

Inhibition and Dissolution as Dual Mitigation Approaches for Colloidal Silica Fouling and Deposition in Process Water Systems: Functional Synergies

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This paper is focused on a dual approach for silica scale control, inhibition and dissolution by use of designed chemical approaches. Inhibitors that are tested include the polyaminoamide STARBURST dendrimers (PAMAM) of generations 0.5, 1.0, 1.5, 2.0, and 2.5. Of these, only the NH_2 -terminated ones (PAMAM-1.0 and 2.0) show significant inhibitory activity, in contrast to COOH -terminated ones (PAMAM-0.5, 1.5, and 2.5), which show virtually no inhibition performance. The synergism between the above dendrimers and an anionic polyelectrolyte (poly(acrylamide-co-acrylate) copolymer) is also described. Addition of poly(acrylamide-co-acrylate) copolymer in silica supersaturated solutions containing PAMAM-1 or 2 alleviates the appearance of silica-PAMAM insoluble precipitates, resulting in stable colloids. The paper also describes silica dissolution approaches, as an alternative to inhibition, by using nonhazardous additives based on polycarboxylates with one to five $-\text{COOH}$ groups (acetate, oxalate, citrate, diethylenetriaminepentaacetate, and others), mixed polycarboxylates/phosphonates (2-phosphonobutane-1,2,4-tricarboxylate), and amino acids (L-histidine and L-phenylalanine). Their reactivity is linked to their chemical structure in this structure/function study. The presence of additional chemical groups (e.g., $-\text{PO}_3\text{H}_2$, $-\text{NH}_2$, or $-\text{OH}$) in the dissolver molecule augments the dissolution process.

Introduction

Mineral scale deposits can become major operational problems for poorly treated process waters.^{1,2} These sparingly soluble electrolytes include calcium carbonate³ and phosphate,⁴ calcium oxalate,⁵ barium⁶ and strontium sulfate,⁷ and others⁸ and are largely dependent on a plethora of variables, such as water chemistry, temperature, pH, etc.⁹ Silica¹⁰ and magnesium silicate¹¹ are especially troublesome because they can cause catastrophic operational failures in process water systems due to deposit formation. 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.¹²

Scale prevention, in principle, can be achieved by use of scale inhibitors (usually phosphonates¹³ in combination with dispersant polymers¹⁴), key components of any well-designed chemical water treatment. Unfortunately, these “traditional” scale control methods (inhibition and crystal modification) applied to crystalline mineral salt precipitates do not apply to silica because it is amorphous.¹⁵ Therefore, designed and well-thought inhibition approaches have to be utilized for silica precipitation and scaling.

Unfortunately, prevention of scale formation is not always possible. At times, system operators are faced with the difficult task of removing hard and tenacious scale deposits from critical system components, such as heat exchangers. Silica deposits can be cleaned mechanically by “sandblasting”, or chemically with $\text{NH}_4\text{F}\cdot\text{HF}$, a process that is not hazardfree.¹⁶ Therefore, an integrated chemical water treatment approach must

include “contingencies” that relate to chemical cleaning of a potentially scaled system.

This paper is a continuation of our research efforts^{17–21} to discover and explore the effectiveness of structurally well-defined scale inhibitors. Its main focus is on (a) use of chemical additives that possess certain dendritic structural features (see Figure 1) for silica scale inhibition and their synergistic behavior with anionic, polyacrylate-based polymers (see Figure 2) and (b) use of environmentally benign chemicals for silica scale dissolution.

Experimental Section

Reagents. STARBURST dendrimers, polyacrylamide-polyacrylate copolymer (PAM-co-AA, 20 wt % acrylamide, average MW 200 000), EDTA (ethylenediaminetetraacetic acid), DETPA (diethylenetriaminepentaacetic acid), DL-malic acid, and L-phenylalanine are from Aldrich Chemical Co., Milwaukee, WI, BTC (butanetetracarboxylic acid) is from Lancaster, Windham, NH, L-histidine is from ACROS, NJ, model colloidal silica for the dissolution studies (AEROSIL 200) is from Degussa, Frankfurt/Main, Germany, acetic and citric acids are from Riedel de Haen, oxalic acid is from E.M Science Merck, 2-phosphonobutane-1,2,4-tricarboxylic acid (commercial name Dequest 7000, 50% w/w active acid) is from Solutia Inc., St. Louis, MO, and ammonium bifluoride, $\text{NH}_4\text{HF}\cdot\text{HF}$, is from Fischer Scientific.

