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Use of antiscalants for mitigation of silica (SiO_2) fouling and deposition: fundamentals and applications in desalination systems

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Abstract

Colloidal silica (SiO_2) is perhaps the most undesirable inorganic deposit formed in process industrial waters, either in bulk or on surfaces, such as membrane heat exchangers or pipelines. Conventional mineral scale inhibitors do not inhibit its formation. Chemical cleaning is difficult and not free from hazards. Research on silica scale formation and prevention is on-going and has led to various chemical approaches. This paper is focused on silica formation, deposition and its inhibition in desalination applications by following designed chemical approaches. More specifically, benchtop screening tests on various silica inhibition chemistries are reported, with emphasis on additives with dendrimeric or polymeric structure and backbone. The inhibition performance of Starburst® polyaminoamide (PAMAM) dendrimers of generations 0.5, 1, 1.5, 2, and 2.5 are investigated in detail. Experimental results show that inhibition efficiency largely depends on structural features of PAMAM's such as generation number and nature of the end groups, as well as dosage levels. Poly(2-ethyl-2-oxazoline) polymers of a variety of molecular weights are also investigated as potential SiO_2 inhibitors. The general scope of silica formation and inhibition in waters relevant to desalination systems is also discussed.

Keywords: Silica fouling; Desalination; Silica inhibition; Dendrimers; Polyethyloxazoline

1. Introduction

Most unsoftened (raw) industrial waters used as feedwaters for reverse osmosis (RO) systems

contain alkaline earth metal cations such as calcium, magnesium, barium, etc. [1,2]. These, particularly calcium, cause enormous problems when combined with polyanions, such as carbonate, phosphate or sulfate, and the solubility

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products of the corresponding salts are exceeded [3]. The major resulting problems are precipitation and deposition of these insoluble mineral salts onto membrane surfaces [4]. Other deposits, although less common, are equally troublesome. These include silica and magnesium silicate (Fig. 1) [5,6]. These phenomena can cause catastrophic operational failures in desalination systems that may lead to costly membrane replacements. Prevention of scale formation is greatly preferred by industrial water users to the more costly, laborious (and potentially hazardous) chemical and mechanical cleaning of the adhered scale, in the aftermath of a scaling event [7].

Scale prevention in principle can be achieved by use of scale inhibitors, key components of any chemical water treatment [8]. These are com-

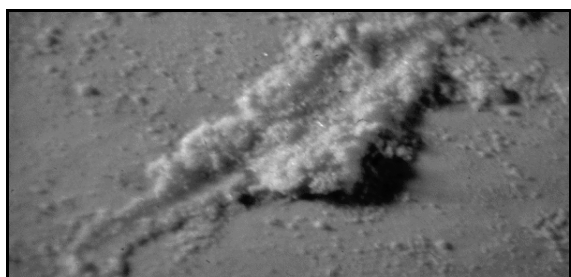


Fig. 1. Silica scale deposit on a RO membrane surface.

pounds (small molecules) that are added to any given treatment in minute (parts per million) quantities and usually work synergistically with dispersant polymers. Popular phosphonates include AMP (amino-*tris*-methylene phosphonic acid), HEDP (1-hydroxyethylidene-1,1-diphosphonic acid), PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid), as well as those that contain a larger number of phosphonate groups [8–13]. Dispersant polymers such as PAA (polyacrylic acid) with its several derivatives are used frequently to disperse water-born scale particles [14]. Unfortunately these traditional scale control methods (inhibition and crystal modification) applied to crystalline mineral salt precipitates do not apply to SiO_2 because it is amorphous.

Silicon is the most abundant element on Earth's crust in the form of several silicon-containing minerals [15,16]. Silica solubility in water is 150–180 ppm (as SiO_2) depending on the specifics of water chemistry. Levels frequently encountered in natural waters are in the range of 1–30 ppm, in well waters 20–100 ppm and in brackish waters in excess of 1000 ppm [17]. High silica levels often lead to undesirable silica formation and deposition in water systems. Silica has been named the “Gordian Knot” of water treatment due to the

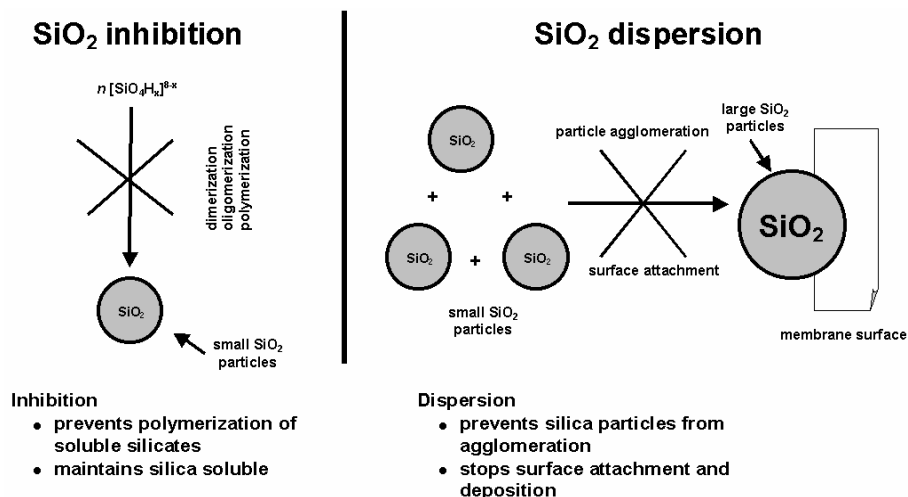


Fig. 2. Approaches to controlling silica precipitation and deposition by use of chemical additives.

unconventional methods one must resort to, in order to effectively mitigate silica fouling [18,19].

Inhibition and dispersion are two general methods of preventing scale and fouling. Inhibition stops scale crystals or particles from forming, whereas dispersion keeps scale particles from being attached onto membrane surfaces. The two are schematically shown in Fig. 2 and refer to silica scale formation and deposition.

