Additive-Driven Dissolution Enhancement of Colloidal Silica. 1. Basic Principles and Relevance to Water Treatment

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ABSTRACT: The effect of various chemical additives (small molecules and polymers) on the dissolution of two kinds of colloidal silica (Aerosil 200 and laboratory-synthesized, SSD) is systematically studied at pH 10. The silica scale dissolvers tested are 5-carboxybenzotriazole (**CBZT**), amino-tris(methylene phosphonic acid) (**AMP**), a phosphino-polycarboxylic acid (**PPCA**), diethylenetriamine pentacarboxylic acid (**DETPA**), a proprietary polymer (**Genesol 40**), poly(acrylic acid) (**PAA**), ethylenedia-mine-tetrakis(methylenephosphonic acid) (**EDTMP**), phosphonobutane-1,2,4-tricarboxylic acid (**PBTC**), sodium metaborate, and *N*-phosphonomethylimino-diacetic acid (**PMIDA**). Of the polymeric additives only **Genesol 40** shows some dissolution activity, dissolving ~280 ppm silica at 10 000 ppm dosage after 72 h. **PBTC** and **DETPA** are the best-performing additives of all those tested. **PBTC** is effective even at the 2500 ppm dosage, as it solubilizes ~290 ppm silica after 72 h. Its efficiency is dosage-dependent. **DETPA** is also an effective silica dissolver. Its behavior is similar to that of **PBTC**. Its best dosage is 7500 ppm, which yields dissolution of 322 ppm silica (after 24 h), 340 ppm (after 48 h), and 333 ppm (after 72 h). SSD silica is a very recalcitrant deposit showing resistance to dissolution even by the most effective additives, **PBTC** and **DETPA**.

■ INTRODUCTION

Silicon is an important element, as it is often used as silica (SiO_2) by several living organisms (mainly diatoms and sponges) in their skeleton.[1] Although the factors that govern formation of biosilica have been at the epicenter of intense research efforts, several aspects of the seemingly simple transformation of silicic acid to silica are still a challenge. On the other hand, the reverse process, silica dissolution to give silicic acid, $Si(OH)_4$ (often called desilicification[2]), has also attracted the attention of several researchers. Desilicification is an important step in silicon recycling on the planet.[3] Often desilicification is induced by bacteria. For example, dissolution of diatom biogenic silica in estuaries and its control by water salinity and bacteria were investigated using the river euryhaline species *Cyclotella mene-ghiniana* as a model.[4] Experiments were also performed in order to remove silicates from an oil shale by a chemoorganohetero-trophic bacterium, *Bacillus circulans*.[5] In addition, the ability of diatoms to dissolve silica has been demonstrated.[6] Also, a technique was reported related to a dissolution study of un-cleaned frustules of *Cyclotella cryptic*.[7]

Colloidal silica also appears as a problematic deposit in industrial water systems. Water is a universal cooling medium because of its cost-effectiveness and high heat capacity.[8] Increasing pressure for water conservation together with environmental concerns has forced operators to limit water discharge and reuse "spent" process water. Water recycling leads to an increase of the concentration of dissolved species to a critical point of precipitation/deposition of insoluble mineral salts. Scale formation is a technical challenge for industrial process water operators and a financial burden for all industries that use water to support their operations.[9]

The chemical nature of scale depends on water chemistry. Carbonates,[10] sulfates[11] and phosphates,[12] colloidal silica,[13] and metal silicates[14] constitute a representative sample of such field deposits. Scale deposit prevention benefits water operators by minimizing the risk for unexpected production shut-downs. In arid areas with high water costs substantial savings can be gained through water conservation.

Colloidal silica deposits present are the most recalcitrant in water treatment and have been called "water treatment's Gordian knot".[15] Such undesirable deposition problems can be avoided after application of chemical water treatment techniques that commonly involve use of additives as inhibitors. Scale control additives are fed into the water in "ppm" quantities and enhance saturation limits of sparingly soluble salts. There is active research that embraces design, discovery, and application of such additives that are nontoxic and readily biodegradable.[16]

Occasionally, preventive measures for scale control fail due to several reasons including instrument malfunction, pH upsets, incompatibility of treatment additives, or human error. At times, system operators are faced with the difficult task of removing hard and tenacious scale deposits from critical equipment surfaces. Silica deposits can be cleaned mechanically by labor-intensive "sandblast-ing", or chemically with $NH_4 \cdot HF_2$ (ammonium bifluoride), a process that presents hazard risks.[17] Therefore, an integrated chemical water treatment approach must include contingencies that consider chemical cleaning as a "recovery option" after a scaling/deposition event.