Silica Inhibition Protocol. Detailed procedures for instruments used, reagents, solution preparation, inhibitor screening test, and silicomolybdate test for soluble silica measurement have been reported elsewhere.¹⁸ All inhibition studies were performed at pH 7.00. This pH was selected because it represents a pH region where silica shows its minimum solubility.¹⁵ In all cases, the term “control” denotes the presence of silicate ion but absence of any other additives.

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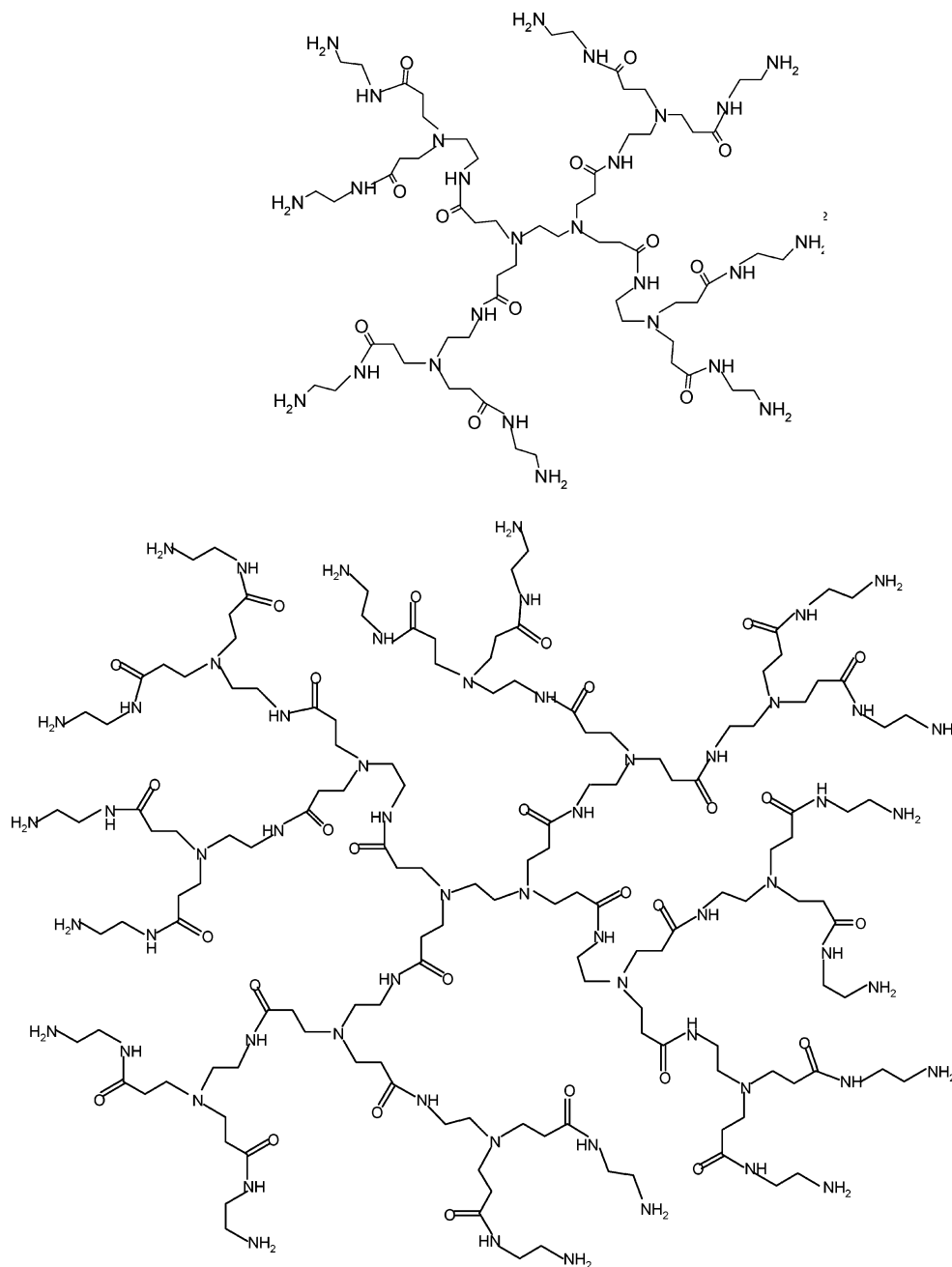


Figure 1. Schematic structure of PAMAM (generation 1, upper) and PAMAM (generation 2, lower), both containing $-\text{NH}_2$ terminal moieties. Note that all amine functionalities are protonated in alkaline pH regions.

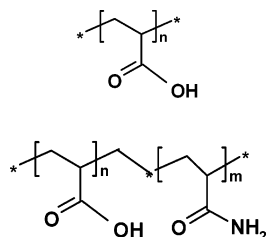


Figure 2. Schematic structures of polyacrylate (PAA, upper) and poly(acrylamide/acrylate) copolymer (PAM-co-AA, lower).