This paper focuses on silica formation and membrane surface fouling and their inhibition/control by using treatment additives that possess either dendritic or polymeric structure. Attention will also be given on the design of this inhibition approach with the ultimate goal to produce tailor-made inhibitors according to the individual scale characteristics.

2. Experimental

2.1. Instruments

IR spectra were recorded on a FT-IR Perkin – Elmer FT 1760. The measurements of soluble silica (SiO_2) made with a HACH 890 spectrophotometer.

2.2. Reagents

Sodium silicate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ was from EM Science (Merck). PAMAM dendrimers generations 0.5–1.0–1.5–2.0–2.5 were from Aldrich Chemical Co. (Milwaukee, Wisconsin, USA) as 20% w/v solutions in methanol, except PAMAM 2.5 that is 10% w/v in methanol. PAMAM's are available under the commercial name Starburst® polymers. Poly(2-ethyl-2-oxazoline) (commercial name Aquazol) polymers were obtained from Polymer Chemistry Innovations Inc. in molecular weights of 5,000, 50,000, 200,000 and 500,000 Daltons. 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, hydrochloric acid 37% was from Riedel de Haen. Potassium bromide (KBr) for

preparation of the IR discs was from Fluka. Acrodisc filters (0.45 μ) were from Pall-Gelman Corporation. In-house, nanopure water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts.

2.3. Solution preparation

A solution containing 500 ppm SiO_2 was prepared by dissolving 4.4 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in 2.5 L nanopure water. 1% (10,000 ppm) stock solutions of the inhibitors in water were also prepared by making the appropriate dilution with nanopure water in case the inhibitor was in solution, or by dissolving 0.1 g of the solid inhibitors in 10 mL nanopure water. The following solutions were prepared for the silica analytical test. (a) 10 g of ammonium molybdate was dissolved in 100 mL water and pH was adjusted between 7–8 with NaOH to avoid its precipitation. (b) HCl 1+1 is prepared by mixing one volume 37% HCl with equal volume water. (c) 8.75 g of oxalic acid was dissolved in 100 mL water. All solutions were kept in polyethylene containers (glass containers must be avoided in order to minimize SiO_2 leaching).

3. Experimental screening protocol

3.1. Control test

100 mL from the 500 ppm SiO_2 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 adjusted to 7.00 ± 0.1 by addition of HCl and NaOH (the change in the resulting volume was about 3%). Then the beaker was covered with plastic membrane and set aside without stirring. The solution was checked for the soluble silica by silicomolybdate method every two hours for the first twelve hours or after 24, 48, 72 h time intervals after the pH reduction to 7.00.

3.2. Inhibitor performance test

100 mL portions of the 500 ppm SiO_2 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. These ranged from 20–40–60–80 ppm and the volumes added were 200–400–600–800 μL .

3.3. Determination of soluble (reactive) SiO_2

All soluble silica measurements are expressed as ppm SiO_2 . Soluble silica was measured using the silico-molybdate spectrophotometric method [20]. According to this method 2 mL filtered sample, with 0.45 μm syringe filter, from the test solution is diluted to 25 mL in the cell, with 1 cm light path. 1 mL ammonium molybdate stock solution and 0.5 mL 1 + 1 HCl are added to the sample cell, the solution is mixed well and left undisturbed for 10 min. Then 1 mL oxalic acid solution is added and mixed again. The solution is set aside for 2 min. After the second time period the spectrophotometer is set at zero absorbance with water as the blank. Finally the sample absorbance is measured at 452 nm as “ppm soluble silica”. The detectable concentrations range is 0–75.0 ppm. In order to calculate the concentration in the original solution the appropriate 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 (about 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. This term includes not only the monomer silicate ion but also oligomeric species such as dimmers, trimers, tetramers, etc. The exact number of reactive units is not known.

4. Results and discussion

4.1. Formation of colloidal silica: general scope

Silica scale formation is a serious problem in waters with high dissolved silica content, used for industrial applications [21,22]. In certain areas of the world, such as the Pacific Rim, Latin America, Texas, New Mexico, South Europe and others, the water used for industrial applications contains high amounts of silica (50–100 ppm, as SiO_2). Silica solubility in water has been measured to be 150–180 ppm, depending on the dissolved species and temperature [15,16]. This imposes severe limits to water users and forces them to either (a) operate at very low cycles of concentration (in the case of open recirculating cooling systems), thus consuming enormous amounts of water, or (b) use chemical water treatment techniques in order to prevent silica scale formation and deposition. It is worth noting that silica and/or silicate deposits are particularly difficult to remove once they form. Harsh chemical cleaning (with hydrofluoric acid) or mechanical removal, are usually required [23–25].

Silica scale formation is favored at $\text{pH} < 8.5$, whereas magnesium silicate scale forms at $\text{pH} > 8.5$ in waters with high Mg^{2+} levels. Silica has “normal” solubility, in contrast with the “inverse” solubility of magnesium silicate [26–28]. Formation of the latter is more pronounced at higher temperatures. When silicate ion polymerizes, it forms a plethora of structural motifs: rings of various sizes, cross-linked polymeric chains of different molecular weights, oligo-meric structures, etc. [29]. The resulting “silica scale” is a complex and amorphous product (colloidal silica), which in fact is a complicated mixture of numerous components, linked randomly through Si–O–Si bonds.

Silica scale prevention can be achieved principally in three ways: (1) by silica removal from make-up water by “hot-lime softening” (precipitation with $\text{Mg}(\text{OH})_2$ or MgCl_2 , followed by filtration) [30,31], (2) by inhibition (retardation or elimination of colloidal silica formation) [32–

34], and (3) by dispersion (elimination of surface attachment of “larger” silica colloids) [35–37]. Inhibition and dispersion are shown schematically in Fig. 2.

This paper focuses on inhibition of silica formation by oligomeric molecules that have a dendritic structure and by polymeric inhibitors. Magnesium silicate scale formation and inhibition are beyond the scope of this article, but will be the subject of a future publication.

