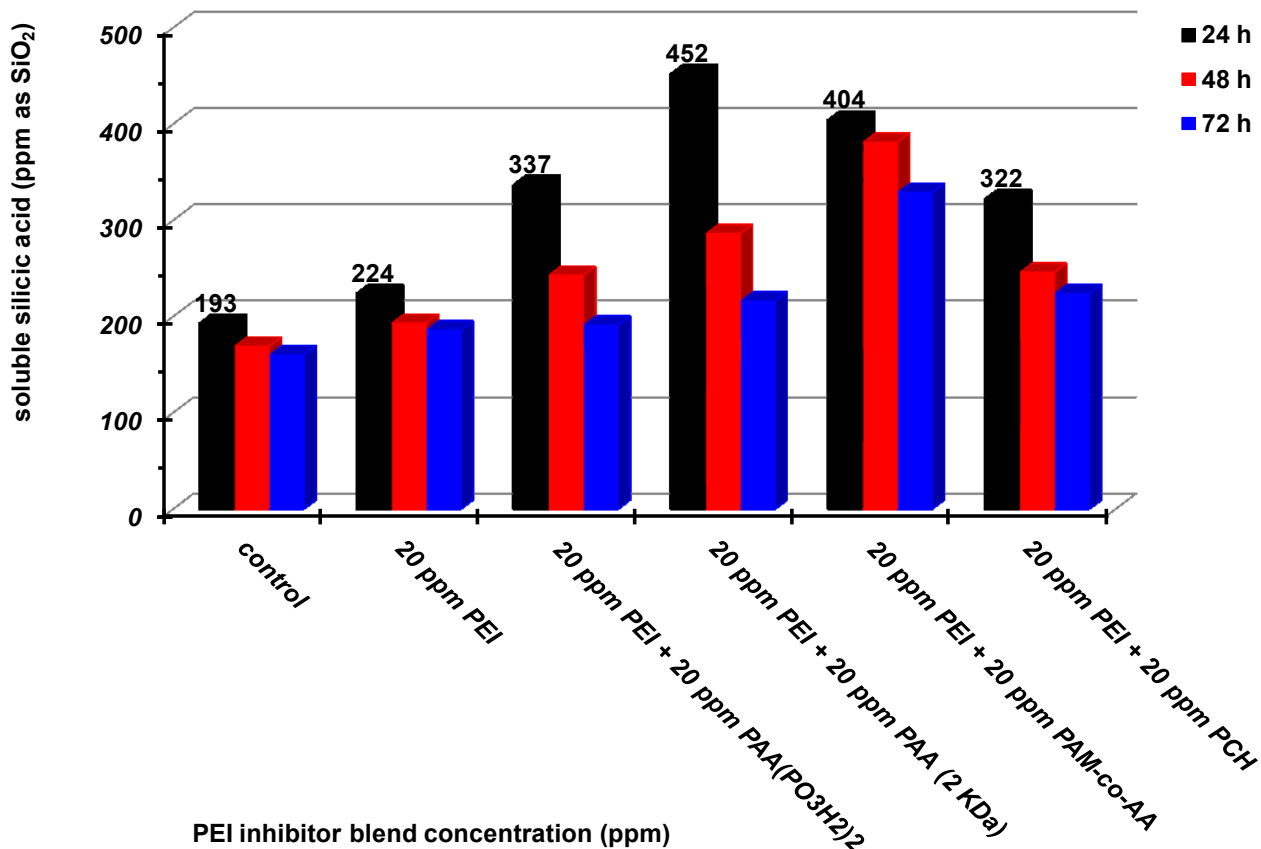


Figure 8. Bar graph with silica inhibition measurements in the presence of PEI (20 ppm) and its synergistic blends with PAA(PO₃H₂)₂, PAA (2 kDa), PAM-co-AA, and PCH (all at 20 ppm).

An important observation is that all co-inhibitors exhibit an enhancement effect on the inhibitory activity of PEI, which is more profound in the 24 h measurements. Specifically, and based on the 24 h results, the following ranking can be put forth for the enhancement effect of the co-inhibitors:

