A structure/function study of polyaminoamide dendrimers as silica scale growth inhibitors

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Abstract: Dendrimers have attracted immense attention during the last decade due to their interesting properties both from a basic and an applied research viewpoint. Encapsulation of metal nanoparticles for catalysis, drug delivery and light harvesting are only some applications of dendrimers that are breaking new ground. A novel application of dendrimer technology is described in the present paper that relates to industrial water treatment. Industrial water systems often suffer from undesirable inorganic deposits. These can form either in the bulk or on metallic surfaces, such as heat exchangers or pipelines. Silica (SiO_2) scale formation and deposition is a major problem in high-silica-containing cooling waters. Scale prevention rather than removal is highly desired. In this paper, benchtop screening tests on various silica inhibition chemistries are reported, with emphasis on materials with a dendrimeric structure. Specifically, the inhibition properties of commercially available STARBURST® polyaminoamide (PAMAM) dendrimers generations 0.5, 1, 1.5, 2, and 2.5 are investigated in detail together with other commonly-used scale inhibitors. Experimental results show that inhibition efficiency largely depends on structural features of PAMAM dendrimers such as generation number and nature of the end groups. PAMAM dendrimers are effective inhibitors of silica scale growth at 40 ppm dosage levels. PAMAM dendrimers also act as silica nucleators, forming SiO_2–PAMAM composites. This occurs because the SiO_2 formed by incomplete inhibition interacts with cationic PAMAM-1 and -2. The general scope of silica formation and inhibition in industrial waters is also discussed.
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Keywords: polyaminoamide dendrimers; silica scale; inhibitors; water treatment; deposit

INTRODUCTION

Dendrimers are well-defined globular macromolecules constructed around a core unit. The term dendrimer derives from the Greek words 'δέντρον' (déndron, meaning 'tree') and 'μέρος' (méros, meaning 'part') and was first coined by Tomalia.[1] He also pioneered the elegant synthesis of the polyaminoamide (PAMAM) dendrimers that were given the name 'starburst polymers'.[2] A schematic structure of PAMAM (generation 1) is shown in Fig 1. Their main structural feature is the growth of the dendrimer branches around a central core (in this case an ethylenediamine) via amide chemical linkages. The dendrimer generation number indicates its degree of growth and branching. More specifically, PAMAM dendrimers of generations 0.5, 1.5, 2.5 possess –COOH termini, and those of generations 1 and 2 have –NH2 termini.

Numerous research groups concentrate their efforts on applying dendrimer chemistry in a plethora of technological applications. Our research efforts are focused on developing new technologies for chemical water treatment in the industrial water treatment field, with an emphasis on scale inhibition and control.[3] The aim of the present work is to exploit dendrimers of various generations as inhibitors of silica polymerization. In addition, knowledge of the structural features that are responsible for the inhibition performance may lead to the design of new silica inhibitors that are more efficient and more cost-effective.

Silica scale formation is a serious problem in cooling waters with high dissolved silica content, as used in industrial applications.[4] Silica and/or magnesium silicate deposition limit industrial water users to a few cycles of operation. Several cooling systems conserve water by operating under conditions of high supersaturation of dissolved species. In certain areas of the world, such as the Pacific Rim, Latin America, Texas, New Mexico, south Europe and others, raw 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.[5] This imposes severe limits to the water-users and forces them to either operate at very low levels of concentration, thus consuming

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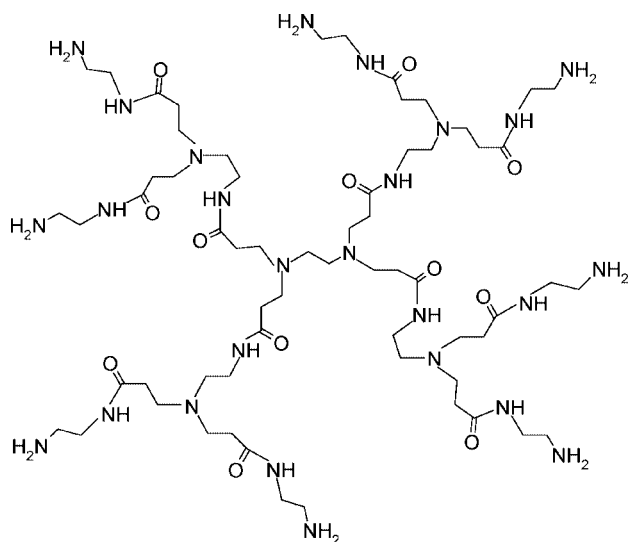E-mail: demadis@chemistry.uoc.gr

Figure 1. Structure of a representative PAMAM dendrimer of generation 1 (8 −NH₂ terminal groups).

enormous amounts of water, or 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.[6]

Silica scale formation is favored at pH < 8.5, whereas magnesium silicate scale forms at pH > 8.5 in waters with high Mg^{2+} levels. Silica has 'normal' solubility, in contrast with the 'inverse' solubility of magnesium silicate. The formation of the former is favored as the temperature increases, while the formation of the latter is more pronounced at higher temperatures. When silicate ions polymerize, they form a plethora of structural motifs: rings of various sizes, cross-linked polymeric chains of different molecular weights, oligomeric structures, etc.[7] 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.

GENERAL SCOPE OF SILICA SCALE PREVENTION AND CONTROL

Certain additives can increase the amount of soluble (reactive) silica beyond its solubility limit. In these sets of experiments, the pH of the test solution was chosen to be ∼7 in order to simulate several industrial cooling systems that operate at pH regions between 7 and 8. Silica solubility increases as pH increases, due to the presence of OH^- ions.