4.2. Silica scale control by use of dendrimers

Dendrimers are well-defined globular macromolecules constructed around a core unit. The term dendrimer derives from the Greek words “δένδρον” (déndron, meaning “tree”) and “μέροϛ” (méros, meaning “part”) and was first coined by Tomalia [38–45]. He also pioneered the elegant synthesis of the polyaminoamide PAMAM dendrimers, which were given the name “starburst polymers” [46,47]. This divergent synthetic strategy involves the growth of success-

ive generations of a dendrimer radially outward from a central core. As the dendrimer grows larger, the end-groups on the surface of the globule become more densely packed and eventually the dendrimer reaches its upper generation limit because of steric hindrance. This phenomenon is known as the “starburst effect” or “de Gennes dense packing” after Pierre-Gilles de Gennes, the French 1991 Nobel Laureate physicist who first discovered it.

This synthetic approach has generated the polyaminoamide (PAMAM) dendrimers. A representative schematic structure of PAMAM (Generation 1.5) is shown in Fig. 3. It was only recently discovered that PAMAM dendrimers form stable interior molecular nanocomposites with metal cations, zero-valent metals, other electrophilic ligands, and semiconductor particles. These materials are actively being investigated in electronics, optoelectronics and catalysis [48].

In summary, numerous research groups internationally focus their efforts on applying dendrimer chemistry in a plethora of technological

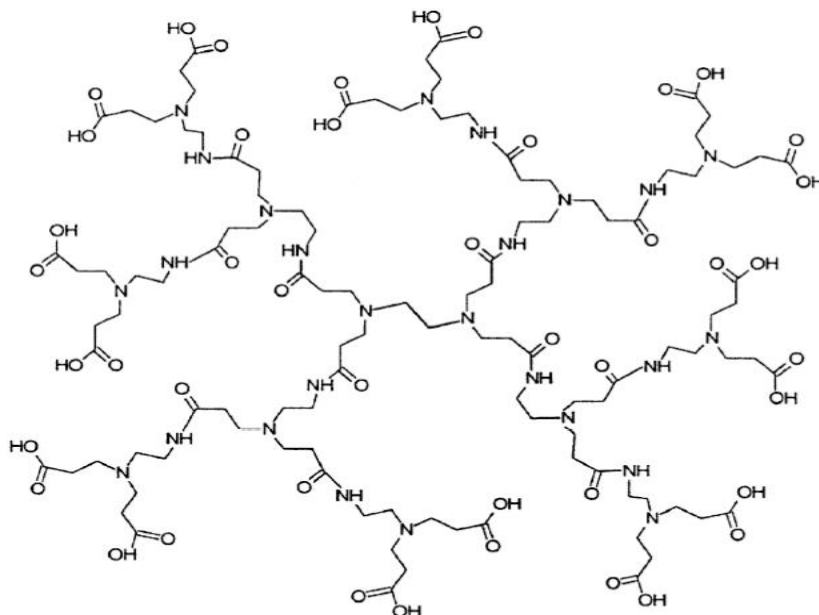


Fig. 3. Schematic structure of PAMAM (Generation 1.5) with 16 –COOH terminal surface groups.

applications. Our research efforts are targeted at developing new technologies for chemical water treatment in the industrial water treatment field. We have studied a novel application of PAMAM dendrimers as inhibitors of silica scale in silica-rich waters.

PAMAM dendrimers are supplied under the commercial trademark Starburst® polymers and offered in two kinds: COOH-terminated (generations 0.5, 1.5, 2.5) and NH₂-terminated (generations 1 and 2). Various dendrimer levels were tested in SiO₂ inhibition experiments. These were 20, 40, 60 and 80 ppm (measured as actives). In Table 1 and Fig. 4 results are presented at 40 ppm dendrimer, whereas the soluble SiO₂ is measured every 2 h for a total period of 12 h. A noticeable drop in soluble SiO₂ from 500 to 385 ppm occurs after 2 h for the control experiment (no additives present). The initial abrupt drop becomes less pronounced as shown in Fig. 4 and eventually 168 ppm of SiO₂ remain soluble. Addition of 40 ppm of dendrimers PAMAM-0.5 and -1.5 have essentially no retarding effect in SiO₂ polymerization. PAMAM-2.5 exhibits low inhibiting efficiency, eventually allowing 191 ppm of SiO₂ to remain soluble, a 23 ppm advantage over the control. PAMAM-0.5, -1.5 and -2.5 have all anionic dendrimers and are (at least) partially deprotonated –COOH groups at the pH of study. In general, anionic inhibitors show virtually no inhibiting

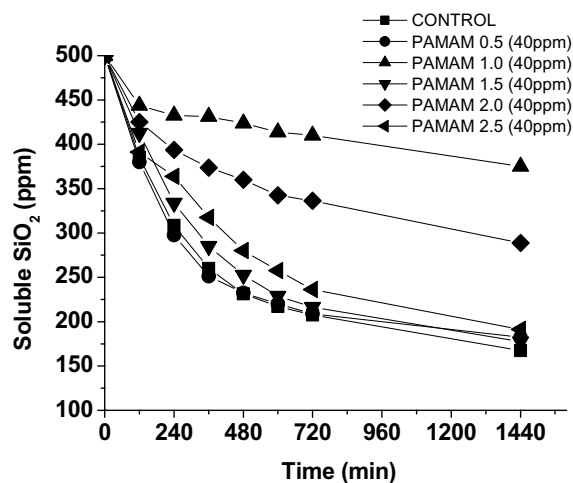


Fig. 4. Solubility enhancement of SiO₂ by PAMAM dendrimers of various generations.

performance in SiO₂ polymerization probably due to charge repulsion between the anionic charges of the inhibitor itself and the negatively charged silicate anions or SiO₂ particles.