Silicic acid polymerizes via condensation polymerization at appropriate pH regions (the pH range 7—10 is relevant to water treatment applications). The product of this polymerization event is a hydrated silica precipitate that transforms into a recalcitrant and tenacious deposit on critical industrial equip-ment. Silica removal by dissolution is a challenge, and the usual
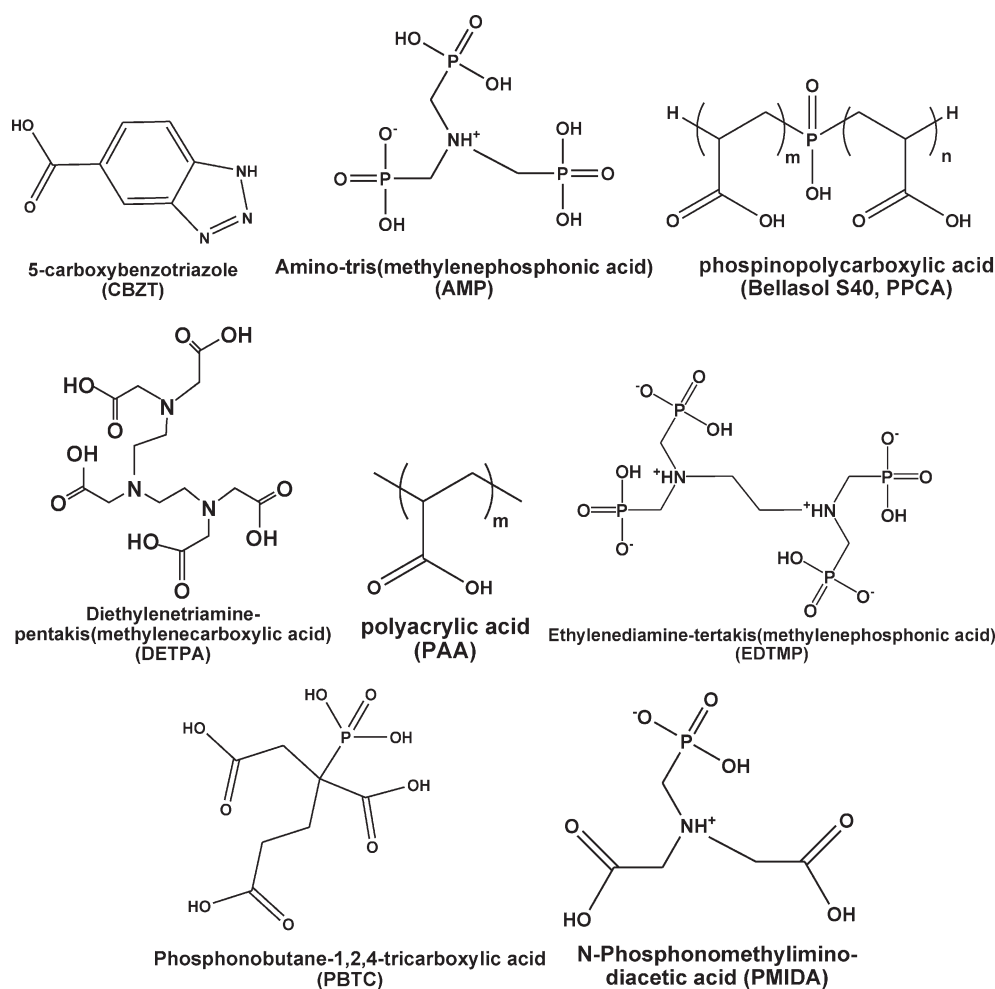
Figure 1. Schematic structures of silica dissolution agents used in this study.

approaches to control it are avoiding supersaturation (leading to water wastage) or pretreatment (with high equipment costs).

Our research is concerned with scale inhibition and dissolution strategies with emphasis on utilization of environmentally benign additives, wherever possible.[18] This paper is the first of a three-part series that deals with some fundamental and practical aspects of silica dissolution. In the first part (this work) we are presenting several desilicification results by a variety of chemical additives in an attempt to identify which chemical groups are important for silica dissolution. In part 2, we focus on environmentally friendly (green) additives. In part 3, we will deal with fluorine-containing additives, in an effort to delineate mechanisms that govern silica dissolution by $NH_4 \cdot HF_2$ (the accepted "industrial standard") and compare it with other F-containing molecules. Parts 2 and 3 will be submitted in due course.

In the present study we used several chemical additives, whose schematic structures are shown in Figure 1.

■ EXPERIMENTAL SECTION

Instruments. IR spectra were recorded on a FT-IR Perkin-Elmer FT 1760 in KBr discs. The measurements of soluble silicic acid were performed on a HACH 890 spectrophotometer from the Hach Co., Loveland, CO. SEM images were collected on a scanning electron microscope LEO VP-35 FEM.

Reagents and Materials. All dissolution additives tested herein are from commercial sources and are used as received. All acidic dissolvers were added to the dissolution reaction medium as acids. They all exist in their deprotonated form at the experiment pH (10.0).

Model colloidal silica is Aerosil 200 from Degussa (water content ~1.5%, BET surface area 200 ± 25 m^2/g). The choice of Aerosil 200 was based on its high surface area and absence (by powder X-ray diffractometry) of crystalline phases. The reagents needed for the silicomolybdate test were prepared as follows: (a) A 10 g sample of ammonium molybdate was dissolved in 100 mL of water, and its pH was adjusted between 7 and 8 with NaOH to avoid precipitation of ammonium molybdate. This solution was kept in an airtight PET container in the refrigerator. (b) HCl 1 + 1 is prepared by mixing one volume 37% HCl with equal volume water. (c) An 8.75 g sample of oxalic acid was dissolved in 100 mL of water. All solutions were kept in PET containers (glass containers must be avoided in order to minimize SiO_2 dissolution and silicate leaching into the test solutions).