In these test waters and at this operational pH magnesium silicate does not pose a problem. Higher pH values are usually avoided because of potential precipitation of magnesium silicate. A similar study using Mg-containing water and higher operational pH values is underway to study the inhibition effectiveness of PAMAM dendrimers in magnesium silicate growth inhibition.

Current practices for combating silica scale growth in industrial waters include:

(a) *Operation at low levels of concentration.* This is a common practice, but one that results in consumption of large amounts of water. It is generally accepted that in a cooling tower operating at pH < 7.5, silica should be maintained below 200 ppm (as SiO_2). For pH > 7.5, silica should be maintained below 100 ppm (as SiO_2). It should be kept in mind that at pH > 7.5 an additional factor should be taken into account, that of Mg levels. In that case, the product (ppm Mg as $CaCO_3$) × (ppm SiO_2 as SiO_2) should be below 20 000.

(b) *Prevention of 'other scale' formation.*[8] This indirect control method interferes with the propensity of silica scale to co-precipitate with other scales. It is based on prevention of other scaling species (such as calcium carbonate or calcium phosphate) and indirectly benefits the whole cooling tower operation.

(c) *Pretreatment.*[9] Silica removal in precipitation softeners is effected through an interaction between silica and a metal hydroxide. Both $Fe(OH)_3$ and $Al(OH)_3$ have shown silica-removing capabilities, although $Mg(OH)_2$ is considered more effective.

(d) *Use of inhibitors or dispersants.*[10] The present paper is focused on silica inhibition, not dispersancy. Inhibition is defined as the prevention of silica oligo- or polymerization. As a result, silica remains soluble or 'reactive'. Dispersion, on the other hand, is the prevention of particle agglomeration to form larger-size particles and the prevention of the adhesion of these particles onto surfaces. Inhibition and dispersion are shown schematically in Fig 2.

A rather small number of products are available commercially for silica scale control in reverse osmosis and cooling water applications.[11−13] Boric acid and/or borate salts have been effectively used to control silica scale in cooling waters. This treatment can achieve up to 300 ppm soluble silica in the recirculating water. Sulfonate-modified, acrylate-based terpolymers have been used as silica dispersants. Patented technology describes a blend that contains a poly(2-ethyl-oxazoline). Polyether polyamino methylene phosphonates in combination with other phosphonates have also been used to prevent silica deposition.[14]

EXPERIMENTAL
Reagents
$Na_2SiO_3.9H_2O$ was from Fischer. PAMAM dendrimers of generations 0.5, 1, 1.5, 2, and 2.5 were purchased from Aldrich Chemical Co (Milwaukee, WI, USA) as solutions in methanol and were used
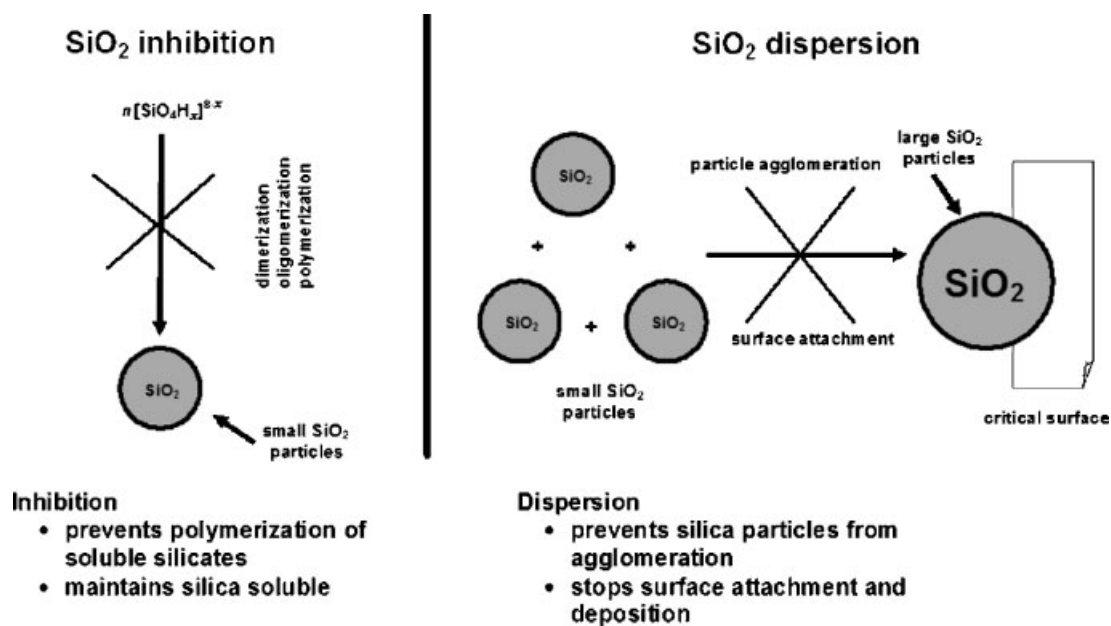
Figure 2. Schematic representation of silica inhibition and dispersion in water systems.

as received. AMP (amino-tris-methylene phosphonic acid), HEDP (1-hydroxyethylidene-1,1-diphosphonic acid), PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid), PAA (polyacrylic acid, MW ~2000 daltons) were from Solutia Inc, and sodium orthoborate was from Fischer. Materials and reagents for the silica analytical test were from the Hach Co. Syringe filters (0.45 µm) were from Millipore Corporation. In-house, doubly distilled water was used for all experiments. This water was tested for silica with atomic absorption spectroscopy and was found to contain negligible amounts.