In contrast to the above results obtained with the –COOH terminated dendrimers, when PAMAM-1.0 or PAMAM-2.0 are present SiO₂ polymerization is inhibited much more efficiently. More specifically, PAMAM-2.0 shows superior performance compared to the control even at the first stages of the experiment allowing 425 ppm of SiO₂ to remain soluble. The drop in soluble

Table 1
Silica inhibition by PAMAM dendrimers at 40 ppm dosage levels in 12 h

Time (min)	Soluble SiO ₂ (ppm)					
	Control (no inhibitor)	PAMAM-0.5	PAMAM-1.0	PAMAM-1.5	PAMAM-2.0	PAMAM-2.5
0	500	500	500	500	500	500
120	385	380	444	413	425	391
240	309	298	433	334	390	364
360	260	251	431	285	374	318
480	231	233	424	253	360	280
600	215	220	414	229	343	258
720	208	209	410	216	336	236
1440	168	183	375	178	289	191

SiO₂ is much less abrupt, an indication that the retarding effect is more enhanced. Eventually, 289 ppm of SiO₂ remain soluble after 24 h, 121 ppm higher than the control.

PAMAM-1.0 is an even more effective inhibitor than PAMAM-2.0. The drop in soluble SiO₂ is significantly delayed and also the final measured soluble SiO₂ (375 ppm) after 12 h is much higher than that with PAMAM-2.0 present (289 ppm) or without any additives present (168 ppm).

The effect of inhibitor dosage level on SiO₂ scale growth was also studied. We have performed experiments where the inhibitor dosage was varied from 20 to 80 ppm and the soluble SiO₂ was measured after 24, 48 and 72 h. From the carboxylate-terminated PAMAMs, only those results with PAMAM-0.5 are presented in Table 2 and Fig. 5. Because of the similarity in behavior of the other carboxylate-terminated PAMAMs the

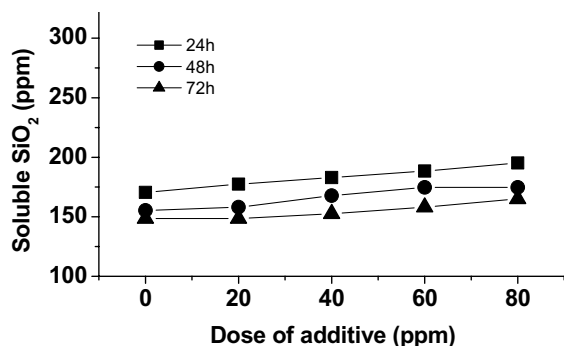


Fig. 5. Solubility dependence of SiO₂ on PAMAM-0.5 dendrimer dosage.

results related to their Dose-Response are not presented here.

At 20 ppm dosage PAMAM-0.5 is ineffective in inhibiting SiO₂ polymerization. Those results are comparable to the control. At 40 ppm dosage the inhibition efficiency is slightly improved. Similar marginal improvement is observed at inhibitor dosage of 60 ppm. Finally, at a dosage of 80 ppm, 195, 175 and 165 ppm soluble SiO₂ are measured in 24, 48 and 72 h, respectively. It is interesting to note that by increasing inhibitor level, soluble SiO₂ is also increased, albeit marginally.

The behavior of the NH₂-terminated dendrimers PAMAM-1.0 and -2.0 was investigated in detail. The results obtained from the dosage dependence of PAMAM-1.0 are presented in Table 3 and Fig. 6. At 20 ppm dosage PAMAM-1.0 is able to partially inhibit SiO₂ formation after 24 h, but its inhibiting ability diminishes after 48 and 72 h, with soluble SiO₂ values indistinguishable from the control. Dramatic changes are observed when 40 ppm of PAMAM-1.0 are present in solution. SiO₂ is strongly inhibited after 24 h, with 384 ppm of it remaining soluble. As time passes, soluble SiO₂ continues to drop but still remains high (336 ppm and 308 ppm after 48 and 72 h, respectively), much higher than the control (147 ppm after 72 h).

At higher inhibitor dosage, 60 ppm, the results present interesting features. After 24 h soluble SiO₂ is 363 ppm, a value slightly lower than the corresponding one at 40 ppm inhibitor dosage. Soluble SiO₂ continues to drop at a higher rate

Table 2

Dose–response relationship for SiO₂ Inhibition by dendrimer PAMAM-0.5

Time (h)	Soluble SiO ₂ (ppm)				
	Control (no inhibitor)	20 ppm PAMAM-0.5	40 ppm PAMAM-0.5	60 ppm PAMAM-0.5	80 ppm PAMAM-0.5
24	171	177	183	188	195
48	155	158	168	175	175
72	149	149	153	158	165

Table 3
Dose–response relationship for SiO₂ inhibition by dendrimer PAMAM-1.0

Time (h)	Soluble SiO ₂ (ppm)				
	Control (no inhibitor)	20 ppm PAMAM-1.0	40 ppm PAMAM-1.0	60 ppm PAMAM-1.0	80 ppm PAMAM-1.0
24	169	208	384	363	342
48	153	154	336	304	283
72	147	143	308	264	253

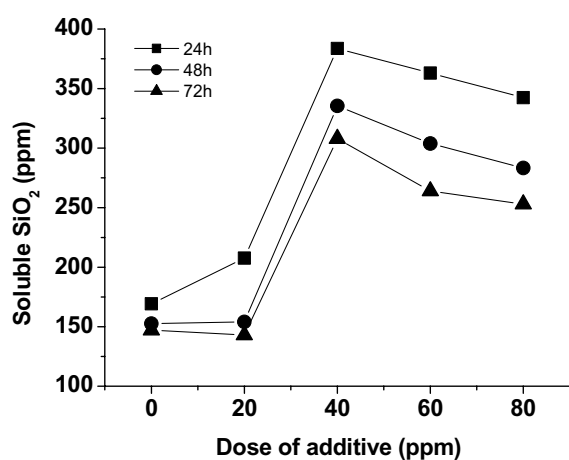


Fig. 6. Solubility dependence of SiO₂ on PAMAM-1.0 dendrimer dosage.

(304 ppm and 264 ppm after 48 and 72 h, respectively), compare to the rate of SiO₂ growth at 40 ppm inhibitor dosage. A similar trend is observed when 80 ppm of PAMAM-1.0 are added, with the difference that soluble SiO₂ values are even lower compared to the 60 ppm inhibitor dosage. This is clearly seen in Fig. 6.