Silica Dissolution Protocol. Glass containers must be avoided to minimize silica leach-out. A quantity of colloidal silica corresponding to 500 ppm expressed as SiO_2 (calculated for 100 mL final solution volume) is placed in a polyethylene container with 80 mL of de-ionized water and a dosage of specific chemical additive (2500–10 000 ppm, depending on the specific run). In

some cases, chemical additives do not dissolve readily; therefore, addition of a small amount of NaOH or mild heating may be necessary to achieve complete dissolution. Solution pH is then adjusted to 10.00 by use of NaOH or HCl solutions (10%). Finally, solutions were diluted up to 100 mL and kept under continuous stirring for up to 72 h. Soluble silica measurements on small samples withdrawn are made at 24, 48, and 72 h. After each measurement, pH is again checked, and in case of deviation from the target value a readjustment is made. In all cases, the term “control” denotes the presence of colloidal silica but absence of any other additives.

Interference Test. Every cleaning additive is tested for its interference with the silicomolybdate spectrophotometric test. A stock solution (500 ppm) of soluble silicate (prepared from commercial sodium silicate) is prepared. To 100 mL of that solution is added a dosage

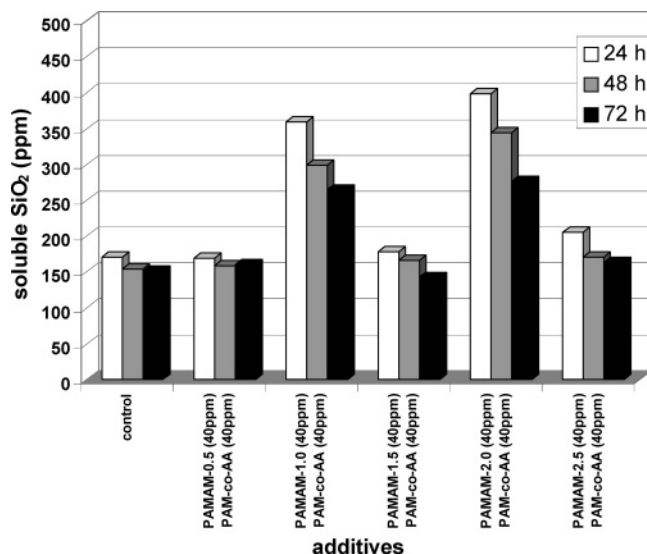


Figure 3. Soluble silica in the presence of combinations of PAMAM dendrimers and PAM-co-AA polymer. Each set of bars represents inhibitory activity based on blends indicated on the x-axis.

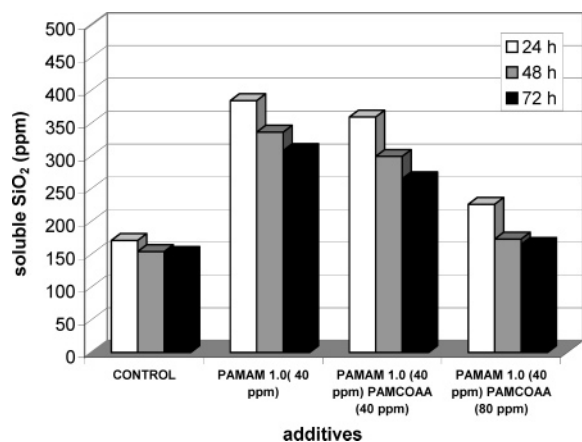


Figure 4. Effect of PAM-co-AA dosage on PAMAM-1 inhibitory action.

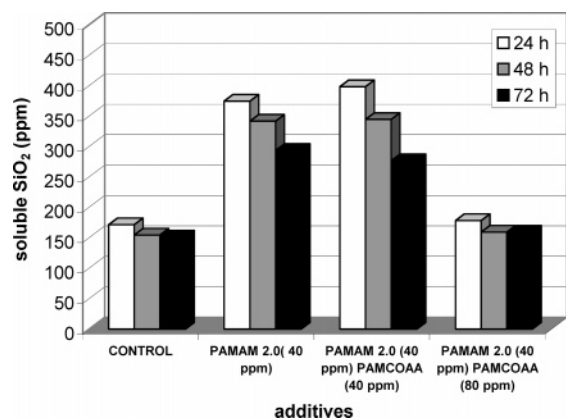


Figure 5. Effect of PAM-co-AA dosage on PAMAM-2 inhibitory action.

of the cleaning chemical. After appropriate dilutions are made, soluble silica is measured, and the results are compared to the expected value of 500 ppm SiO₂. Additives that interfere with the silica measurement test are rejected.

