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“Green” scale inhibitors in water treatment processes: the case of silica scale inhibition

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ABSTRACT

This paper focuses on scale control approaches using a number of “green” silica scale inhibitors. These findings may be of interest to chemists and engineers in the fields of cooling and boiler water, pulp and paper, detergents, oil, gas, etc. In light of increasing environmental concerns, this research acquires significant interest. Also, in this paper, the effects of biological and synthetic polymers on the formation of amorphous silica are discussed. The importance of synergies between polyelectrolytes on silica inhibition is also discussed. A specific example of a zwitterionic polymer phosphonomethylated chitosan (PCH) is further analyzed for its inhibitory activity. Specifically, the ability of PCH to retard silicic acid condensation at circumneutral pH in aqueous supersaturated solutions is explored. Furthermore, the effects of either purely cationic (polyethyleneimine, PEI) or purely anionic (carboxymethylinulin) polyelectrolytes on the inhibitory activity of PCH are systematically studied. It was found that the action of inhibitor blends is not cumulative. PCH/PEI blends stabilize the same level of silicic acid as PCH alone in both short-term (8 h) and long-term (72 h) experiments. Lastly, six polyethylene glycol polymers are used as silica scale inhibitors. Their Molecular Weights range from 1,550 to 20,000. There is a profound dependence of inhibitory performance on the additive Molecular Weight. However, this dependence seems to be less significant for Molecular Weights > 10,000. Mechanistic implications will be discussed as well.

Keywords: Water treatment; Green additives; Silica scale; Scale inhibitors; Polyethylene glycol; Inulin

1. Introduction

Nature directs the formation of amorphous hydrated silica (biosilica) in living organisms, such as marine/freshwater diatoms and terrestrial plants via the important process of biosilicification [1–3]. One can put this in perspective by considering that the gross production of biogenic silica in surface waters was estimated to be ~240 ± 40 terramoles of silicon per year. This means, marine biological systems process the breathtaking amount of about 6.7 gigatonnes of silicon annually [4]. Biosilicification is a unique kind of biomineralization.

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Its uniqueness and differentiation from a plethora of other biogenic, metal-containing minerals (e.g. calcite, aragonite, vaterite, octacalcium phosphate, hydroxyapatite, iron sulfides, etc.) lies not only with the simple, albeit unique, structure of the final product, amorphous silicon dioxide (silica), but also with the intricate (and enigmatic) mechanism of its formation. Whereas metal carbonate and phosphate solids are crystalline ionic materials whose formation is governed by cation–anion association and solubility equilibria, silica is an oxide of amorphous nature formed by a complicated inorganic polymerization process that is controlled by organic macromolecules, resulting in "exotic" morphologies at the micron scale [5].

Amorphous silica appears as a recalcitrant deposit in industrial water systems that operate with fresh water high in silicon content (either soluble or colloidal silica). There are no established methodologies for preventing silica deposit formation. In addition, cleaning and removal of silica deposits from a fouled system require either chemical approaches (using hydrofluoric acid) or mechanical methods (requiring system shut-downs and several man hours). It is imperative, therefore, that silica inhibition must be resorted to, as (perhaps) the only environment-friendly and cost-effective approach.

Our on-going research efforts in the silicification area focus on the inhibitory effects of polymeric molecules on colloidal silica formation by studying the stabilization of silicic acid by these polymers [6–12]. In a biomimetic approach, we utilize information available on biomacromolecule-induced biosilica formation in order to design, synthesize, and utilize macromolecules that may have inhibitory activity on colloidal silica formation, thus extending the life of soluble silicic acid prior to its self-condensation to form colloidal silica.

We have selected to utilize chitosan-based biopolymers [13,14], Fig. 1, as additives that may stabilize silicic acid and delay its self-condensation to yield amorphous silica. More specifically, in this paper, we study the polymer chitosan on which animomethylenephosphonate groups have been grafted by a Mannich-type reaction [15]. Furthermore, PCH is synthesized from chitosan in an efficient and low-cost manner, and also has low-aquatic toxicity.

2. Experimental protocols

2.1. Instrumentation

IR spectra were recorded on a FT-IR Perkin–Elmer FT 1760. Measurements of soluble silicic acid were carried out using a HACH 890 spectrophotometer from the Hach Co., Loveland, CO, USA. SEM images were collected on a scanning electron microscope LEO VP-35 FEM.