Preparation of Synthetic Silicon Dioxide (SSD). A quantity of $NaSiO_3 \cdot 5H_2O$ (5 g) was dissolved in 90 mL of nanopure water at ambient temperature. The pH of the solution was adjusted to 7.0 ± 0.1 by addition of 80% v/v HCl solution under vigorous stirring. At this point a gel formed, as the solution volume reached ~100 mL. Within 10 min stirring was not possible,
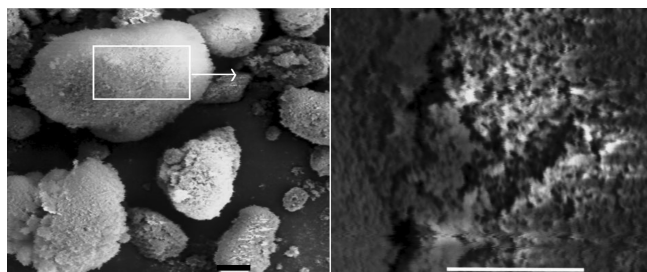
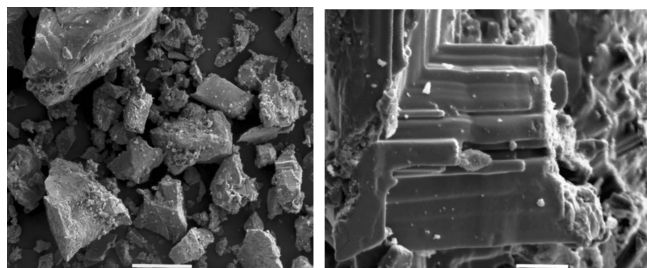**Figure 2.** SEM images of Aerosil 200. The bars on the images are both 10 μm.

Figure 3. SEM images of SSD (synthetic silicon dioxide). The bars on the images are 100 μm for the left, and 10 μm for the right image.

and the reaction was stopped. The gel was then dried in the oven at 85 °C overnight to yield a white solid. This was ground to a fine powder and then washed with copious amounts of nanopure water to remove byproduct NaCl, and finally dried again in the oven for 24 h. Water content was determined to be ~1.5—2.0% (by thermogravimetry) due to rapid surface adsorption of water. BET surface area was measured to be ~100 ± 30 m^2/g.

Silica Dissolution Protocol. Glass containers must be avoided in order to minimize silica leach-out. A quantity of colloidal silica corresponding to 500 ppm as silica (for 100 mL final solution volume the calculated silica weight is 50 mg) is placed in a polyethylene container together with 80 mL of deionized water and a dosage of specific chemical additive (2500—10 000 ppm, depending on the specific run). We chose to calculate additive dosages based on "ppm" rather than "mg" or "mmol" in order to be consistent with the nomenclature used in the water treatment field. Then, solution pH is adjusted to 10.0 by use of NaOH solution (10% v/v). The specific pH (10.0) was chosen for the following reasons: (a) This is the maximum operational pH for real water systems that operate without pH control. (b) All dissolution additives are in their deprotonated state at that pH. (c) Also, preliminary experiments (not reported here) showed that the SiO$_2$ dissolution rates are too slow for any practical experimental setup. Finally, solutions were diluted up to 100 mL and kept under continuous stirring for a total of 72 h. Soluble silica measurements on small samples withdrawn are made at 24, 48, and 72 h with the silicomolybdate spectrophotometric test.[19] After each measurement pH is again checked, and in the case of pH shift from the target value a readjustment is made. Such deviations were seldom. Dissolution experiments were also run at shorter times (8 h), and sampling was more frequent (every 1 h).

Interference Test. Every cleaning additive is tested for its interference with the silicomolybdate spectrophotometric test. A stock solution (500 ppm, expressed as "ppm SiO$_2$") of soluble silica (prepared from commercial sodium silicate) is prepared by dissolving 4.4 g of Na$_2$SiO$_3$·5H$_2$O in 2.5 L of nanopure water.
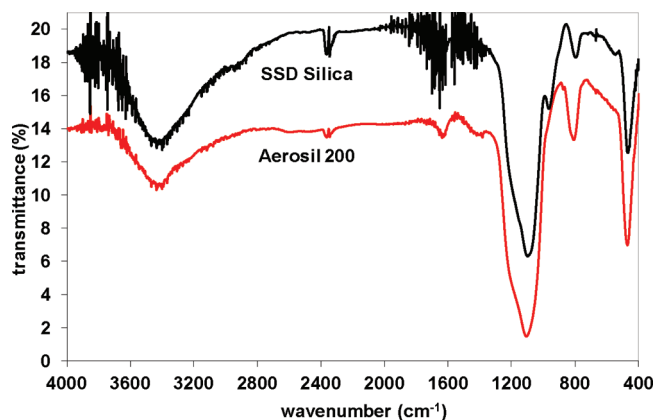

Figure 4. FT-IR spectrum of Aerosil-200 and laboratory-synthesized SSD silica in KBr pellets.

Table 1. Band Assignments in the FT-IR Spectrum of a Aerosil-200 or SSD

vibration (cm^{-1})	band assignment
3600—3300	water stretching bands + ν(O—H) from Si—OH
1650	H$_2$O deformation
~1208 (sh)	asymmetric stretching Si—O and Si—O-(Si)
1124	asymmetric stretching Si—O and Si—O-(Si)
973 (sh)	Si—O$^-$ asymmetric
820	Si—O$^-$ symmetric
479	O—Si—O deformation

The pH of the above solution was 11.50. To 100 mL of that solution is added a dosage of the cleaning chemical (2500—10 000 ppm). After appropriate dilutions are made, soluble silica is measured with the silicomolybdate spectrophotometric test.[19] The results are compared to the expected value of 500 ppm. Additives that interfere with the silica measurement test are rejected. Results showed that **AMP** and **EDTMP** above the dosage of 5000 ppm interfere with the silica quantification.