Results

High dissolved silica content in process waters used for industrial applications leads to supersaturation and

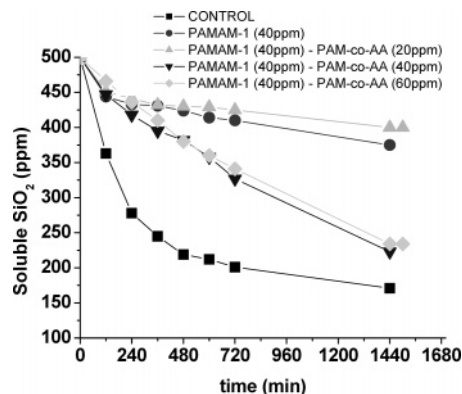


Figure 6. Effect of PAM-co-AA dosage on PAMAM-1 inhibitory action within the first 12 h.

formation of colloidal silica that deposits onto critical surfaces, forming hard and tenacious deposits that are not easily removed.²² Silica scale may require unconventional means for its mitigation and control. Certain approaches utilize polymeric chemical additives (often based on modifications of the commonly used polyacrylates) to “condition” the water to prevent silica scale formation and deposition, albeit with partial success.^{23–25} Silica and/or silicate deposits are particularly difficult to remove and usually require harsh chemical cleaning (e.g., with hydrofluoric acid) or mechanical removal (e.g., by sandblasting). The amorphous nature of silica renders crystal modifiers ineffective, because these molecules (usually phosphonates or mixed phosphonates/carboxylates) are active only on crystalline surfaces.²⁶ Their functionality lies with their ability to adsorb onto nanocrystalline nuclei and position themselves in such a way that eventually poison further crystal growth. Thus, discovery of molecules that would exhibit predictable inhibitory action in silica polymerization is a nontrivial task, and one may have to resort to potential inhibitors with “exotic” molecular structures.

Use of Dendrimeric Molecules in Synergism with Anionic Polyelectrolytes for Silica Scale Inhibition. The principal structural feature of a polyaminoamide (PAMAM) dendrimer is the growth of its branches around a central core (in this case, an ethylenediamine) via amide chemical linkages.²⁷ 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. We recently reported our initial results on the use of dendrimers for silica scale control.^{17–19} Those findings revealed that the –COOH terminated dendrimers (generations 0.5, 1.5, and 2.5) show virtually no activity as inhibitors. In contrast, the –NH₂ terminated analogues (generations 1 and 2) are potent SiO₂ scale inhibitors. Schematic structures of PAMAM-1 and 2 dendrimers are shown in Figure 1.

Despite the excellent performance of PAMAM 1 and 2 as colloidal silica growth inhibitors, these dendrimers suffer from a serious disadvantage: the silicate levels that are not inhibited lead to formation of large colloidal silica particles that entrap the dendrimers.²⁸ This also leads to active inhibitor depletion from solution, resulting in drop of inhibitory activity in the bulk. Visual observations show that these particles appear as white flocculent precipitates at the bottom of the test containers (vide infra in Figure 8). Chemical analyses of these amorphous precipitates (as proven by X-ray Diffraction

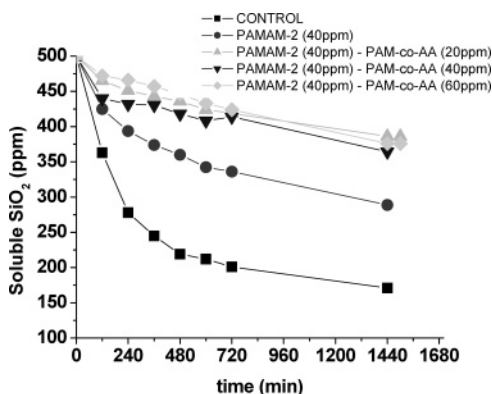


Figure 7. Effect of PAM-*co*-AA dosage on PAMAM-2 inhibitory action within the first 12 h.

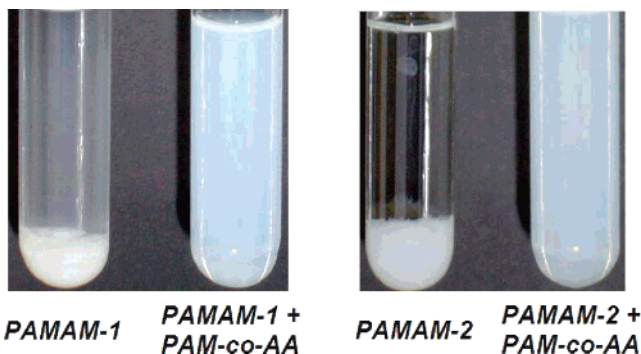


Figure 8. Visual observations of the effect of PAM-*co*-AA on dispersing SiO₂-PAMAM precipitates.

studies on powdered samples²⁸) showed that they are mainly composed of SiO₂ (>90%), with the remaining being organic material, undoubtedly dendrimer. EDS²⁸ and FT-IR spectroscopy also verified the dominant presence of SiO₂ (several characteristic bands²⁸), but also proved the presence of entrapped PAMAM dendrimers (the amide $\nu(\text{C}=\text{O})$ appears at 1645 cm⁻¹).