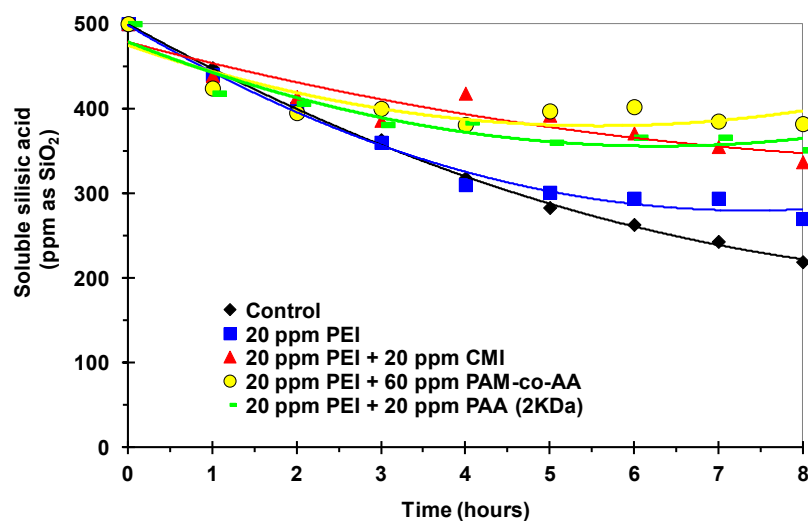
$$\text{PCH} < \text{PAA}(\text{PO}_3\text{H}_2)_2 < \text{PAM-co-AA} < \text{PAA (2 kDa)}$$

It is important to note, however, that PAM-co-AA is able to enhance the inhibitory activity of PEI beyond the 24 h limit. Specifically, the synergistic blend “20 ppm PEI + 20 ppm PAM-co-AA” maintains 381 ppm silicic acid after 48 hours, and 329 ppm silicic acid after 72 hours. Hence, this combination is more suitable for good inhibition results on a longer time scale.

Lastly, we selected the three co-inhibitors PAA (2 kDa) (20 ppm), PAM-co-AA (60 ppm) and CMI (20 ppm) and studied them for their inhibitory enhancement of PEI (20 ppm) in “short-term” experiments (8 hours). These results are presented in Table 6 and Figure 9 in short-term experiments.

Table 6. Silica inhibition measurements with 20 ppm PEI and its blend with PAA (2 kDa) (20 ppm), PAM-co-AA (60 ppm) and CMI (20 ppm).

Time (hours)	Control	Inhibitor Blend Composition			
		20 ppm PEI	20 ppm PEI + 60 ppm PAM-co-AA	20 ppm PEI + 20 ppm PAA (2 kDa)	20 ppm PEI + 20 ppm CMI
1	448	344	439	424	418
2	395	323	414	395	406
3	363	314	386	400	381
4	318	303	418	381	384
5	283	301	392	397	360
6	263	294	371	402	366
7	243	294	355	385	366
8	219	259	337	382	351

**Figure 9.** Silica inhibition measurements with 20 ppm PEI and its blend with PAA (2 kDa) (20 ppm), PAM-co-AA (60 ppm) and CMI (20 ppm).

It becomes evident that the inhibitory enhancement of PEI in the presence of co-inhibitors that was observed in the “long-term” experiments (3-days, Table 5, Figure 8) is confirmed in the “short-term” experiments (8 hours). All three co-inhibitors (PAA (2 kDa), PAM-co-AA and CMI) exert similar enhancement effects, however, PAM-co-AA was added at 60 ppm concentration, whereas the other two, PAA and CMI, were utilized at 20 ppm concentration.

Conclusions/Perspectives

In this paper we reported the inhibitory efficiency of polyethyleneimine (PEI) and its multifunctional synergistic mixtures with anionic polyelectrolytes for the control of silica scale. PEI is proven to be an “acceptable” silica scale inhibitor in 10 ppm addition (Figures 3 and 4). However, the excess of cationic charge causes the formation of precipitates that consist of silica-inhibitor aggregates and clusters. A blend of PEI and CMI (10 ppm each) is proven to be most efficient, stabilizing almost 165 ppm additional silicic acid than that stabilized by PEI alone.

PEI at 20 ppm is marginally effective due to the increase of cationic charge (compared to the 10 ppm dosage) in solution. Again, the extensive cationic charge on the polymer backbone may be detrimental to its inhibitory activity, and this may, in part, be corrected and improved by the use of secondary, anionic polymer add-ons. In this case, PAM-co-AA, CMI and PAA (2KDa) were proven to be the most beneficial for PEI. Synergistic blends with the aforementioned anionic molecules relieve the excess cationic charge and stabilize silicic acid up to 382 ppm (PAA 2kDa 20 ppm) after 8 hours.

The results presented herein strongly support the conclusion that inhibition of silica scale is a demanding task, often requiring “exotic” approaches and strategies. Towards this goal, several other inhibitor molecules are under investigation in our laboratory [42, 43].

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