■ RESULTS

Characterization of Aerosil-200 and SSD. Both Aerosil 200 and SSD silica were characterized by SEM, EDS, and FT-IR. The SEM images for both silica samples are shown in Figures 2 and 3. Those in Figure 2 (especially the left image) show that silica particles are nonuniform in size and have rounded corners. Their texture appears smooth; however, upon higher magnification the particles appear porous. This feature will prove significant (*vide infra*).

Particles of SSD silica are also irregular and nonuniform. Their surface is smooth, as evidenced by the right image in Figure 3.

Both Aerosil-200 and SSD silica exhibit identical FT-IR spectra, shown in Figure 4, and the band assignments are in Table 1. The positions and peak intensities agree very well with spectral characteristics published in the literature.[20] Integration of the broad band in the region 3000—3700 cm^{-1} assigned to absorbed water shows that SSD silica has ~60% more water than Aerosil 200. Sample characterization by EDS showed presence of Si and O at the expected levels (data not shown).

Effect of Additives on Silica Dissolution during "Long-Term" Experiments. In the experiments described herein stirred
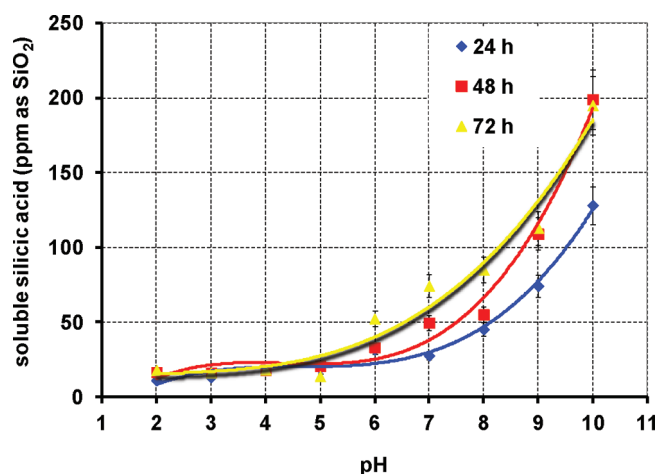
Figure 5. Effect of pH on colloidal silica dissolution.

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[19] after 24, 48, and 72 h (long-term experiments), or every hour for 8 h (short-term experiments) of dissolution time. We first studied the effect of pH (in essence of OH^- anions) on silica dissolution (Aerosil 200). The results are shown in Figure 5. It is apparent that at pH regions <5 silica dissolution does not take place. Upon pH increase there is a dissolution enhancement, which reaches ∼200 ppm levels at pH 10. Silica dissolution is also time-dependent, and requires prolonged contact times.

The results of silica dissolution in the presence of silica dissolvers are presented in Figure 6. The measurement methodology followed for silica is based on the quantification of "soluble" (or "reactive") silica after dissolution experiments are performed for at least 24 h. Colloidal silica is completely unreactive to the silicomolybdate spectrophotometric 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. These results obtained for silica dissolution in the absence of any additives need to be surpassed by satisfactorily performing additives. Examination of Figure 6 shows that additives **AMP**, **PMIDA**, and **PAA** are not effective silica dissolvers. In the case of AMP the drop in silicic acid levels as the dose of **AMP** increases is due to the interference of **AMP** with the quantification test. Soluble silica levels in the presence of **PAA** are lower than those in "control" solutions. The proprietary polymer **Genesol 40** shows a dose-dependent cleaning performance, as silicic acid levels increase with its dosage. It gives best results at 10 000 ppm dosage after 72 h. **PPCA**, a phosphino-polycarboxylate polymer, reacts very slowly with colloidal silica, as evidenced by the virtual absence of dissolution activity in the first 48 h. After 72 h and at doses of >5000 ppm, it achieves ∼250 ppm silica dissolution. Besides the **AMP** triphosphonate, **EDTMP** (a tetraphosphonate) was also tested. **EDTMP** is a very effective silica dissolver even at "lower" doses, as it achieves solubilization of ∼300 ppm silicic acid at 2500 ppm dose. Unfortunately, as its level increased in experiments with higher doses of **EDTMP**, its interference with the silicomolybdate test did not allow further quantification of its efficiency. **CBZT** achieves

dissolution of ∼240 ppm silica at 2500 ppm levels, but its performance does not improve upon dose increase.

The behavior of sodium metabate as silica dissolver is dose dependent. At 2500 ppm levels it does not affect silica dissolution. However, at 5000 ppm levels it achieves dissolution of ∼250 ppm of silicic acid. Further dose increase to 10 000 ppm does not improve performance.

Lastly, the polyanionic dissolvers **PBTC** (a phosphono-tricarboxylate) and **DETPA** (a pentacarboxylate) were both very effective dissolvers. **PBTC** is effective even at the 2500 ppm dosage, as it solubilizes ∼290 ppm silica after 72 h. Its efficiency is dosage-dependent. At 7500 ppm concentration it indices dissolution of 274 ppm silica (after 24 h), 316 ppm (after 48 h), and 341 ppm (after 72 h). Further additive concentration increase is not advantageous. **DETPA** is also an effective silica dissolver. Its behavior is similar to that of **PBTC**. Its best dosage is 7500 ppm, which yields dissolution of 322 ppm silica (after 24 h), 340 ppm (after 48 h), and 333 ppm (after 72 h).

Effect of Additives on Silica Dissolution during "Short-Term" Experiments. From the additives presented above, we selected the most effective ones for further study. Thus, the dissolution efficiency of **PBTC** and **DETPA** was studied in "short-term" experiments, in which solution sampling was done every hour for the first 8 h of the dissolution reaction. The results are shown in Figure 7.