Formation of SiO₂-PAMAM precipitates occurs due to association of anionic silica particles and cationic PAMAM-1 or 2 dendrimers. To combat this problem, we resorted to utilization of anionic polymer additives that could work in synergism with the dendrimer inhibitors. Herein, we describe the effect of a poly(acrylamide-acrylate) copolymer (PAM-*co*-AA, Figure 2) on dendrimer PAMAM-1 or 2 inhibitory performance. Figure 3 shows results obtained from experiments performed where both PAMAM dendrimers and PAM-*co*-AA were both present in solution. It is obvious that the inhibition activity of all -COOH terminated dendrimers is indistinguishable from the control. It should be noted that PAMAM-0.5, 1.5, and 2.5 exhibit virtually no inhibitory activity when used alone. Addition of PAA (Figure 2) or other anionic polyelectrolytes has a similar synergistic effect; however, this will be described in more detail in a future publication.

In contrast, solutions containing either PAMAM-1 or 2 show remarkably high levels of soluble silica. When PAMAM 1 is used at 40 ppm levels together with 40 ppm PAM-*co*-AA, 359 ppm of soluble silica is measured within 24 h. This level drops at 299 and 265 ppm after 48 and 72 h, respectively. This drop in soluble silica levels occurs invariably regardless of the presence of inhibitor. When PAMAM 2 is used with PAM-*co*-AA, 398 ppm soluble silica is measured after 24 h, 344 ppm after 48 h, and 276 ppm after 72 h. It is worth mentioning

that soluble silica levels are higher in solutions containing PAMAM 2 + PAM-*co*-AA than those containing PAMAM-1 + PAM-*co*-AA.

The effect of PAM-*co*-AA dosage was studied in more detail. Results presented in Figures 4 and 5 show that, by comparison, PAMAM-1 is a slightly better inhibitor than PAMAM-2. When PAMAM-1 (40 ppm) is combined with PAM-*co*-AA (40 ppm), its activity slightly drops from 384 ppm soluble SiO₂ to 359 ppm (in 24 h). When an 80 ppm dosage of PAM-*co*-AA is used, the activity drops dramatically to 226 ppm (in 24 h).

Combination of 40 ppm of PAM-*co*-AA and 40 ppm of PAMAM-2 actually slightly increases its performance from 374 ppm (when PAMAM-2 is applied alone) to nearly 400 ppm. However, a dosage increase of PAM-*co*-AA to 80 ppm has an adverse effect and considerably decreases activity down to 178 ppm in 24 h.

The effect of PAM-*co*-AA polymer was also investigated within the first 12 h of silica formation. The results are shown in Figures 6 and 7. This time, polymer dosages of 20, 40, and 60 ppm were studied, while dendrimer dosage was maintained at 40 ppm. Use of 20 ppm PAM-*co*-AA appears to have no significant effect on the performance of PAMAM-1 within the first 240 min. There is some differentiation in inhibitory activity from 240 to 720 min. The combination 40 ppm PAMAM-1 + 20 ppm PAM-*co*-AA maintains 425 ppm soluble silica after 720 min, as compared to 410 ppm when PAMAM-1 is used alone. Combinations of 40 ppm PAMAM-1 + 40 ppm PAM-*co*-AA and 40 ppm PAMAM-1 + 60 ppm PAM-*co*-AA present almost indistinguishable inhibitory activity. There is a clear drop in maintaining soluble silica, achieving ~330 ppm after 720 min. It should be noted, however, that these combinations maintain 130 ppm soluble silica over the control.

Combinations of PAM-*co*-AA and PAMAM-2 present some interesting features that are different from those with PAM-*co*-AA and PAMAM-1. All dosages of PAM-*co*-AA appear to exhibit an effect similar to the performance of PAMAM-1. Drop of inhibitory activity is not observed even with the highest (60 ppm) polymer dosage (Figure 7). It is important to notice that the inhibitory activity of PAMAM-2 actually increases in the presence of PAM-*co*-AA, in contrast to PAMAM-1 that is less active with PAM-*co*-AA (except for the case where 20 ppm PAM-*co*-AA dosage is used).