2.2. Materials

Schematic structures of the polymers used in this study are shown in Fig. 1. Polyethyleneimine (PEI, branched, MW 70 kDa, ~25% primary amines, ~50% secondary amines, and ~25% amines) was from Polysciences. PCH was synthesized according to published procedures [16–18]. Carboxymethylinulin (CMI), (proprietary MW, between 2 and 3 KDa) was from Solutia Inc. (Belgium). CMI can be prepared from the biopolymer inulin via a carboxymethylation step [19]. The average Molecular Weight for PCH was found ~254 KDa. Solid samples of polyethylene glycol (PEG) polymers were commercial samples. PEG 1550, PEG 6000, and PEG 20000 were from SERVA Electrophoresis GmbH (Germany), and PEG 2000, PEG 10000, and PEG 12000 were from Alfa Aesar (USA).

2.3. Methods

The protocols for all experiments and measurements described, herein, have been reported in detail elsewhere [20]. Molybdate-reactive silicic acid was measured using the silicomolybdate spectrophotometric method [21–25], which has a ± 5% accuracy. Reproducibility was satisfactory.

3. Results and discussion

Our research efforts have been focusing on utilization of "natural" or "synthetic" polymeric additives that influence (inhibit or direct) colloidal silica formation. In particular, we have placed significant attention on: (a) the inhibitory effect that polymeric additives have on silica precipitate formation, while they delay silicic acid polymerization, (b) the use of non-toxic, environment-friendly, "green" chemical additives that can enhance silicic acid solubility, (c) exploiting the significant observation (by other research groups and us) that cationic additives have profound effects on silica particle formation, and (d) delineating various process variables that may affect additive effectiveness, notably, minimizing polymer dosage while maximizing inhibitory performance.

The use of PCH, a zwitter ionic polymer, that is derived from renewable sources acts as an effective inhibitor of colloidal silica formation. Below, results are presented on the inhibitory effects of PCH alone, and in combination with a purely cationic (PEI) polymer or a purely anionic (CMI) polymer.