The above curves clearly indicate that the dissolution is faster for **PBTC** than for **DETPA** during the first stages. For **PBTC** there is a discernible differentiation of dissolution efficiency between different doses (something that is also reflected on the 24 h results in the "long-term" experiments). This differentiation is poor in the case of **DETPA**.

Differences in Dissolution between Aerosil 200 and SSD Silica. An interesting theme to explore is whether the silica features play a role in dissolution rates. Thus, we compared the dissolution efficiency of **PBTC** on two kinds of silica, Aerosil 200, and laboratory-synthesized (SSD) silica. The results are given in Figure 8, and they are quite revealing. SSD silica is poorly responsive to dissolution by hydroxyl ions at pH 10. In fact, after 24 h only ∼90 ppm are dissolved, in comparison to dissolution of ∼130 ppm of Aerosil 200 under the same conditions. SSD is also unresponsive to dissolution induced by **PBTC**. The dissolution efficiency barely exceeds that of the control. At the high dose of 10 000 ppm, **PBTC** can dissolve ∼180 ppm silica after 72 h. Compare this to dissolution of 330 ppm Aerosil 200 under the same experimental conditions.

The textural features of SSD silica are most likely responsible for the fact that it is recalcitrant to dissolution. As shown in Figure 3 SSD particles appear dense and compact, in contrast to hose of Aerosil 200. The surface area of Aerosil 200 is approximately double that of SSD silica. Therefore, the particle coverage in the case of Aerosil 200 is much more effective than that of SSD silica. In both cases additives cannot penetrate into the particle, but can only achieve dissolution through surface interactions.

■ DISCUSSION

Silica dissolution is driven by hydrolysis according to the following reaction:[21]

$$SiO_2(s) + 2H_2O \rightarrow Si(OH)_4$$
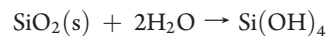
Enhancement of silica dissolution is directly proportional to pH increase, as shown in Figure 5. However, silica deposit

chemical cleaning, which requires prolonged contact times and high levels of OH$^-$ ions, is not a simple task. This is because at high pH regions metallic corrosion of critical system components becomes a significant issue. The "industry standard" for removing silica deposits is ammonium bifluoride, $NH_4 \cdot HF_2$. Although the mechanism of action is not precisely known, formation of water-soluble fluorine-containing "Si compounds" in acidic pH regions has been invoked.[17] A detailed study of the effects of $NH_4 \cdot HF_2$ on silica dissolution will be presented in part 3 of this series. In spite of the effectiveness of $NH_4 \cdot HF_2$, meticulous attention needs to be paid to issues such as hazard potential (generation of HF *in situ*) and acid-induced metallic corrosion (cleanings must be performed at low pH's). Therefore, alternative and more environmentally friendly ways to remove silica deposits are being sought. This series of three papers is a continuation of our studies on chemical dissolution of silica.[22]

The mechanism of hydroxyl ion-induced silica dissolution has been studied.[23]

$$\equiv Si\text{-}O\text{-}Si \equiv \; + H_2O \xrightarrow{\;OH^-\;} 2 \equiv Si\text{-}OH$$
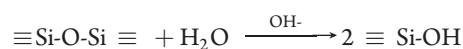
OH$^-$ acts as a nucleophile attacking a tetrahedral Si center on the surface of a silica particle. This can be schematically shown in the following, Figure 9.

It is therefore possible to visualize a similar attack mechanism with the participation of a carboxylate or a phosphonate group, as shown in Figure 10. This concept also takes into account literature reports, see below.

Similar reaction pathways have been proposed by Lambert et al. for an alkoxide-type attack,[24] by Ansell et al. for a carboxy-type attack,[25] and by Quin et al. for a phosphonate attack on silica surface.[26]