The dependence of SiO₂ inhibiting performance on PAMAM-2.0 dendrimer dosage is presented in Table 4 and Fig. 7. Again, at 20 ppm dosage PAMAM-2.0 can only marginally inhibit SiO₂ growth and only within the first 24 h. At later times, its performance at 20 ppm deteriorates and is essentially indistinguishable from the control. When 40 ppm inhibitor are present there is a “jump” in performance, with 374, 341 and 293 ppm at 24, 48 and 72 h, respectively).

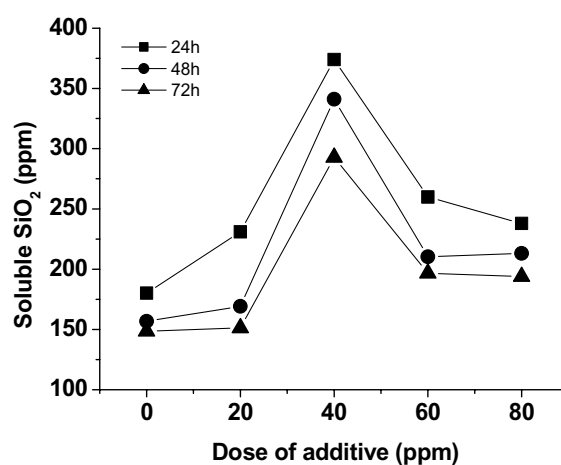


Fig. 7. Solubility dependence of SiO₂ on PAMAM-2.0 dendrimer dosage.

Increasing PAMAM-2.0 dosage to 60 ppm appears to have an adverse effect on its inhibiting ability. Only 260 ppm soluble SiO₂ are measured at 24 h, a 114 ppm difference from the analogous measurement with 40 ppm inhibitor present. A similar phenomenon is observed at 80 ppm dosage. It is important to note that in general all soluble SiO₂ measurements done with PAMAM-2.0 as inhibitor are lower than those done with PAMAM-1.0 as inhibitor (see Tables 3 and 4 and Figs. 6 and 7).

The downward trend in soluble SiO₂ values as added PAMAM-1.0 or -2.0 inhibitor levels increase beyond the 40 ppm level is at first look somewhat unexpected and in contrast with observations noted with the COOH-terminated PAMAM's (Table 2 and Fig. 5). A possible explanation certainly lies with the nature of the

Table 4
Dose–response relationship for SiO₂ inhibition by dendrimer PAMAM-2.0

Time (h)	Soluble SiO ₂ (ppm)				
	Control (no inhibitor)	20 ppm PAMAM-2.0	40 ppm PAMAM-2.0	60 ppm PAMAM-2.0	80 ppm PAMAM-2.0
24	180	231	374	260	238
48	157	169	341	210	213
72	149	151	293	197	194

dendrimer terminal groups. Both PAMAM-1.0 and -2.0 are NH₂-terminated dendrimers. These external groups can be protonated at the experimental pH, thus creating positive surface charge and rendering the dendrimer positively charged. It is this “form” of the dendrimer that interacts with soluble SiO₂ and associates with it in a such way that SiO₂ growth is inhibited.

4.3. Silica scale control by use of poly(2-ethyl-2-oxazoline) polymers

The experiments carried out with the PAMAM dendrimers as inhibitors prompted us to consider other macromolecules that possess similar structural features to the dendrimers (eg. amide bonds), but are more cost effective. We resorted to polymers called poly(2-ethyl-2-oxazolines) (commercial name Aquazols), Fig. 8 [49]. They will be referred to polyethyloxazolines from now on for simplicity.

Polyethyloxazolines are available in molecular weights 5,000, 50,000, 200,000 and 500,000. The inhibition test followed was exactly the same as

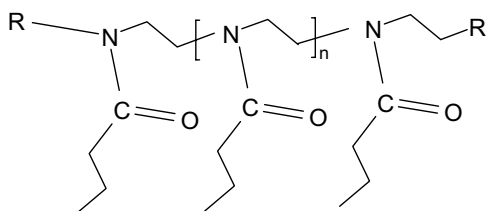


Fig. 8. Schematic structure of polyethyloxazoline (Aquazol) polymers.

that used for the dendrimers. In Table 5 and Fig. 9 inhibition results are presented with polymer dosage of 40 ppm. All polymers show good inhibition results with Aquazol 5 being the least effective. It appears that all the other Aquazol's exhibit very similar inhibition properties that are independent of their molecular weight.

The dependence of SiO₂ inhibition on polyethyloxazoline polymer dosage level was also studied and the results are collectively presented in Table 6 and Fig. 10. Certain features in Fig. 10a–d are worthy of further discussion. First, the dose–response relationship is “normal”, in contrast to the dendrimer inhibition behavior. This means that as inhibitor dosage increases, inhibition efficiency improves as well. At 20 ppm inhibitor

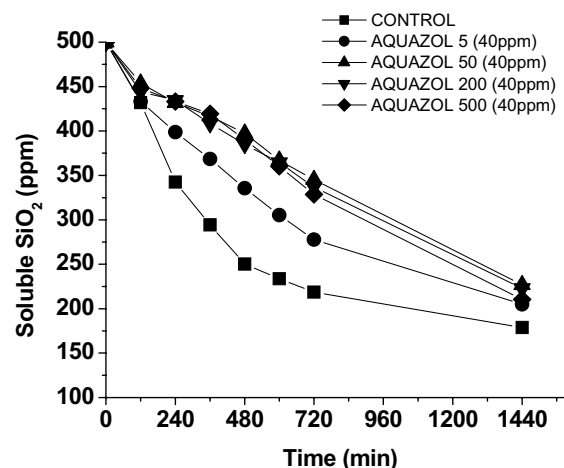


Fig. 9. Solubility enhancement of SiO₂ by polyethyloxazoline polymers at 40 ppm dosage levels in 12 h.