Solution preparation
A 500 ppm solution of sodium silicate (expressed as SiO_2) was prepared by dissolving 0.236 g of solid $Na_2SiO_3 \cdot 9H_2O$ in 100 cm^3 silica-free, doubly distilled water and was kept in a plastic container (glass containers must be avoided in order to minimize silicate ion leach-out). Stock solutions (1% (10 000 ppm as actives) of the inhibitors in water were also prepared.

Screening tests
Control
A volume of the silicate stock solution (100 cm^3) was placed in a plastic beaker and charged with a Teflon-covered magnetic stir bar. The pH of this solution was measured and found to be ~11.5. Gaseous CO_2 from a compressed cylinder was bubbled through a fritted glass outlet into the silicate solution. A relatively slow sparging rate was necessary in order to avoid large pH drifts. The pH started to decrease due to carbonic acid formation. The CO_2 sparger was removed when the pH reached 8.5. Because of the dissolution of CO_2 over time into the solution, the pH continued to decrease without the sparger present. Equilibrium pH values were ~7. The contents of the plastic beaker

were placed in a plastic bottle, which was capped and set aside. Solutions were tested for reactive (soluble) silica by the HACH (silicomolybdate) method (see below) after 24, 48, and 72 h time intervals.

Inhibitor test
The above procedure was followed except that before CO_2 sparging, 0.4 cm^3 of 1% inhibitor solution was added to the silicate stock solution. This gave a final concentration of inhibitor of 40 ppm. Sparging and sampling procedures were the same. Samples were withdrawn from undisturbed solutions.

Soluble (reactive) silica measurements
The silica analytical test method used in the experiments was the High Range (0–100 ppm) silicomolybdate method provided by the HACH Company.[14] According to this method, a 2.5 cm^3 sample of the test solution is diluted to 25 cm^3 in the sample cell. The molybdate reagent is then added to the sample cell solution, followed by the powder acid reagent. The solution is mixed well until all solids have dissolved. After 10 min, solid citric acid is added to the sample cell and after the solid dissolves the solution is set aside for an additional 2 min. At that time, the sample absorbance is measured with a DR2000 spectrophotometer at 452 nm, and the 'ppm soluble silica' value is shown on the instrument display. Following the same procedure, another 2.5 cm^3 sample was filtered through a 0.45 µm syringe filter before adding the Hach test reagents, and tested for reactive silica as above.

The Hach test measures 'soluble' ('reactive') silica. It does not measure 'colloidal' silica.[15] It is worth noting that the term 'reactive' silica does not represent only monomeric silica (silicate ion). It also includes other 'oligomeric species' such as dimers, trimers, tetramers, etc. It is not clear where the cut-off is.

For all practical purposes of this paper, we will assume that the Hach test results are associated with all forms of reactive silica except colloidal. The screening and testing procedures were reproduced at least three times and the relative error was within ±5%.

RESULTS AND DISCUSSION
Silica inhibition by PAMAM dendrimers
Test solutions of 500 ppm silica were utilized in this study. These conditions are considered to be 'high stress' with respect to silica supersaturation. Most industrial cooling systems operate at <200 ppm silica, with no added inhibitor, and no higher than 300 ppm silica when a silica inhibitor is present. Use of these 'high stress' conditions was necessary in order to differentiate between inhibitor efficiencies. Solubility of silica is directly proportional to temperature, in contrast to many other 'inorganic' scales such as calcium carbonates[16] and sulfates[17] and calcium phosphates[18,19] commonly encountered in industrial water systems. Ambient temperatures were used for these experiments. Solutions were tested after 24, 48 and 72 h of polymerization time. All samples were tested by the Hach method either from bulk water. From filtered water (through 0.45 μm filter).

A variety of different dendrimer chemistries were tested by the experimental set-up described in the Experimental section. Under the experimental conditions all denrdimer inhibitors showed efficacy higher than the control for inhibition of silica polymerization. These results are summarized in Tables 1 (24 h), 2 (48 h), and 3 (72 h), and shown in Figs 3 and 4. All runs described herein were reproduced at least three times.

The silicomolybdate method allows for the determination of soluble or 'reactive' silica after the supersaturated solution has been standing for at least 24 h at a pH appropriate for silica polymerization and relevant to industrial cooling water applications. Also, by using CO_2 gas as the 'reagent' to decrease pH, introduction of other ions is avoided. In addition, CO_2 allows for rather high values of 'M Alkalinity' (~800 ppm, as HCO_3^-), not unusual in cooling water applications.