Polymeric additives are in general poor silica dissolvers. This may be due to poor interaction of the polymeric chain with the
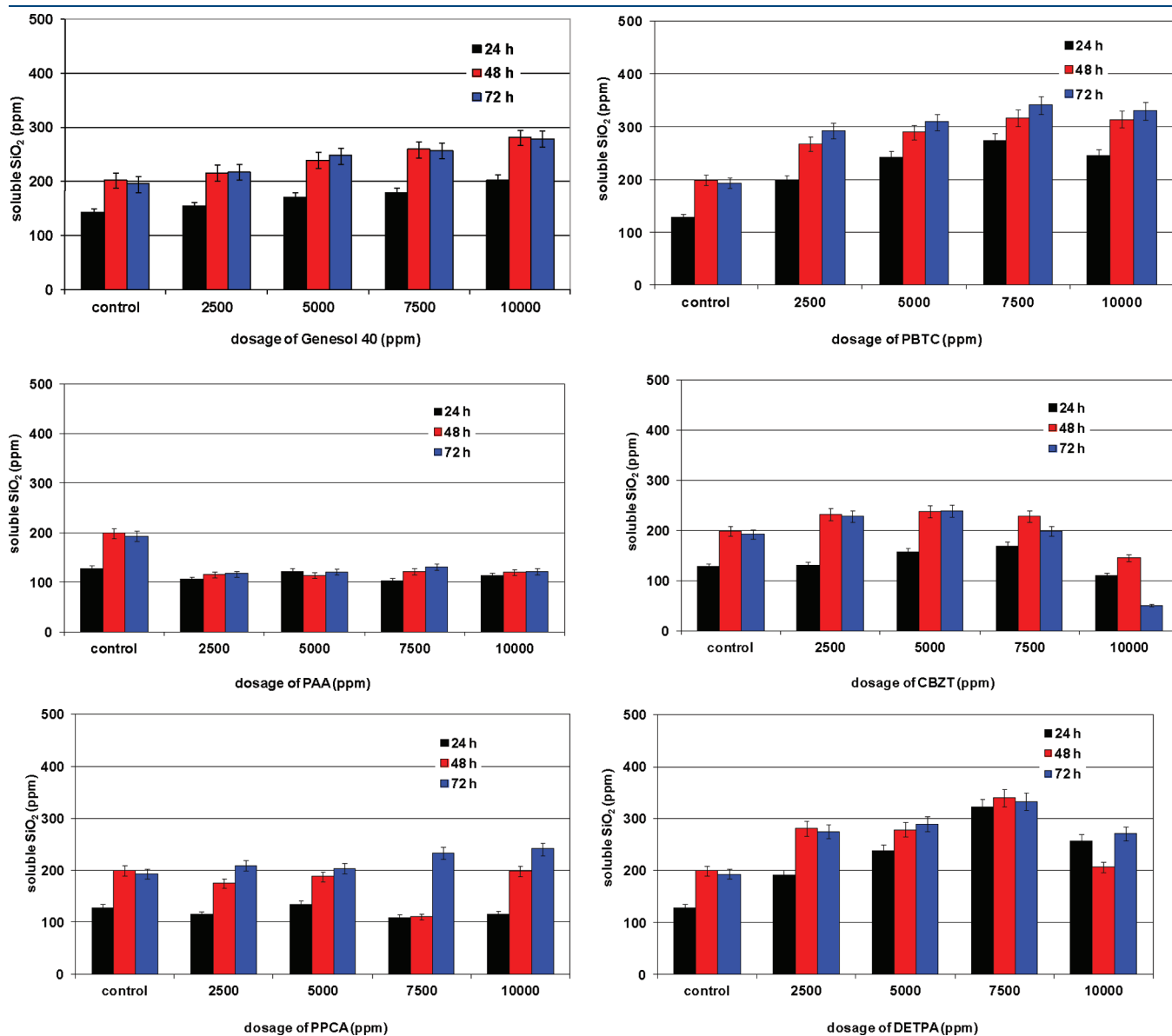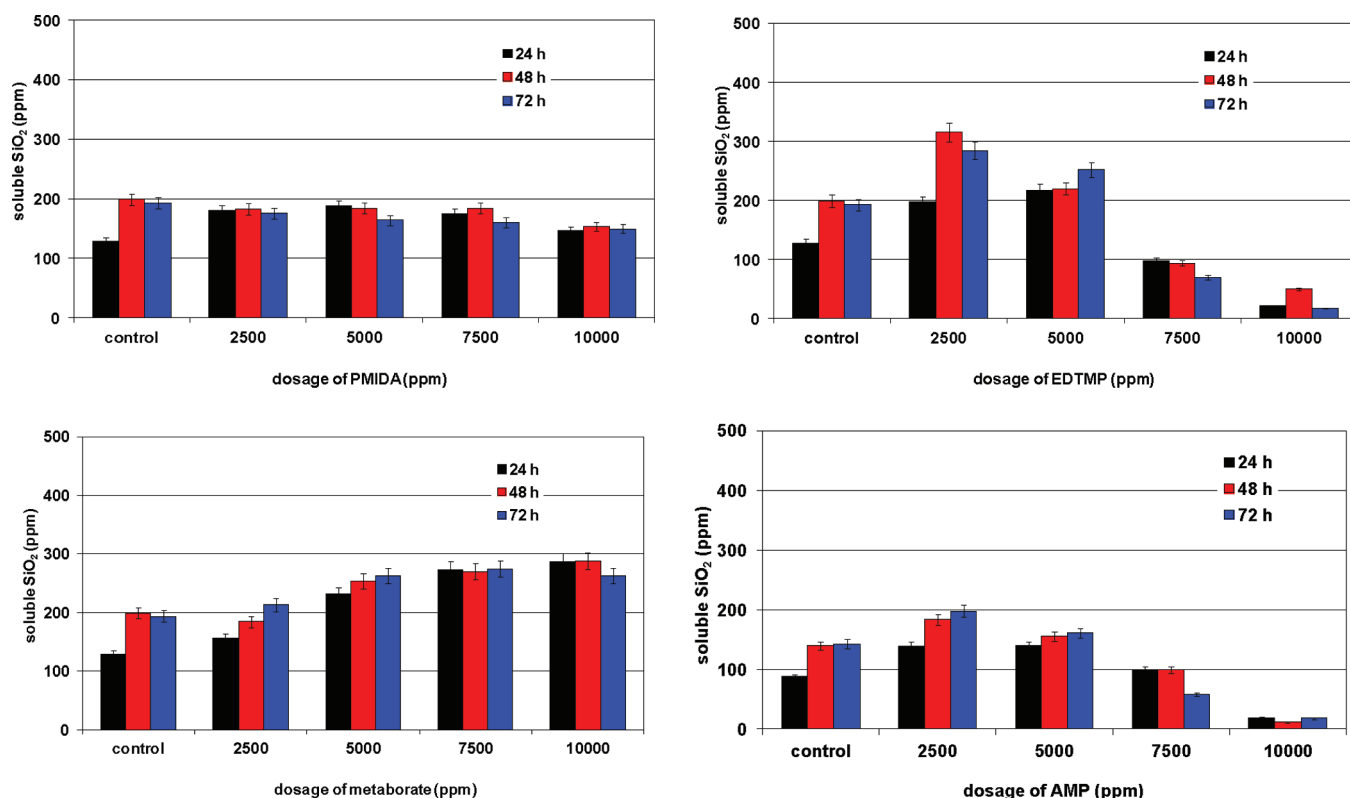