Table 5
SiO₂ inhibition by polyethyloxazoline polymers at 40 ppm dosage levels in 12 h

Time (min)	Soluble SiO ₂ (ppm)				
	Control (no inhibitor)	Aquazol 5	Aquazol 50	Aquazol 200	Aquazol 500
0	500	500	500	500	500
120	432	433	454	444	448
240	342	399	432	435	436
360	294	369	417	408	419
480	250	336	397	385	391
600	234	305	367	364	360
720	219	278	345	337	329
1440	179	205	227	223	210

Table 6
SiO₂ Inhibition by polyethyloxazoline polymers at various dosage levels in 24, 48 and 72 h

Inhibitor	Dosage level (ppm)	Time of measurement		
		24 h	48 h	72 h
Aquazol 5	0	171	151	150
	20	182	161	146
	40	212	172	160
	60	271	186	171
	80	314	208	180
Aquazol 50	0	161	150	142
	20	177	155	144
	40	195	158	154
	60	245	169	160
	80	267	188	171
Aquazol 200	0	171	150	143
	20	180	157	146
	40	204	158	151
	60	272	179	169
	80	304	191	173
Aquazol 500	0	172	154	155
	20	173	150	149
	40	208	164	153
	60	259	180	160
	80	286	191	173

dosage inhibition efficiency is low, barely higher than the control.

At 40 ppm dosage all polymers improve in retarding SiO₂ growth at 24 h. This tendency is more evident than 60 ppm inhibitor are present.

There appears to be a “jump” in inhibitor performance at this level. At 80 ppm inhibitor level there is even better SiO₂ inhibition, with Aquazol 5 being more efficient than the others. All inhibitors show markedly decreased efficiency after 48 h and maintain SiO₂ soluble at levels higher than the control, but much lower than those at 24 h. It should be noted that after 72 h the soluble SiO₂ levels are essentially similar to those measured at 48 h. This means that the inhibitor efficiency albeit reduced, is still maintained.

4.4. Silica-PAMAM composite precipitates

In solutions containing NH₂-terminated PAMAM's (1 and 2) small amounts of flocculant precipitate forms after ~24 h of polymerization. Chemical analysis of the composite showed that it is mainly silica (>90%). Fig. 11 shows a SEM image and the EDS spectrum of that composite material. The amor-phous nature of the deposit is evident based on visual observations from the SEM image as well as the XRD spectrum shown in Fig. 12. FT-IR spectroscopy showed presence of silica (several characteristic bands) [50,51], but also presence of the PAMAM dendrimers (the amide $\nu(\text{C}=\text{O})$ appears at 1645 cm⁻¹). Spectral assignments are found in Table 7. Two representative spectra are shown in Fig. 13 in a comparative manner.

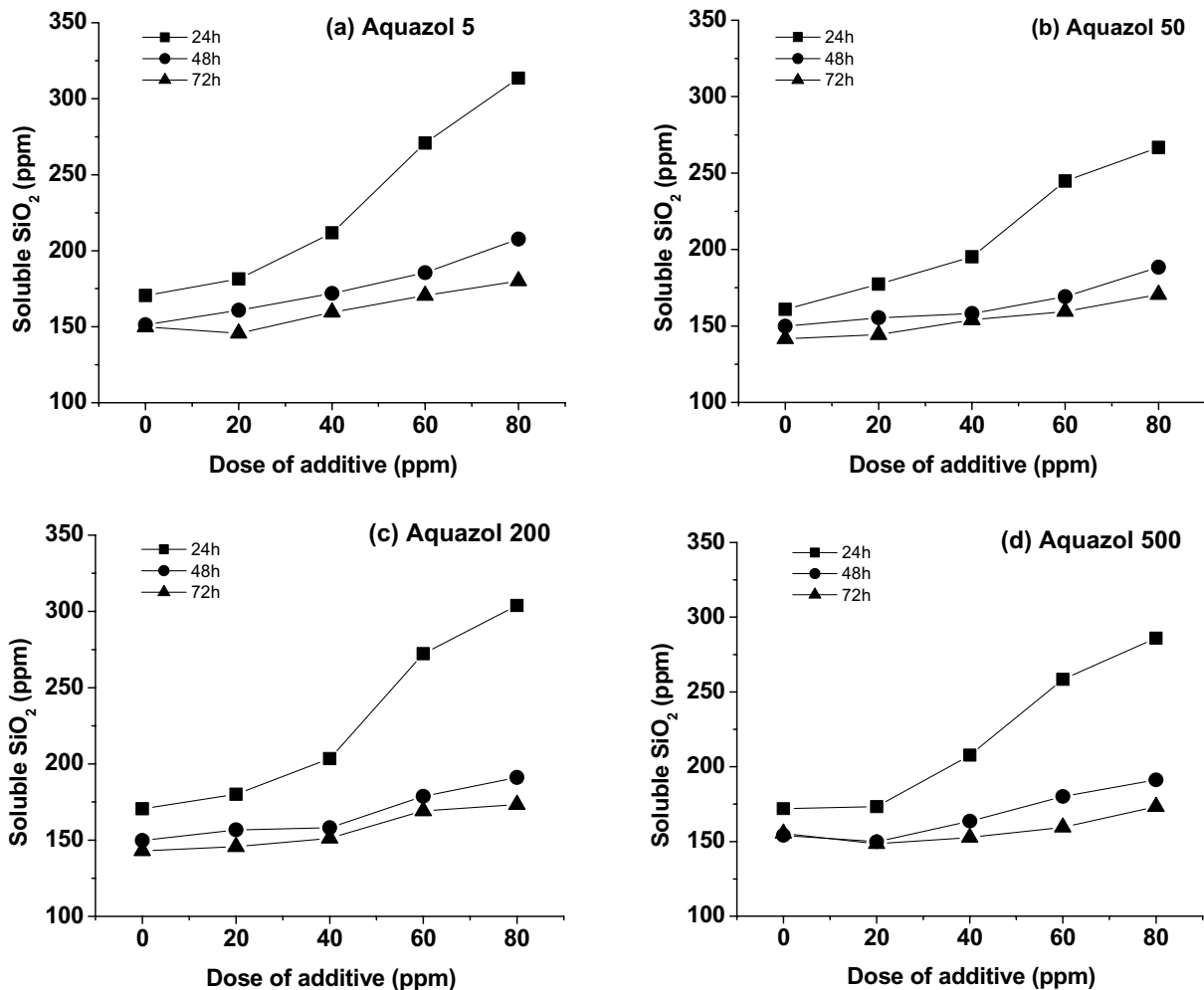


Fig. 10. Solubility dependence of SiO₂ on Aquazol-5 (a), 50 (b), 200 (c), and 500 (d) polymer dosage.