Table 1. Soluble silica after 24 h

Generation	Soluble silica in bulk (ppm)	Filtered soluble silica (ppm)	End group	Number of end groups
Control (no inhibitor)	213	213	—	—
0.5	248	177	−COOH	8
1	434	329	−NH₂	8
1.5	262	215	−COOH	16
2	305	257	−NH₂	16
2.5	388	335	−COOH	32

Table 2. Soluble silica after 48 h

Generation	Soluble silica in bulk (ppm)	Filtered soluble silica (ppm)
Control	160	156
0.5	208	143
1	340	271
1.5	196	154
2	231	205
2.5	299	240

Table 3. Soluble silica after 72 h

Generation	Soluble silica in bulk (ppm)	Filtered soluble silica (ppm)
Control	153	147
0.5	205	143
1	284	232
1.5	174	135
2	202	184
2.5	224	172

24-Hour results
Silica polymerization in the control solution gave 213 ppm soluble silica (both filtered and bulk). PAMAM-0.5 gave only marginal inhibition allowing 248 ppm silica to remain soluble. However, after filtration only 177 ppm soluble silica was measured, indicating that there may be reactive silica associated with insoluble particles >0.45 μm. PAMAM-1 was very efficient in inhibiting silica polymerization, giving 434 ppm of reactive silica in solution, and 329 ppm after filtration. The inhibition efficiency of the next generations of PAMAMs appeared to be lower. PAMAM-1.5 showed about the same efficiency as PAMAM-0.5, allowing 262 ppm silica to remain soluble (215 ppm after filtration). PAMAM-2 and PAMAM-2.5 gave values of 305 ppm and 388 ppm soluble silica, respectively.

48-Hour results
Silica polymerization continued after 48 h. In the control solution, soluble silica dropped to 160 ppm (loss of 53 ppm). Inhibition efficiencies of all PAMAM dendrimers also dropped after 48 h of polymerization time. PAMAM-0.5 gave 208 ppm soluble silica (loss of 40 ppm), and only 143 ppm after filtration. PAMAM-1 solubilized 340 ppm, after a dramatic loss of 103 ppm soluble silica (271 ppm filtered). Gradual loss of inhibitory activity was observed in results with PAMAM-1.5, -2, and -2.5, giving 196 ppm, 231 ppm, and 299 ppm, respectively.

72-Hour results
Loss of polymerization inhibition performance continued after 72 h. Soluble silica in the control solution appeared to be stabilized at ~150 ppm. The same was observed for PAMAM-0.5, which allowed 205 ppm of silica to remain soluble (a drop of only 3 ppm from the 48 h measurement. It is noteworthy that the amount of
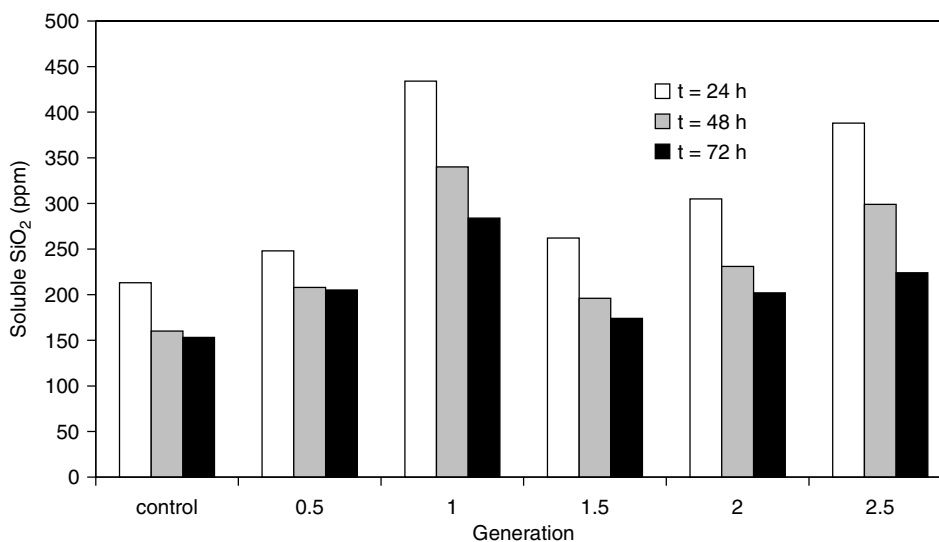
Figure 3. Reactive silica destabilization (loss) over time (in bulk samples).
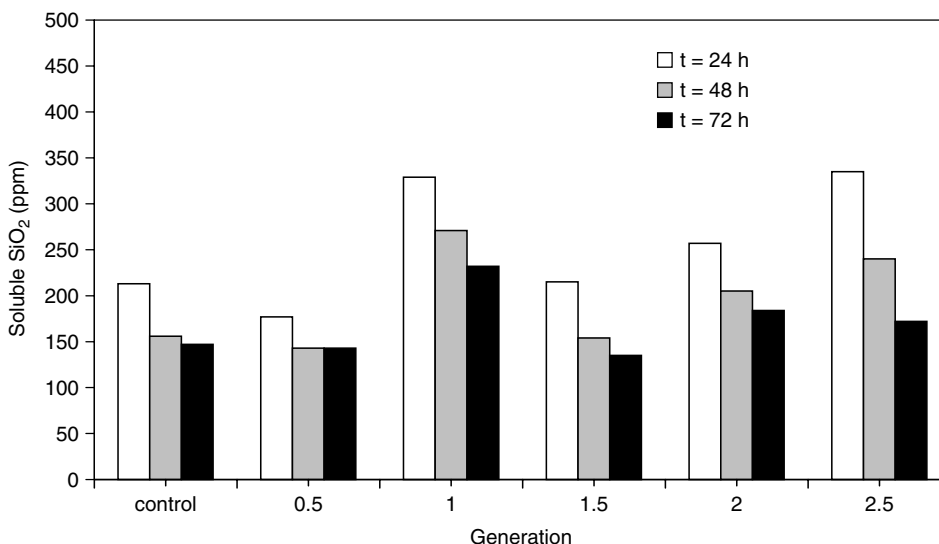

Figure 4. Silica growth inhibition by PAMAM dendrimers (filtered through a 0.45 μm filter).

soluble silica in the filtered solution was 143 ppm, the same as in the 48 h measurement. PAMAM-1 maintained soluble silica at 284 ppm, whereas PAMAM-1.5, -2, and -2.5 gave 174 ppm, 202, and 224 ppm soluble silica respectively. An important observation is that in solutions containing any of the PAMAM dendrimers soluble silica was found at higher levels than in those containing no inhibitor after 72 h of polymerization time. The drop in soluble silica is summarized collectively in Tables 4 and 5.