Figure 6. Continued

Figure 6. Dose−response graphs of silica dissolution experiments for various additives, as indicated.

silica particle surface. The anionic polyelectrolytes contain carboxylate groups that are attached onto a polymeric chain, whose limited motion in solution renders itself an ineffective nucleophilic reagent. **CBZT** contains a deprotonated −COO⁻ group, which could attack the silica surface. However, the presence of the aromatic fused system renders the −COO⁻ group less nucleophilic and less prone to attack a Si center. Sodium metaborate is more effective at >5000 ppm dosage, and this may be due to formation of borosilicate species in solution, as reported before.[27]

The phosphonate additives, **AMP** and **EDTMP**, are poor silica dissolvers, with the exception of **EDTMP** at 2500 ppm dosage. It is possible that these additives that have exclusively phosphonate groups on their backbone are not effective because they form stable covalent bonds with the silica surface and remain attached onto the particle.[28] In a sense, they "protect" the silica particle from further attack.

In order to carry out a more useful comparison between the various additives, a graph can be constructed that presents the dissolution efficiency of all additives. Dissolution efficiency is defines as follows:

$$\text{dissolution efficiency (\%)} = \frac{(A - C)}{(500 - C)} \times 100$$

Here, A is the measured soluble silicic acid at 72 h (in ppm) after dissolution by an additive at 5000 ppm dosage, and C is the measured soluble silicic acid at 72 h (in ppm) after dissolution for the "control" (no additive present).

The results of such calculation are presented in Figure 11.

Mechanistically, the additive must first interact with the silica particle in a "surface complexation" fashion. In order to confirm that during the initial stage of silica dissolution the additive has to approach and interact with the silica surface, we carried out an experiment in which the silica surface was first protected by a cationic polyelectrolyte. Colloidal silica was first reacted with a cationic polymer, polyethyleneimine, PEI (MW 10 000 Da, containing primary, secondary, and tertiary amine groups in approximately 25/50/25 ratio).[22b] Attachment of cationic polymers onto silica surfaces is well established.[29] Coverage of the silica surface by the cationic polymer would be expected to block and inhibit surface complexation by the dissolution additive. The dissolution protocol described in the Experimental Section was followed. Indeed, silica dissolution (no dissolvers present) dropped to 16% efficiency in 24 h, in the presence of 500 ppm PEI, compared to 24% with no PEI present. Even in the presence of **PBTC** (2500 ppm), dissolution only reached 69 ppm silica within 24 h (14% efficiency), compared to 198 ppm (40%) for uninhibited silica. Higher **PBTC** dosages did not show any beneficial effect in increasing soluble silica levels. It appears that blockage of the silica surface by cationic polymers is an irreversible process and is not alleviated by dosage increase of **PBTC**.

It was stated before that an increase in the number of −COOH groups on the dissolver backbone does not have an obvious effect in dissolution efficiency.[22b] 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 that **DETPA** (five −COOH groups). The nature of additional groups in the dissolver molecule also appears to be important. When −COOH and −PO₃H₂ groups

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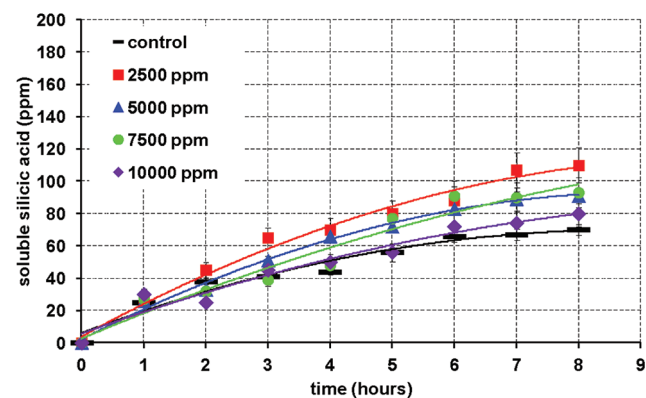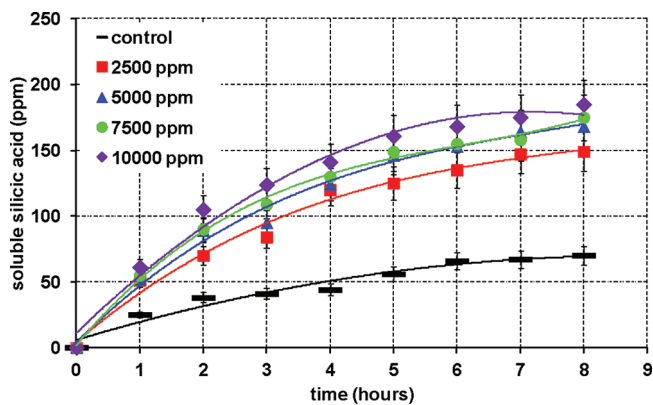dx.doi.org/10.1021/ie201703b |*Ind. Eng. Chem. Res.* 2011, 50, 12587–12595

Figure 9. Attack of an OH⁻ anion on a surface exposed Si center.