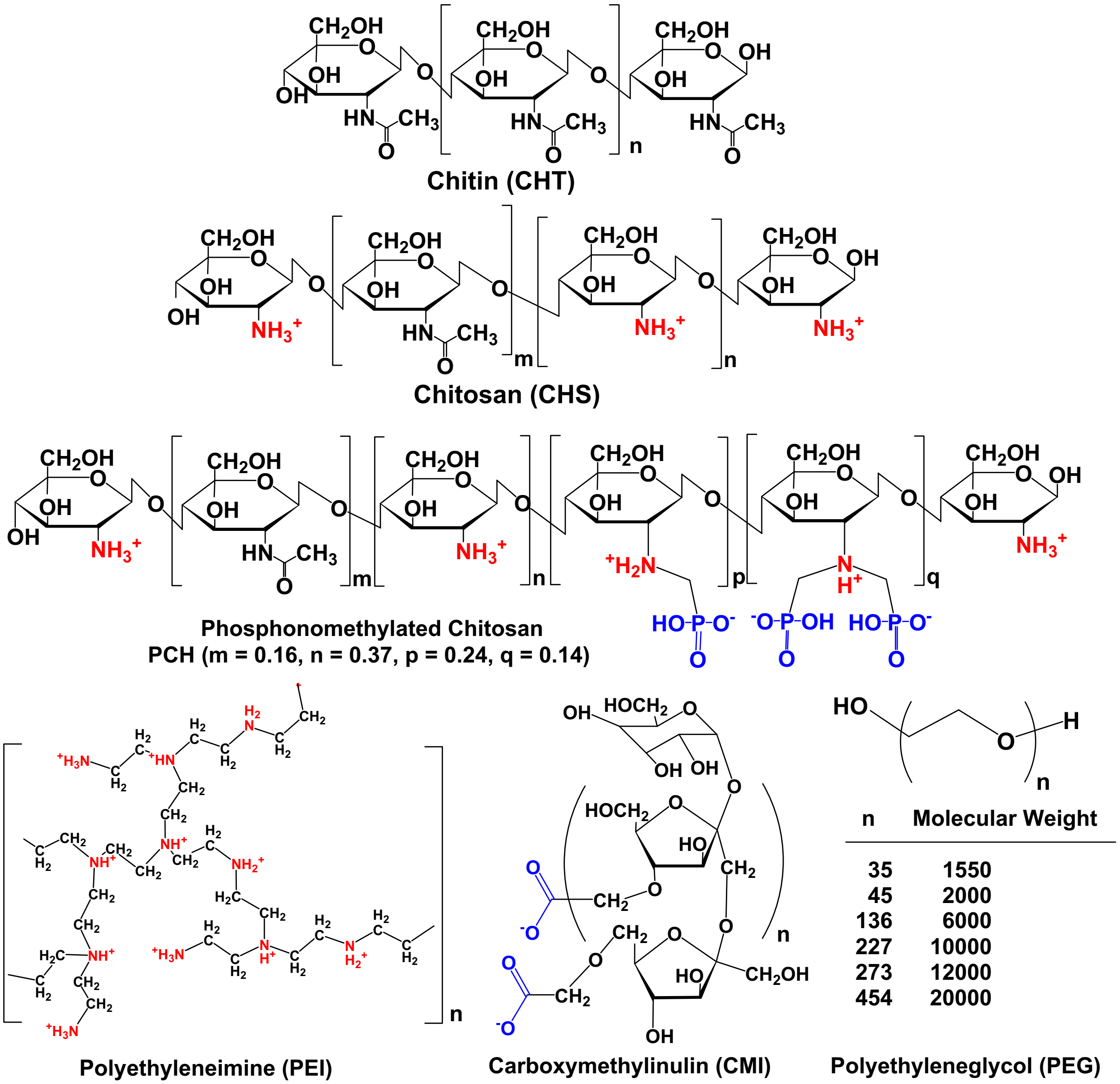

Fig. 1. Schematic structures of chitin (CHT), chitosan (CHS), PCH, PEI, CMI, and PEG. Cationic groups are highlighted in red, anionic in blue.

3.1. Silica inhibition by phosphonomethylated chitosan

Phosphonomethylated chitosan (PCH) was tested for its ability to stabilize silicic acid and influence amorphous silica formation in "short-term" experiments (8 h) at dosages 40, 150 and 200 ppm. The results are presented in Fig. 2. Silicic acid condensation appears to be independent of additive dosage within the first 8 h. Soluble silicic acid reaches a value of ~350 ppm after 8 h. Compared to control solutions not containing PCH this results in ~150 ppm additional silicic acid stabilization.

The long-term silicic acid stabilization by PCH was studied over a 72 h time period with sampling every 24 h. The effect of various dosages of PCH (10, 20, 40, 60, 100, 150, and 200 ppm) on silica formation is shown in Fig. 3. An immediate observation is that PCH can only delay silicic acid condensation over the course of 72 h, thus only partially inhibiting silica formation.

These experiments reveal that there is a dosage-dependence (in contrast to 8-h experiments) on silicic acid stabilization that reaches a maximum at 150 ppm PCH (296 ppm silica compared with 176 ppm of the "control"). This translates to 120 ppm silicic acid

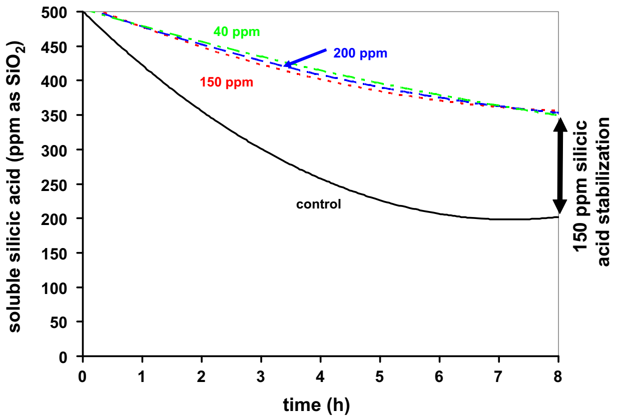

Fig. 2. Effect of PCH levels on colloidal silica inhibition in short-term (8 h) experiments.