PAM-*co*-AA is an anionic polyelectrolyte that readily associates with cationic PAMAM-1 or 2 in solution. Thus, its deprotonated -COO⁻ groups partially "neutralize" the positive charge on the dendrimer's peripheral -NH₃⁺ groups. This, in turn, alleviates formation of SiO₂-PAMAM precipitates. When the anionic polymer is added in excess (80 ppm), the negative charge exceeds the positive, resulting in deactivation of the dendrimer inhibitor with concomitant drop of inhibitory activity. It should be noted that presence of positively charged groups is not the only property necessary for activity. Studies²⁸ with cationic species such as NH₄⁺ or (CH₃CH₂)₄N⁺ as potential silica inhibitors show that these "small" cationic molecules are completely inactive in preventing silica polymerization. Positive charge sites in PAMAM-1 or 2 dendrimers are positioned in such a way that they effectively "interfere" with silicate ion polymerization, thus resulting in inhibition of silica growth. Therefore, the overall structure and topology of the inhibitor molecule certainly plays a profound role.

In Figure 8, dramatic visual observations of the effect of PAM-co-AA addition are shown. There is no precipitate formed except a light dispersion that does not settle, but persists for several months.

Use of Additives for Dissolution of Colloidal Silica. Dissolution of silica is hydrolysis driven. Addition of OH⁻ ions can dissolve silica at high pH regions.^{22,29} However, metallic corrosion of critical system components becomes an issue when silica deposit cleaning requires prolonged times and high concentration of OH⁻ ions. The acceptable “industry standard” for removing silica deposits is ammonium bifluoride, NH₄F·HF. Although the precise mechanism of action is not known, formation of soluble fluorine-containing Si compounds has been invoked.¹² This approach is not free of problems such as hazard potential and acid-driven metallic corrosion (because cleanings must be done at low pH's). Therefore, safer, more environmentally friendly ways to remove silica deposits are desirable.

Stirred suspensions containing colloidal silica and the dissolution additive at various concentrations are vigorously stirred at a fixed pH of 10 and then tested for soluble silica by the silicomolybdate spectrophotometric method^{30,31} after 24, 48, and 72 h of dissolution time. Results are presented in Table 1 and include performance characteristics of NH₄F·HF. This measurement methodology allows for determination of “soluble” or “reactive” SiO₂ after dissolution experiments are performed for at least 24 h at appropriate pH's, relevant to industrial water systems and applications. Colloidal silica is completely unreactive to the test.

After 24 h, in control solutions (no additive present) dissolution proceeds until ~120 ppm silica is solubilized (24%). Silica dissolution continues after 48 and 72 h, allowing soluble silica levels to increase to 150 ppm (30%) and 190 ppm (38%), respectively. Presence of 2500 ppm of any additive listed in Table 1 enhances silica dissolution within the first 24 h in a wide range, from 139 ppm (BTC) to 206 (L-histidine). This enhancement is more pronounced after 48 and 72 h of dissolution time. The fact that silica dissolution is enhanced in the presence of the additives described herein points to the hypothesis that the dissolution effect is not solely due to hydrolysis by OH⁻ ions.

Additive dosage appears to have an effect in only some cases. For example, in the case of acetic acid, dosage increase to 10 000 ppm results in silica dissolution enhancement that reaches 286 ppm (57%) in 24 h as compared to 151 ppm (30%) for the 2500 ppm dosage (an increase of 27%). Similar observations can be made for citric acid that solubilizes 380 ppm silica (76%) in 24 h. In the cases of oxalic acid, BTC, and DL-malate, dosage increase has only a marginal effect on dissolution. Higher dosages of ammonium fluoride have actually a detrimental effect on silica dissolution that is evident particularly in the 10 000 ppm case, allowing only 109 ppm silica to dissolve. Similar observations are noted for a dosage increase in NH₄F·HF.

Silica dissolution is also a factor of time. It is enhanced as dissolution time proceeds. The most dramatic demonstration of this effect is in the case of 10 000 ppm of DETPA that gives 206 ppm soluble silica after 48 h and 271 ppm SiO₂ after 72 h, an enhancement of 13%.