Figure 7. Silica dissolution by **PBTC** (upper) and **DETPA** (lower) during the first stages (8 h).
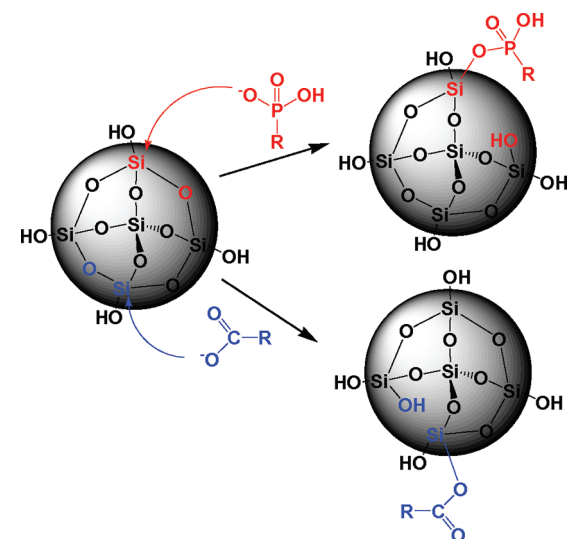
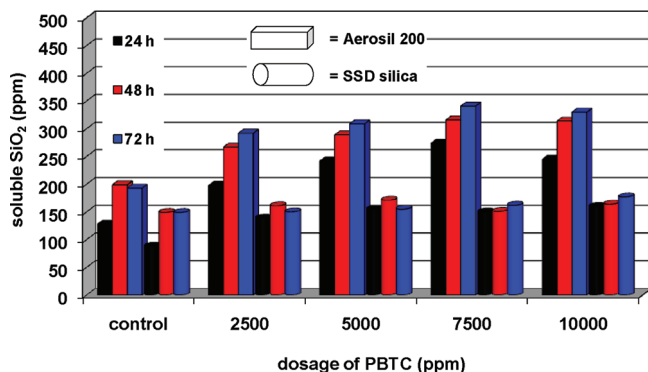**Figure 10.** Attack of a −COO⁻ or a −PO₃H⁻ anion on a surface exposed Si center.

Figure 8. Comparison of dissolution efficiency of **PBTC** on two kinds of amorphous silica: parallelepipeds, Aerosil 200; cylinders, SSD silica.
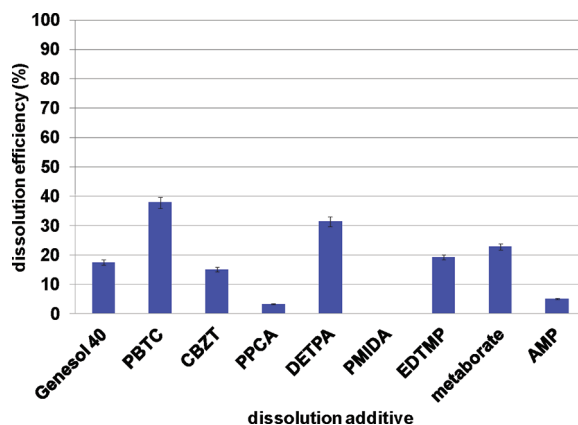
Figure 11. Dissolution efficiency for the additives tested in this work.

are present in the same molecule, **PBTC**, there appears to be higher dissolution efficiency.

Growth of crystalline scale deposits is controlled by use of phosphonate inhibitors,[30] or polyacrylate polymers and derivatives.[31] Inhibition is believed to occur through stereospecific adsorption of inhibitor molecules onto crystallographic planes of a growing nucleus, resulting in "poisoning" further growth and crystallite agglomeration. The amorphous nature of silica scale in process waters renders 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. Dissolution methods for silica scale are much less developed that those for "traditional" scales
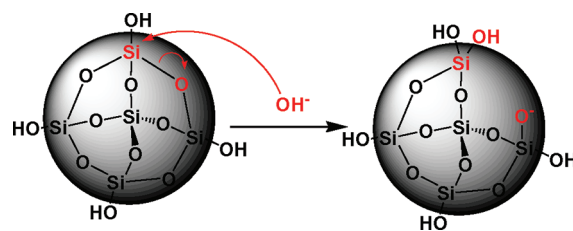
such as calcium carbonates and sulfates, barium and strontium sulfate, etc., that commonly involve use of chelants for metal ion abstraction through surface complexation.[32] Therefore, available techniques for silica scale dissolution must complement preventive approaches.

■ CONCLUSION

The chemical degradation of the Si—O bond framework either in amorphous silica,[33] quartz,[34] or other silicate-containing minerals[35] has been studied intensively in order to get fundamental

insight and also for technological applications.[36] The principal findings of this work are summarized below: (1) Anionic additives that possess at least one —COOH group are effective silica scale dissolvers at >2500 ppm dosage levels. (2) Their chemical structure affects dissolution performance. (3) Dosage increase improves performance only in some cases. (4) Presence of additional groups (e.g., —PO$_3$H$_2$) in the dissolver molecule augments the dissolution process. (5) The first step of silica dissolution is surface complexation. This can be severely inhibited by appropriate cationic reagents.

Colloidal silica deposits present a challenge for a plethora of industrial water applications including heat exchangers, reverse osmosis membranes, piping, etc. Dissolution of such silica deposits by chemical cleaning using chelating agents[37] presents a number of issues that relate to performance and environmental compliance. Green dissolution approaches should be further developed,[38] and such environmentally benign chemical technologies are an ongoing effort in our laboratories.

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