Colloidal SiO₂ alone shows a limited number of bands, as shown in Table 7. The spectra of SiO₂-PAMAM composite precipitates in Fig. 13 show additional bands associated with the presence of the dendrimer in the composite. A reliable comparison can be made with the spectra of the PAMAM dendrimers that are also shown in Fig. 13. Formation of these composite precipitates can be prevented by addition of copolymers based on a polyacrylate backbone. Such results will be published in due course.

4.5. Mechanism of silica inhibition

Amorphous silica formation is governed by several equilibria [52]. Silica deposition results from silicic acid self-condensation. This reaction is first-order and is catalyzed by OH⁻ in the pH range of 5–10. It has been reported that the reaction yielding a silicic acid dimer is kinetically slow, in contrast to the reaction giving trimer, tetramer, pentamer, etc., which are very fast. All these equilibria are very sensitive to pH and tend to be accelerated by metal ions that form hydroxides, e.g. Fe²⁺, Mg²⁺ or Al³⁺ [53].

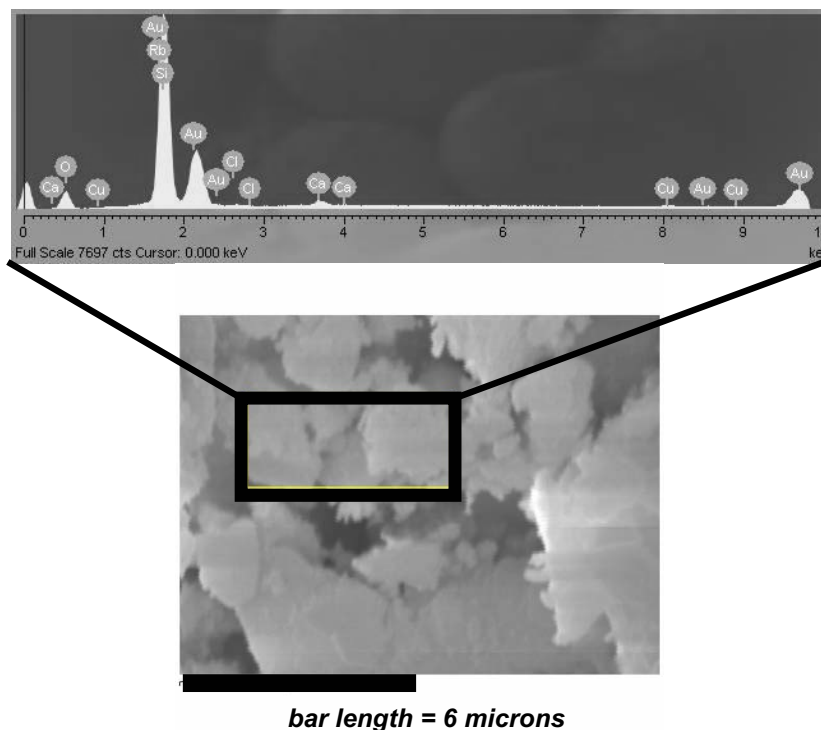


Fig. 11. SEM image of a SiO_2 -PAMAM-2 precipitate (lower) and EDS spectrum of the area in the box (upper) The EDS spectrum shows dominant presence of Si and O originating from SiO_2 with insignificant amounts of impurities and filming elements (e.g. Au) also being present.

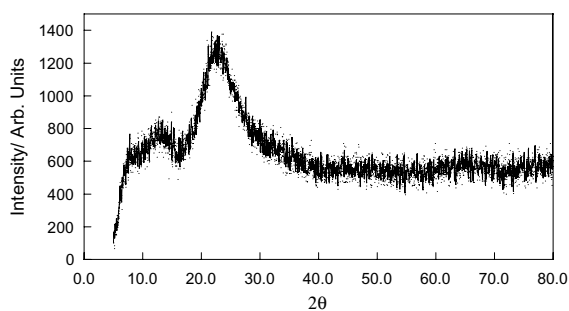


Fig. 12. X-ray powder pattern spectrum of a SiO_2 -PAMAM-2 precipitate showing its amorphous character.

Polymerization of silicic acid is believed to occur through a SN_2 mechanism involving a deprotonated Si-O^- and the Si center of $\text{Si}(\text{OH})_4$. Inhibition of this step should be critical in inhibiting silica scale formation. There are reports

Table 7

Band assignments in the infrared spectrum of a SiO_2 -PAMAM-2 precipitate

Vibrations (cm^{-1})	Band assignments
3600–3300	Water stretching bands + ν (O–H) from Si–OH
3000–2800	N–H ($-\text{NH}_3^+$ from PAMAM 2)
1645	Symmetric $\nu(\text{C}=\text{O})$ from amide bonds
1630	H_2O deformation
1434	Asymmetric $\nu(\text{C}=\text{O})$ from amide bonds
1210	Asymmetric stretching Si–O and Si–O–(Si)
1100	Asymmetric stretching Si–O and Si–O–(Si)
956	Si-O^- asymmetric
788	Si-O^- symmetric
464	O–Si–O deformation