The effect of the number of -COOH groups present in the chemical structure of the cleaner molecule can be seen by examining Table 1. An increase in the

Table 1. Effect of Various Additives on the Dissolution of Colloidal Silica

dissolution additive ^a	pH	dosage (ppm)	soluble SiO ₂ (ppm)		
			24 h	48 h	72 h
control	10	0	120	150	190
		2500	151	219	254
		5000	154	216	199
acetate	10	7500	175	245	243
		10 000	286	367	360
		2500	164	220	241
		5000	165	217	205
oxalate	10	7500	198	246	193
		10 000	155	219	239
		2500	142	226	267
		5000	186	228	271
citrate	10	7500	166	216	253
		10 000	380	370	407
		2500	139	202	246
		5000	140	226	228
BTC ^b	10	7500	146	198	219
		10 000	147	210	202
		2500	305	301	308
		5000	340	345	348
EDTA ^c	10	7500	347	363	391
		10 000	341	371	381
		2500	191	281	275
		5000	237	279	289
DETPA ^d	10	7500	322	340	333
		10 000	257	206	271
		2500	198	267	292
		5000	242	289	309
PBTC ^e	10	7500	274	316	341
		10 000	245	314	330
		2500	206	259	268
		5000	241	283	282
L-histidine	10	7500	249	298	304
		10 000	245	283	298
		2500	135	235	249
		5000	146	210	205
DL-malate	10	7500	147	227	213
		10 000	142	191	199
		0	17	51	10
		2500	506	409	501
ammonium bifluoride	4	5000	403	455	443
		7500	198	312	400
		10 000	87	110	67
		2500	276	281	285
ammonium fluoride	10	5000	289	305	309
		7500	219	265	279
		10 000	109	116	131
		2500	202	248	253
L-phenylalanine	10	5000	187	246	245
		7500	230	301	282
		10 000	231	264	264

^a The structures of all dissolver additives are given in the Supporting Information. ^b BTC = 1,2,3,4-butanetetracarboxylate. ^c EDTA = ethylenediamine-tetracarboxylate. ^d DETPA = diethylenetriaminepentaacetate. ^e PBTC = phosphonobutane-1,2,4-tricarboxylate.

number of -COOH groups does not have an obvious effect on dissolution efficiency. For example, acetate (one -COOH group) at 10 000 ppm dosage is more active than oxalate (two -COOH groups). EDTA (four -COOH groups) is more efficient than DETPA (five -COOH groups).

The nature of additional groups in the dissolver molecule also appears to be important. When one -COOH group is replaced with a -PO₃H₂ group in the molecule of BTC, the resulting structure, PBTC, appears to exhibit higher dissolution efficiency. L-Histidine and L-phenylalanine (one -NH₂ group at α-position to a -COOH group) are more active particularly in lower dosages than acetate that does not possess such structural features. Both PBTC and citrate possess three

–COOH groups, but differ in that PBTC has an additional $-\text{PO}_3\text{H}_2$ group, whereas citrate has a $-\text{OH}$ group. This difference allows PBTC to exhibit higher dissolution efficiency than citrate at dosages <7500 . However, at 10 000 ppm levels, citrate appears more effective.

Growth of crystalline scale deposits is controlled by use of phosphonate inhibitors,³² or polyacrylate polymers and derivatives.³³ Mineral scale inhibitors achieve inhibition by stereospecific adsorption onto crystallographic planes of a growing nucleus after a nucleation event, resulting in “poisoning” further growth and crystallite agglomeration.³⁴ The amorphous nature of silica scale in process waters renders the effectiveness of “classical” mineral scale inhibitors questionable. Control of silica scale can be achieved either by preventive approaches or dissolution techniques in the aftermath of scale deposition. Inhibition methods for silica scale are much less developed than those for “traditional” scales such as calcium carbonates and sulfates, barium and strontium sulfate, etc., that commonly involve use of chelants for metal ion abstraction through surface complexation.^{35,36} Therefore, available techniques for silica scale dissolution must complement the preventive methods.

Although the precise mechanism of colloidal silica dissolution is not known, it is established that hydroxyl ions play a catalytic role in the process.³⁷ It is reasonable to assume that chemical groups that are strongly anionic, such as $-\text{COO}^-$ and $-\text{PO}_3^{2-}$, may react with Si centers in the amorphous network of SiO_2 in a fashion similar to that of OH^- . Formation of silicate esters, $\text{R}-\text{C}(\text{O})\text{O}-\text{SiO}_x$, may be a possibility, and such possible pathways are currently investigated. Literature examples of such Si–O interactions either in the solid state or in solution include silicate-oxalic acid,³⁸ silicate-tropolone and silicate-3-hydroxypyridine-4-one,³⁹ silicate-catechol,^{40–46} and silicate-pyrogallol.⁴⁷

Discussion

Formation of colloidal silica is a result of several, complicated equilibria.⁴⁸ These are sensitive to solution pH and temperature and tend to be affected by the presence of metal ions that form hydroxides, e.g., Fe^{3+} , Mg^{2+} , or Al^{3+} .^{49–53} The key step in silica formation is silicic acid self-condensation and is catalyzed by OH^- in the pH range of 5–10. Heterogeneous colloidal silica formation involves condensation between Si–OH groups formed at the material surface and Si–OH of dissolved silicate species present in bulk water.