The *rate* of loss of soluble silica can be examined comparatively if soluble silica (in ppm) is plotted vs time. This can be seen in Fig 5. It immediately becomes evident that colloidal silica grows at a slower rate in the presence of PAMAM-0.5 than in any of the other PAMAM dendrimers. Also, PAMAM-2.5 accelerates the growth of colloidal silica when compared with the control.

In solutions containing $-NH_2$-terminated PAMAM dendrimers a white floc formed after ∼24 h of

Table 4. Stabilization of silica (in bulk samples, in ppm) vs time

Generation	Time (h)		
	24	48	72
Control	213	160	153
0.5	248	208	205
1	434	340	284
1.5	262	196	174
2	305	231	202
2.5	388	299	224

polymerization time. Table 6 shows observations after a 72 h reaction time. Physicochemical analysis (elemental analysis and EDS) of this floc showed that it was mainly silica (>90%) with small amounts of organic material, certainly PAMAMs. The presence of PAMAMs in the floc was verified by FT-IR spectroscopy by following the ν(C=O) band of the amide bond at 1645 cm^{-1}. The presence of silica in the
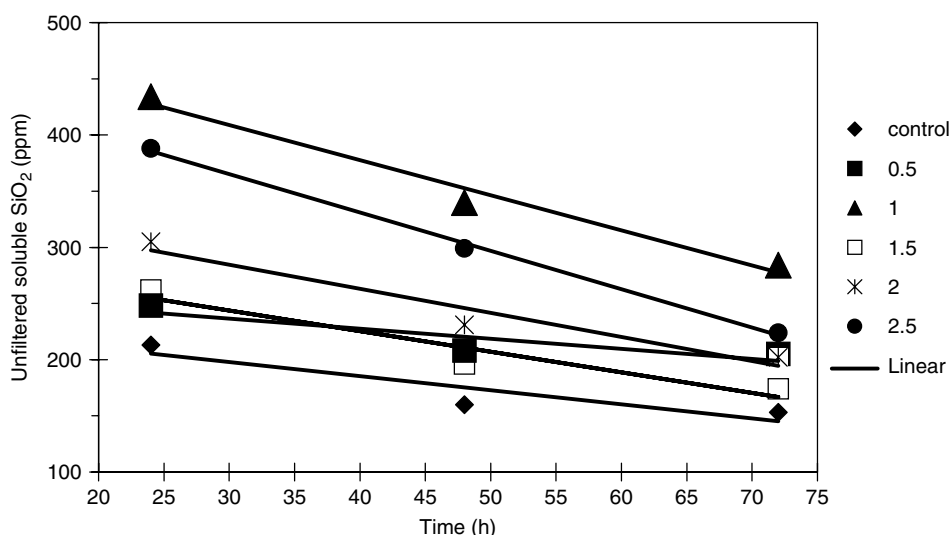
Figure 5. Silica destabilization slopes (in bulk samples) by various generation dendrimers.

Table 5. Stabilization of silica (in filtered samples, in ppm) vs time

	Time (h)		
Generation	24	48	72
Control	213	156	147
0.5	177	143	143
1	329	271	232
1.5	215	154	135
2	257	205	184
2.5	335	240	172

Table 6. Visual observations after 72 h

Generation	Observations
Control	Clear solution, no turbidity
0.5	Clear solution, no turbidity
1	High turbidity, a lot of settled deposit
1.5	Little turbidity, very little deposit
2	High turbidity, a lot of settled deposit
2.5	Little turbidity, very little deposit

deposit was also confirmed by the Si−O−Si vibration as a characteristic strong band at ~1050 cm^{-1}.

At relatively low dosages (10–20 ppm) the PAMAM dendrimers were inefficient in inhibiting silica polymerization to an appreciable extent. In fact, the amounts of soluble silica were essentially no different from the control (no inhibitor). At 40 ppm inhibitor dosage there was a jump in inhibition performance. Higher dosages of all inhibitors (60 and 80 ppm) were tested. All −COOH-terminated PAMAM dendrimers showed slight increases in silica inhibitory efficiency. An increase in dosage of −NH$_2$-terminated PAMAM compounds, however, resulted in a reduction of inhibitory power. This can be explained by the increase in positive charge in solutions containing PAMAM-1 and PAMAM-2.

SiO$_2$ stabilization by PAMAM dendrimers with −COOH termini

There appears to be a relationship between PAMAM generation, terminal group and silica stabilization. Figure 6 shows soluble silica drop vs time for three PAMAMs containing a −COOH terminus. PAMAM-0.5 and PAMAM-1.5 offered little additional stabilization compared with the control (153 ppm soluble silica after 72 h). However, silica loss in solutions containing PAMAM-0.5 was limited (loss of 43 ppm between 24 and 72 h), compared with that for solutions containing PAMAM-1.5 (88 ppm between 24 and 72 h). Silica stabilization was maintained for PAMAM-0.5 and PAMAM-1.5 after 48 h (loss of 3 ppm for PAMAM-0.5 and 22 ppm for PAMAM-1.5). Silica loss over time was more dramatic for PAMAM-2.5 (164 ppm between 24 and 72 h, and 75 ppm after 48 h). PAMAMs of smaller size containing −COOH as terminal group seem to offer a relatively small inhibition effect, at least initially, but they tended to offer more effective stabilization over longer periods of time. As the dendrimer molecular size increased, the initial silica stabilization (388 ppm for PAMAM-2.5 after 24 h) was rapidly diminished (299 ppm after 48 h, and 224 ppm after 72 h).