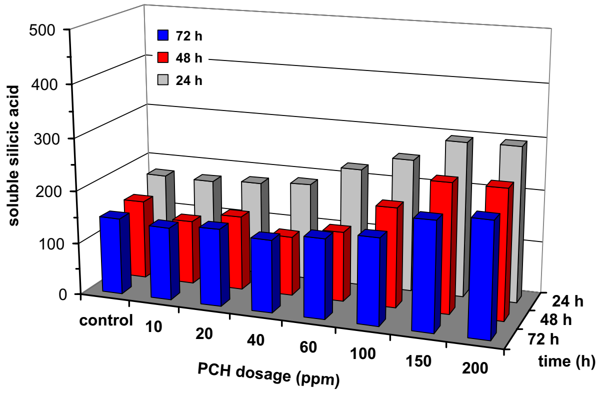

Fig. 3. Stabilization of silicic acid in the presence of PCH in long term (24–48–72 h) experiments.

stabilization (over the control) for the first 24 h. Low dosages (10 and 20 ppm) exhibit virtually no long-term inhibitory effects.

There seems to be a sharp reduction in inhibitory action after 24 h. This has been observed numerous times in our experiments with a variety of additives. Specifically, for the 150 ppm dosage, there is a 50 ppm drop in silicic acid levels between 24 and 48 h. The same is true for the 200 ppm dosage. As will be discussed extensively later, a reason for the reduction in inhibitor activity is PCH entrapment in the colloidal silica matrix. This results in unavailability of sufficient PCH in solution to continue inhibition and in further drop in silicic acid levels.

3.2. Silica inhibition by a blend of PCH and cationic PEI

The inhibitory effects of combinations of PEI and PCH were tested in silicic acid polymerization. The "short-term" and "long-term" results are shown in Fig. 4. In spite of its profound structural differences to PCH, the inhibitory action of PEI (20 ppm) appears to be comparable with that of PCH (40 ppm), with only minor differences. PEI is only slightly less active than PCH within the first 4 h of condensation. Addition of PEI and PCH combinations to silicic acid solutions give also marginal differences in performance, compared with that of PEI alone, or PCH alone. It is noteworthy that there appears to be no discernible synergy between the two additives for inhibitory activity enhancement. Furthermore, the effect of PEI and PCH (when both present in solution simultaneously) is not cumulative. If that was the case then PEI (at 20 ppm dosage) and PCH (at 40 ppm dosage) should inhibit silica formation quantitatively, reaching 500 ppm soluble silica. The results show that ~350 ppm remains soluble when the above combination of inhibitors is present.

This observation demonstrates the interaction of PEI and PCH in solution, presumably due to an electrostatic attraction and/or hydrogen bonding between the anionic phosphonate groups on the PCH backbone and the protonated cationic amine groups on the PEI [26]. The resulting "combined" dual polymeric inhibitor formed by polyanion–polycation association does not exhibit any enhanced inhibitory activity, compared with that of its components, PEI and PCH.

Long-term silicic acid polymerization studies further confirm these results. This should be contrasted to observations noted on increased inhibitory activity of combinations of cationic PAMAMs and polyanionic electrolytes, such as carboxylate-based polymers [10–12]. Fig. 4 shows that addition of 20 ppm of PEI to solutions containing 20 ppm PCH has virtually no beneficial effect on inhibitory activity of 20 ppm PCH. Further PCH dosage increase (up to 60 ppm), while maintaining 20 ppm PEI dosage has actually a small but measurable detrimental effect.

3.3. Silica inhibition by a blend of PCH and anionic CMI

It is well established that anionic polymers do not affect silicic acid polymerization. There is only one report in the literature of the inhibitory activity of a genuinely anionic polymer, phosphinopolycarboxylic acid (PPCA, a polyacrylate-based polymer), causing stabilization of 325 ppm soluble silicic acid, albeit at very high dosage (1,000 ppm) [27]. CMI alone does not affect silicic acid condensation at dosage levels up to 200 ppm (see third set of bars in Fig. 5).