Although silica polymerization is governed largely by pH, it is not an easily “cured” foulant by resorting to pH adjustments. Silica solubility is very high at pH's >10 , where it is mainly in the form of monomeric silicate, but this pH regime is impractical and is not an operational option for several water systems, including open recirculating cooling systems.

As monomeric silicate ion polymerizes, it forms a deposit on a solid surface where the $[\text{Si}(\text{OH})_{4-x}]^{x-}$ condenses with any solid surface possessing $-\text{OH}$ 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, and whose surface is covered with metal oxide/hydroxide films. Once the

receptive surface is covered with silica scale, additional silica layers are deposited on an already formed silica film.

The precise mechanism of silica inhibition is poorly understood. Any “interference” with the condensation reaction may lead to silica scale growth inhibition. A relevant example is silica inhibition by orthoborate ion, which reacts with soluble silicate ions (monomeric or oligomeric) to form borosilicates.⁵⁴ These borosilicate products are more soluble in water than SiO_2 /metal silicates. PAMAM dendrimers combined with anionic polyelectrolytes seem to have a significant inhibitory effect on silica formation, most likely at its earlier stages where the reaction products are monomeric or oligomeric silicates.

Anionic PAM-co-AA assists the action of PAMAM-1 and 2 by alleviating formation of insoluble SiO_2 –PAMAM precipitates. This most likely occurs by partial neutralization of the positive charge that exists in $-\text{NH}_3^+$ surface groups. However, if PAM-co-AA dosage exceeds 40 ppm, the activity of PAMAM-1 and 2 drops dramatically. In that case, PAM-co-AA's negative charge “overwhelms” the dendrimer and poisons its inhibitory ability.

Colloidal silica dissolution is a challenging task when applied to deposits in process cooling systems. Alternative chemistries exploited herein involve polycarboxylates and carboxylate/phosphonate hybrids. These show variable activities, with 2-phosphonobutane-1,2,4-tricarboxylate being the most effective dissolver. Colloidal silica dissolution is catalyzed by hydroxyl ions. However, their function is assisted by the presence of additives in a fashion that is not entirely clear. Formation of silicate esters, $\text{R}-\text{COO}-\text{SiO}_x$, may be a possibility, and this will be examined by various spectroscopic methods in the future.

Conclusions/Perspectives

This work is part of our continuing research effort to identify and exploit novel chemical technologies to effectively control scale growth in process waters.^{17–21,55} The principle findings are summarized below:

- (1) PAMAM-1 and 2 (with $-\text{NH}_2$ surface groups) dendrimers are effective inhibitors of silica scale growth.
- (2) PAMAM 1 and 2 dendrimers form SiO_2 –PAMAM insoluble precipitates.
- (3) Combination of PAMAM-1 and 2 dendrimers with anionic polyelectrolytes such as PAM-co-AA inhibits these precipitates and results in stable colloids.
- (4) Additives that possess at least one $-\text{COOH}$ group are effective cleaners of silica scale at >2500 ppm dosage levels.
- (5) Their chemical structure affects dissolution performance.
- (6) Dosage increase improves performance only in some cases.
- (7) The presence of additional groups (e.g., $-\text{PO}_3\text{H}_2$, $-\text{NH}_2$, or $-\text{OH}$) in the dissolver molecule augments the dissolution process.

Scale inhibition by use of chemical additives is an established approach to control water-formed scale deposits. However, as pressure for water conservation is increased (particularly in arid areas), water reuse is an unavoidable choice by water system operators. This water recycling leads to increased dissolved solids levels, resulting, in turn, in troublesome mineral deposits that cannot be controlled by conventional inhibitors. Thus,

research to discover or design and synthesize new and improved chemical additives for scale inhibition is thriving. In addition, increased environmental concerns may soon mandate use of environmentally acceptable water additives that certainly draw increased attention from researchers in this field.

Colloidal silica deposits present a challenge for a plethora of industrial water applications including heat exchangers, reverse osmosis membranes, piping, etc. Inhibition or dissolution of such silica deposits by designed chemical approaches presents a number of issues that relate to performance and environmental compliance. "Green" inhibition and dissolution chemical technologies should be further developed, and this is an ongoing effort in our laboratories.

Acknowledgment

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Supporting Information Available: Detailed tables with all data described in the paper, spectroscopic characterization of silica-PAMAM precipitates, and effect of NH_4^+ and $(\text{CH}_3\text{CH}_2)_4\text{N}^+$ on silica polymerization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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