SiO$_2$ aggregation ability of PAMAM dendrimers

PAMAM dendrimers act as silica scale growth inhibitors, but at the same time they act as reactive *and* colloidal silica aggregators. This is consistent with the appearance of a white precipitate after 72 h of silica polymerization time, indicating formation of large particles. However, formation of colloidal silica is not always accompanied by the appearance of a visual precipitate.

Filtration through a 0.45 μm filter allows the separation of 'small' (<0.45 μm) and 'large' (>0.45 μm) silica particles. As noted before, measurements with the Hach test give the total reactive silica, regardless of particle size. Therefore, using this test and
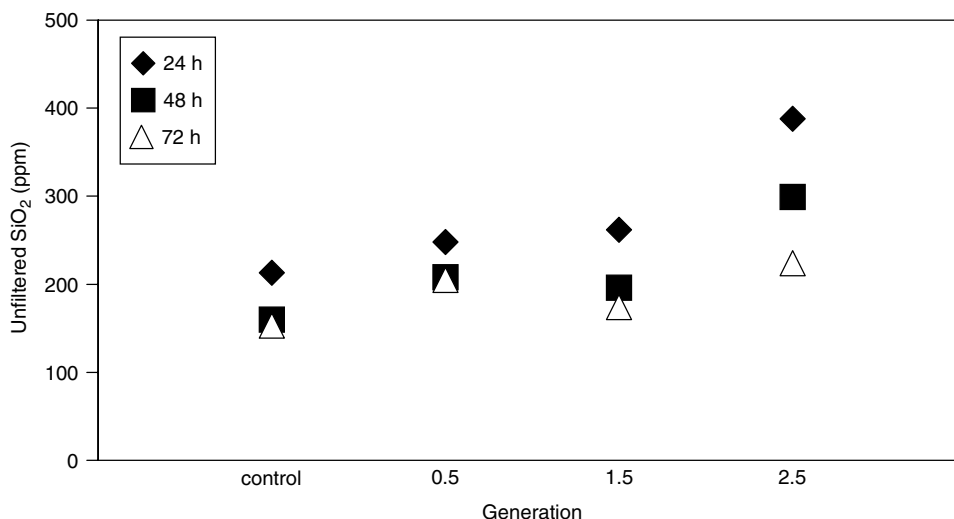
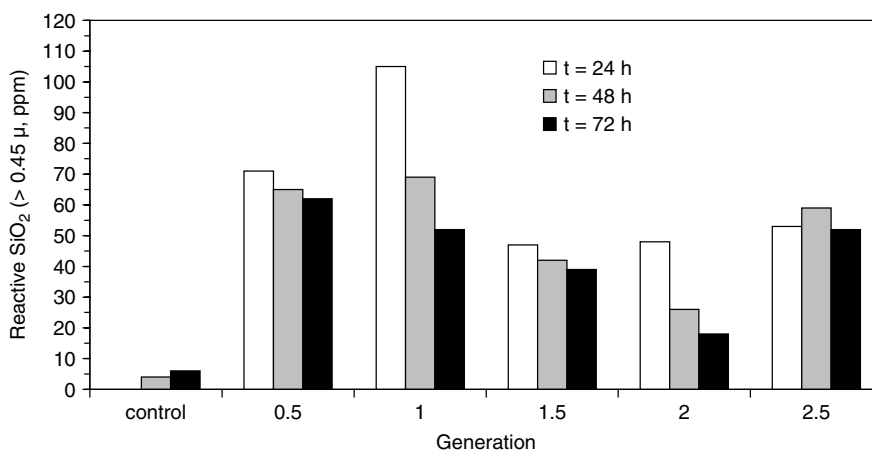**Figure 6.** Reactive silica stabilization by PAMAM dendrimers with −COOH terminal groups.

Figure 7. Reactive SiO$_2$−PAMAM composites >0.45 µm.

measuring the total reactive silica, in the bulk and in a filtered solution, gives the level of silica particles of size >0.45 µm that are reactive to the Hach test. These measurements are plotted in Fig 7. Based on IR measurements, these particles contain PAMAM, and thus they can be envisioned as dendrimer−silica organic−inorganic hybrid composites. The silica associated with these composites is not in the colloidal form because they are reactive to the Hach test. Whether silica is in a monomeric or oligomeric form is unknown at this point. It is possible that silica is associated with the dendrimer in such a way (either embedded within the dendrimer, or at the periphery), that it is still 'reactive'.

Figure 8 shows that in the absence of an inhibitor (control) virtually no reactive silica particles >0.45 µm formed under the specific experimental conditions. In the presence of PAMAMs there was a dramatic change in the course of silica particle formation. Each generation showed different aggregation ability for the above particles. For example, within a 24-h time period PAMAM-0.5 caused the formation of 71 ppm of reactive silica particles, whereas PAMAM-1 was a better aggregator, forming 105 ppm of those particles.