We recently reported that CMI can enhance the inhibitory activity of PCH at <8 h silicic condensation times, when the two polymers act in combination in solution (50 ppm PCH and >50 ppm CMI) [12]. In this

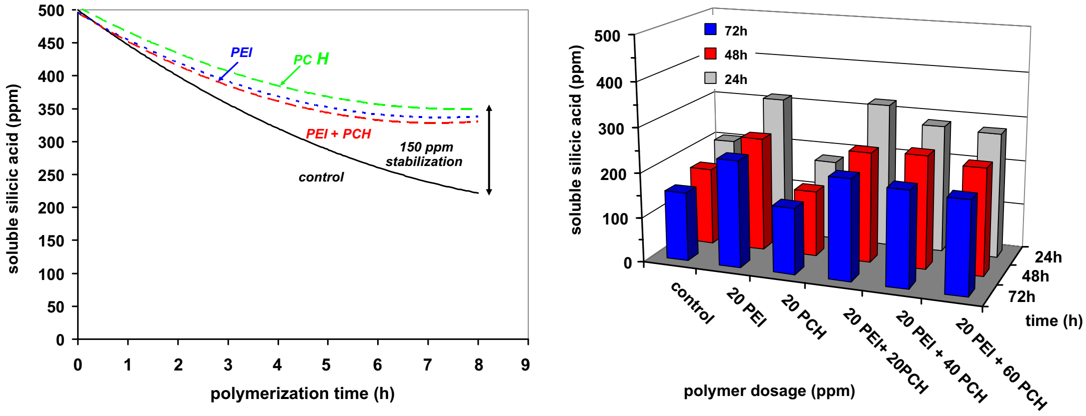

Fig. 4. Synergistic action of PEI and PCH in colloidal silica inhibition in "short-term" experiments. PEI, 20 ppm dosage; PCH, 40 ppm dosage (left). Effect of PCH dosage (20–40–60 ppm) with constant PEI dosage (20 ppm) on colloidal silica inhibition in "long-term" experiments (right).

context, we investigated whether this beneficial synergy has a life time beyond 8 h. Thus, when PCH is combined with CMI in "long-term" silicic acid condensation experiments, a substantial reduction in its inhibitory activity is noted (see Fig. 5).

Addition of 50 ppm CMI to 150 ppm PCH causes a 100 ppm (from 342 to 241 ppm) reduction in silicic acid stabilization after 24 h polymerization time. Further CMI dosage increase to 100 ppm results in complete "deactivation" of PCH's inhibitory activity. Additional CMI dosage increase exerts no further effects, as silicic acid levels are identical to the "control" experiment. The observed detrimental effects on PCH inhibitory activity are somewhat expected. Similar observations have been noted on the effect of polyanionic polymers (polyacrylate, poly(acrylamide-*co*-acrylate), and CMI) on amine-terminated, cationic polyaminoamide (PAMAM) dendrimers [28].

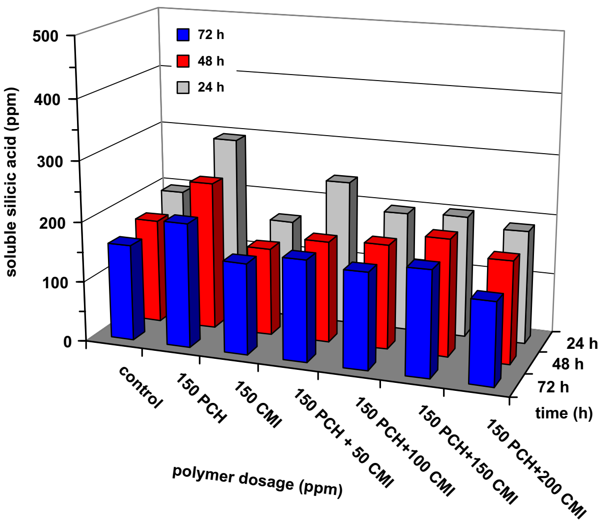

Fig. 5. Effect of CMI dosage (0–50–100–150–200 ppm) with constant PCH dosage (150 ppm) on colloidal silica inhibition in long-term experiments.

3.4. Silica inhibition by PEG inhibitors

The inhibitory activity of PEG inhibitors depends on their MW. It increases almost linearly up to MW = 10,000 and then it levels-off. Representative 3D experiments with PEG of MW = 20,000 are shown in Fig. 6.