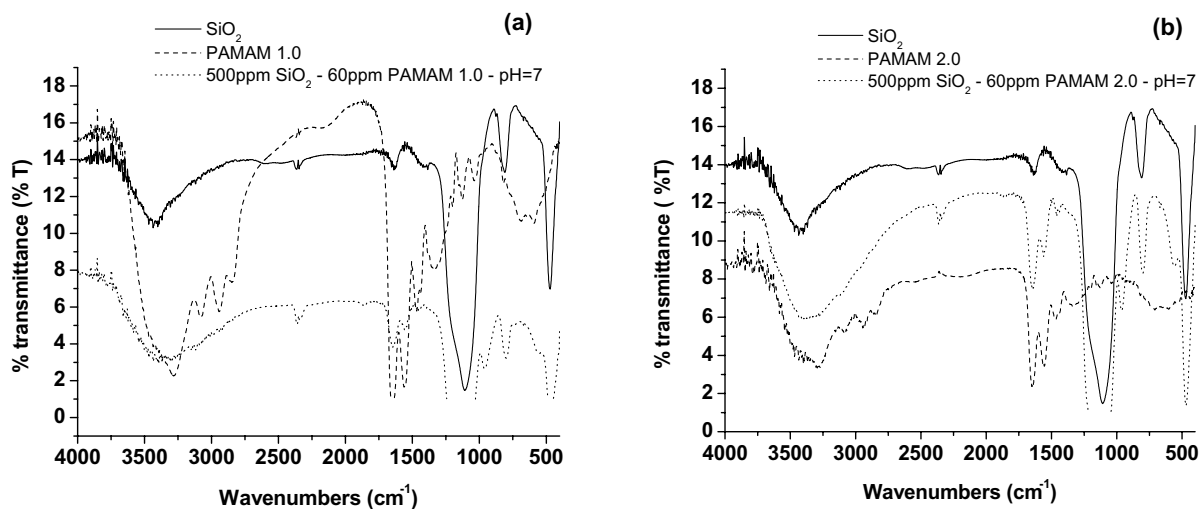
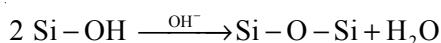


Fig. 13. FT-IR spectra of SiO₂-PAMAM-1 (a) and SiO₂-PAMAM-2 (b) composites precipitated out from solutions containing 60 ppm inhibitor dosages.

indicating that orthosilicates hydrolyze more rapidly than other silicate species (e.g. disilicates, chain silicates, cross-linked oligomers and polymers), indicating that bridging oxygens are much more resistant to attack than non-bridging oxygens. Above pH 2 this mechanism involves polymerization with condensation, catalyzed by OH⁻ according to the following reaction:



Silica scale formation involves condensation between Si-OH groups formed at the material surface and Si-OH of the dissolved silicate present in water. Hayakawa et al. reported that condensation between the Si-OH units formed at a glass surface and dissolved Si-OH can be the dominant mechanism [54].

Silica polymerization although dependent on pH, presents a much lower sensitivity to pH changes than the formation of other sparingly soluble salts. This is consistent with the fact that silica is not an easily “cured” foulant by pH adjustments. For example CaCO₃ scale can be virtually eliminated by operating a process water system at lower pH’s, e.g. –7. For high silica-containing

waters, operation at higher pH’s generates the problem of “magnesium silicate” scale. Lowering the pH (by feeding acid) does not eliminate the problem. It just “shifts” it from “magnesium silicate” to “silica”. Low operational pH has the additional disadvantage of increasing corrosion rates of metallic surfaces, ultimately leading to materials failure [55]. Silica solubility is very high at pH’s >10, but this pH regime is impractical and is not an operational option for desalination systems.

Dissolved silica precipitates out of solution principally in three ways:

Surface deposition. As a deposit on a solid surface where the [Si(OH)_{4-x}]^{x-} condenses with any solid surface possessing –OH groups. If the surface contains M–OH moieties (M = metal) this reaction is further enhanced. Such pronounced silica deposition phenomena in the water treatment industry are observed on metallic surfaces that have suffered severe corrosion, whose surface is covered with metal oxides/hydroxides. Once the receptive surface is covered with silica scale, additional silica is deposited on an already formed silica film.

Bulk precipitation. As colloidal silica particles grow by the condensation reaction they collide

with each other and agglomerate forming larger particles.

In living organisms [56]. This form of silica is called biogenic and appears in certain micro-organisms that have the ability to deposit silica from highly *undersaturated* solutions. Such a subject is not relevant to the present study and will not be discussed further.

The precise mechanism of silica formation is not well understood. Any interference with the condensation reaction may lead to silica scale growth inhibition. A relevant example is silica inhibition by orthoborate, which reacts with silicate ions to form borosilicates [57–59]. These products are more soluble in water than silica/metal silicates. This technology has been applied in open recirculating cooling water systems. PAMAM dendrimers and AQUAZOL polymers seem to have a profound deleterious effect on the silica condensation reaction, most likely at its earlier stages where the reaction products are oligomeric silicates. Spectroscopic techniques that may assist in delineating the silica inhibition mechanism include ^{27}Si NMR. Such options will be investigated in the future.

5. Conclusions

The purpose of this work is to identify and exploit novel dendrimer chemistries as effective SiO_2 scale growth inhibitors in process waters. The principle findings are summarized as follows:

- (1) PAMAM dendrimers are effective inhibitors of SiO_2 scale growth.
- (2) Their structure (generation number and nature of end groups) affects inhibitory activity in a profound way.
- (3) The NH_2 -terminated dendrimers, PAMAM 1 and 2 are much more effective SiO_2 scale growth inhibitors. The optimum dosage is 40 ppm.
- (4) PAMAM 1 and 2 dendrimers also form SiO_2 -PAMAM composite precipitates after prolonged periods. These composites have been

characterized. Formation of such materials having dendrimer entrapped within the SiO_2 matrix obviously depletes the solution from active inhibitor and may explain deterioration of the inhibitor performance over time.

- (5) Polyethyloxazolines are also effective SiO_2 inhibitors, but their performance is less dependent on structural features.

A number of studies have appeared in the literature describing the immobilization of PAMAM dendrimers onto solid surfaces that include silica [60–66], gold [67–70] and mica [71], mostly by utilizing multistep wet chemical strategies. Some of these approaches include chemical modification of either the “core” or the “branches” of dendrimers to improve their ultimate physicochemical properties. Such an approach may also be applicable in the present field. For example, based on the results described here, it is obvious that $-\text{NH}_2$ terminal groups have a detrimental effect on dendrimer inhibition performance. Based on the results presented herein, inhibition rather than dispersion is a more likely approach for dendrimer and polymer utilization as silica control agents in water systems.

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