PAMAM-1.5, -2, and -2.5 aggregated 47, 48, and 53 ppm of those particles, respectively after 24 h. After 72 h, solutions containing PAMAM-1 or PAMAM-2, *both containing −NH$_2$ terminal groups*, appeared to lose a large portion of these particles, ∼50% for the former and 62% for the latter. It is reasonable to conclude that these reactive silica composites converted to colloidal silica (either as colloidal silica−dendrimer hybrids or unassociated, 'free' colloidal silica). PAMAM-0.5, -1.5, and -2.5, all containing −COOH as terminal groups, were able to inhibit the above transformation, thus maintaining (within experimental error) the initial levels of reactive silica composites.

Figure 8 shows the amount of colloidal silica present in solutions containing PAMAMs. It appears that in the presence of PAMAMs a significantly lower amount of silica existed in the colloidal form. For example, PAMAM-1 in 24 h aggregates only 66 ppm of silica, but this number increased to 160 ppm after 48 h, and finally it reached 216 ppm. PAMAM-0.5 seems to affect silica aggregation rather insignificantly, as compared with the control. Silica solutions containing no inhibitor showed no visible precipitate after 72 h of polymerization time. When a PAMAM was
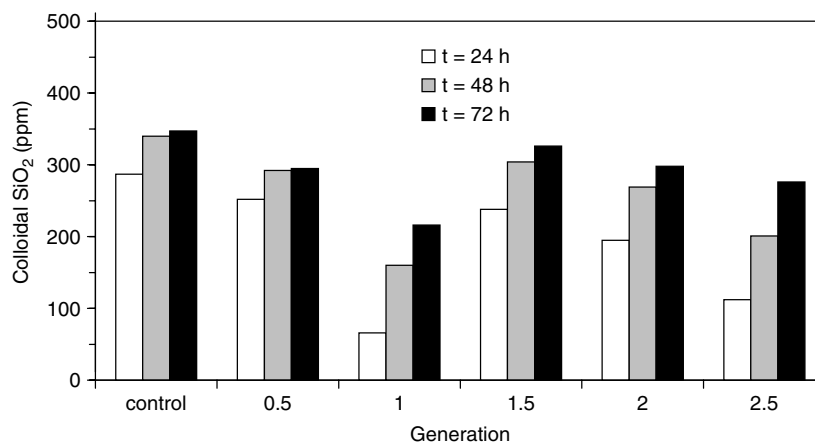
Figure 8. Aggregation of colloidal silica by PAMAM dendrimers.

present there was a visible turbidity (except for PAMAM-0.5), however the solution's appearance varied with the type of PAMAM. PAMAM-1 and -2 (with $-NH_2$ terminus) caused the formation of relatively large amounts of a white precipitate, whereas PAMAM-1.5 and -2.5 (with $-COOH$ terminus) caused virtually no precipitation, only causing a minor turbidity to the solution appearance. These visual observations are shown in Table 6. As noted above, chemical analysis of this flocculent material showed that it is mainly silica (>90%), also confirmed by FT-IR spectroscopy ($Si-O-Si$ vibration at $\sim 1050\,cm^{-1}$). PAMAM molecules are incorporated into the precipitate, as verified by FT-IR spectroscopy (appearance of $\nu(C=O)$ band of the amide bond at $1645\,cm^{-1}$). Incorporation of PAMAM in the SiO_2−dendrimer composite causes loss of 'active' inhibitor in solution. This is most likely the main cause of inhibition activity drop over time.

Effect of cations

Polyvalent metal ions present in the feedwater can adsorb onto colloidal silica particles and accelerate particle agglomeration and eventual precipitation and fouling. The adverse effect of those ions on silica precipitation emphasizes even more the importance of silica inhibition, rather than its dispersion. Dispersion of colloidal silica becomes exceedingly challenging at higher supersaturations, where concentrations of metal ions, such as calcium and magnesium, are very high (the situation worsens in the presence of iron or aluminum). It has been reported before that the presence of cations, such as Ca^{2+} and Mg^{2+}, does not significantly affect silica polymerization, unless operational pH favors formation of magnesium silicate[20,21] (Calcium silicate[22] does not form due to its relatively high solubility at normal Ca^{2+} and silica levels in industrial waters). In the present study it was investigated whether the same cations had any effect on silica formation in the presence of PAMAMs. It was found that for Ca levels up to 400 ppm and Mg levels up to 200 ppm, PAMAMs inhibited silica equally well as without Ca^{2+}/Mg^{2+} present (data not shown here).

Comparison of PAMAM dendrimers with other scale inhibitors

Mineral scale prevention can be achieved by use of threshold scale inhibitors, key components of any chemical water treatment.[23] These are compounds that are added to any given treatment in minute (ppm) quantities and usually work synergistically with dispersant polymers.[24] Phosphonates (or organic phosphates) belong to a fundamental class of such compounds.[25] These usually (although not always) contain multiple phosphonate groups ($R-PO_3H_2$, R = organic chain), most commonly found in their deprotonated form, due to the relatively high pH of the water. Some common commercially available phosphonates are PBTC, HEDP and AMP. Low molecular weight polyacrylates are also commonly used as scale inhibitors. Mineral scale inhibitors are thought to achieve scale inhibition by adsorbing onto specific crystallographic planes of a growing crystal nucleus after a nucleation event. This adsorption prevents further crystal growth and agglomeration into larger aggregates.[3]

The amorphous nature of silica scale that forms in cooling systems renders use of the above mineral scale inhibitors ineffective. This was confirmed in inhibition tests. Table 7 shows inhibition results at the same inhibitor level (40 ppm actives). All 'classical'

Table 7. Stabilization of silica (in bulk samples) vs time in the presence of 40 ppm inhibitor

Inhibitor	Soluble silica (in ppm, after 24 h)
Control	213
PAMAM-0.5	248
PAMAM-1	434
PAMAM-1.5	262
PAMAM-2	305
PAMAM-2.5	388
HEDP	215
AMP	220
PBTC	208
PAA	220
Orthoborate ion	200

threshold scale inhibitors showed no additional inhibitory activity against silica formation, compared with the control. Orthoborate, which was shown to exhibit good inhibition properties against silica deposition but at much higher levels (~100 ppm actives),[26] also showed no significant performance under the test conditions.