PEG is an effective silica inhibitor even at the low dosage of 20 ppm. There is a gradual increase of inhibitory activity upon PEG concentration increase. However, above 40 ppm no further enhancement is observed. Similar observations can be noted for the short-term (8 h) results (see Fig. 7). A 20 ppm dosage has a minor effect, whereas increase to 40 ppm substantially

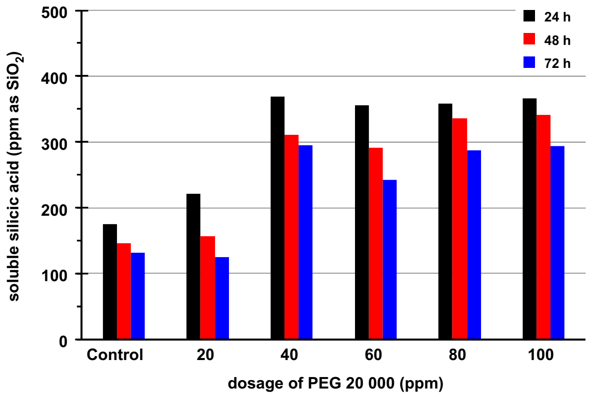

Fig. 6. Effect of PEG dosage (20–40–60–80–100 ppm) on colloidal silica inhibition in long-term experiments.

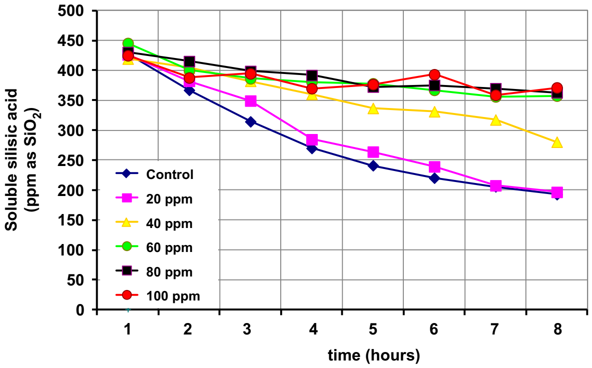

Fig. 7. Effect of PEG of MW 20,000 levels on colloidal silica inhibition in short-term (8 h) experiments.

improves inhibitory efficiency. Further dosage increase offers additional stabilization, but the dosages 60, 80, and 100 ppm are virtually indistinguishable.

4. Conclusions/Outlook

The purpose of this work is to identify and exploit novel polymeric structures that are able not only to direct silica morphogenesis, but also to maintain high silicic acid concentrations for an extended period of time before silica deposition occurs. This is directly linked to silicon transport to and within the cell, during which relatively high “Si” concentrations must be maintained for a period of time. It should be noted that there is also an intense interest in the water treatment industry, where chemical technologies for effective silica scale growth in process waters are still an unsolved problem.

The principle findings are summarized as follows:

(1) PCH can maintain soluble silicic acid levels beyond the calculated level at >60 ppm dosages.
(2) PEI maintains higher silicic acid levels compared with PCH, at lower (10 ppm) levels.
(3) PCH/PEI combinations are effective inhibitors of silicic acid condensation at rather low levels (20 ppm each).
(4) CMI appears to have detrimental effects on the inhibitory activity of PCH.
(5) PCH, with ammonium/phosphonate-containing structural features also acts as a silica aggregator forming SiO_2–PCH composites with subsequent loss of inhibitor efficiency over time due to inhibitor entrapment within the amorphous 3D silica matrix. These composites could be envisioned as colloidal silica particles “glued” together with PCH.
(6) PEG polymers show good inhibition performance. PEG 20000 keeps ~350 ppm silica soluble after 8 h.

Dependence of inhibition ability on particular structural features of the inhibitor molecule is of great importance [29]. In addition, intimate blends of different inhibitor molecules may offer advantages and enhanced inhibitory activity based on structural and functional synergies [30]. Structure/activity relationships may help in the rational design of inhibitors with precise structures and topologies that may show, ideally, predictable inhibition performance [31,32]. Inhibition of silica growth most probably occurs at the early stages of silicic acid polymerization. Unfortunately, there is little information available at the molecular level on the silicate oligomers formed. Such data would be of great importance, because they would greatly facilitate inhibitor design and improvement [33,34].

Acknowledgments

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