Silica speciation vs pH

Silica scale formation is favored at pH values <8.5, whereas magnesium silicate scale forms at pH values >8.5. Silica has 'normal' solubility, which increases proportionally with temperature. In contrast, magnesium silicate exhibits 'inverse' solubility characteristics. When silicate ions polymerize, they form a plethora of structural motifs, including rings of various sizes, cross-linked polymeric chains of different molecular weights, oligomeric structures, etc.[7] The resulting 'silica scale' is a complex and amorphous product (colloidal silica), which in fact is a complicated mixture of the above components, linked together by $Si-O-Si$ bonds.

Silica is an undesirable scale for several reasons. It severely impedes heat transfer. It is tenacious, and costly (and potentially hazardous) to remove. It is extremely prone to co-precipitate with other scales, particularly iron (hydr)oxides. It often is the limiting reason for not achieving high cycles of concentration.

The amorphous character of silica deposits precludes the use of conventional crystal modification technologies. Molecules such as phosphonates that are effective mineral scale threshold inhibitors provide virtually no benefit for silica scale inhibition. They can only have an indirect benefit by maintaining a cooling tower free of other deposits that can act as precipitation nuclei for silica or catalyze silica precipitation in the bulk.

Mechanism of silica inhibition

Amorphous silica formation is governed by several equilibria. 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 reactions 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, eg Fe^{2+}, Mg^{2+} or Al^{3+}.

Polymerization of silicic acid is believed to occur through an SN_2 mechanism involving a deprotonated $Si-O^-$ and the Si center of $Si(OH)_4$. Inhibition of this step should be critical in inhibiting silica scale formation. There are reports indicating that orthosilicates hydrolyze more rapidly than other silicate species (eg 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:

$$2\ 'Si-OH' \xrightarrow{OH-} 'Si-O-Si' + H_2O$$
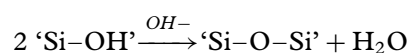
Silica scale formation involves condensation between $Si-OH$ groups formed at the material surface and $Si-OH$ of the dissolved silicate present in water. Hayakawa et al reported that condensation between the $Si-OH$ units formed at a glass surface and dissolved $Si-OH$ can be the dominant mechanism.[27]

Silica polymerization is governed largely by pH. Unfortunately, silica is not an easily 'cured' foulant by pH adjustments. For example $CaCO_3$ scale can be virtually eliminated by operating a cooling tower system at lower pH values. With high-silica-containing waters, operation at higher pH values 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.[28] Silica solubility is very high at pH values >10, but this pH regime is impractical and is not an operational option for cooling tower systems.

Dissolved silica precipitates out of solution principally in three ways:

(1) 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.

(2) Bulk precipitation. As colloidal silica particles grow by the condensation reaction they collide with each other and agglomerate, forming larger particles.

(3) In living organisms. This form of silica is called biogenic and appears in certain microorganisms 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 still 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. These products are more soluble in water than silica/metal silicates. PAMAM dendrimers 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. It may be possible that NH_2-terminated analogs (most likely in a $-NH_3^+$ form in pH ranges examined) associate with negatively charged silicate ions or small silica oligomers, and thus prevent further particle growth. PAMAMs with $-COOH$ terminus apparently cannot function in a similar manner due to charge repulsions between the deprotonated surface carboxylate groups and the silicate ions or oligomers. The efficiency of the $-COOH$-terminated PAMAM-2.5 inhibitor (the largest in size) may be related to possible stabilization of soluble silica within the dendrimer internal voids. This hypothesis is reminiscent of a similar type of stabilization of metallic Cu nanoclusters within the internal spaces found in the PAMAM framework.[29,30] At present the current test for measuring soluble SiO_2 is inefficient in differentiating SiO_2 'outside' the dendrimer from that 'inside' it.

CONCLUSIONS

The principal purpose of this work was to identify and exploit the chemistry of novel dendrimers that would be effective in silica scale growth inhibition in high-silica cooling waters. The major conclusions can be summarized as follows:

(1) PAMAM dendrimers are effective inhibitors of silica scale growth at the optimum dosage level of 40 ppm.
(2) Their structure (generation number and nature of terminal groups) affects inhibitory activity.
(3) PAMAM dendrimers also act as silica aggregators forming $SiO_2-PAMAM$ composites.
(4) Loss of inhibitor is observed over time due to coprecipitation and inhibitor entrapment within the silica matrix.

Based on the results described herein, it is obvious that $-NH_2$ terminal groups are responsible for inhibition, but also have a detrimental effect on dendrimer inhibition performance, since they generate silica–dendrimer insoluble composites. Additional results (not shown here) show that interaction of PAMAM dendrimers with *pre-formed* silica colloids (5–50 nm size) leads to precipitate formation, which would be detrimental when used in water treatment. Therefore, inhibition rather than dispersion is a more likely approach for dendrimer utilization as silica control agents in water systems.

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