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Environmentally benign chemical additives in the treatment and chemical cleaning of process water systems: Implications for green chemical technology

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Abstract

Supersaturated process waters high in silicates frequently result in deposition of colloidal silica or metal silicate salts. Silica cannot be inhibited by conventional phosphonate mineral scale inhibitors. Chemical cleaning poses hazards and requires operational shut-downs. This paper is focused on a dual approach for silica scale control, inhibition of colloidal silica formation and colloidal silica dissolution in water technology applications by use of designed chemical approaches. The additives used for silica inhibition were polyaminoamide dendrimers (PAMAM) and polyethyleneimine (PEI), in combination with carboxymethyl inulin (CMI) and polyacrylate (PAA) polymers. In principle, silica inhibition is a function of time and inhibitor dosage. Amine-terminated PAMAM-1 and 2 dendrimers as well as PEI combined with anionic polymers, such as CMI and PAA, seem to have a significant inhibitory effect on silica formation, most likely at its earlier stages where the reaction products are oligomeric silicates. CMI and PAA assist the inhibitory action of PAMAM-1 and 2 and PEI by alleviating formation of insoluble SiO_2-PAMAM precipitates. This most likely occurs by partial neutralization of the positive charge that exists in $–NH_3^+$ surface groups. Increase of anionic polymer dosage above a certain threshold has a detrimental effect on the activity of the cationic inhibitors. In that case the polymer's negative charge "overwhelms" the cationic charge of the inhibitor and poisons its inhibition ability. For silica dissolution, acetic, oxalic, citric acids, histidine and phenylalanine were used as potential replacements of ammonium bifluoride ($NH_4F·HF$). Silica dissolution is dependent in a rather unpredictable fashion on the structure of the dissolver, time and dosage. This paper continues

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our research efforts in the discovery, design and application of antiscalant additives that have mild environmental impact. These chemicals are also known as "green additives".

Keywords: Water treatment; Silica; Scale formation; Green additives; Inhibitors; Polymers; Scale removal

1. Introduction

Industrial process water systems are often plagued by deposition problems that originate from a variety of deposits, organic or inorganic [1]. The latter, often known as mineral scale deposits, can become major operational issues for poorly treated process waters. Some of these, such as silica, are especially troublesome because they can cause catastrophic materials failures and operational shut-downs. Industrial and potable water users and operators are often faced with a challenging dilemma: is it preferable to prevent deposits from forming, or is it better to clean the deposits after they form? Cost considerations are usually the decision criterion, although other factors are taken into account as well (eg. potential hazards of cleaning chemicals). Scale prevention in principle can be achieved by use of scale inhibitors, key components of any chemical water treatment [2]. Unfortunately, these traditional scale control methods (inhibition and crystal modification) applied to crystalline mineral salt precipitates *do not apply to* SiO_2 *because it is amorphous*. Therefore, much more well-thought inhibition approaches have to be utilized for controlling silica scale. Increasing environmental concerns and discharge limitations have imposed additional challenges in treating process waters. Therefore, the discovery and successful application of chemical additives that have mild environmental impact has been the focus of several researchers [3]. This paper focuses on use of "green" inhibitors in synergistic action with "green" polymers for (a) silica/silicate scale inhibition, and (b) for silica scale dissolution. This research is part of our on-going investigation on the discovery and application of scale inhibitors in industrial process waters [4–12].

2. Experimental section

Detailed procedures for instruments, reagents, solution preparation, inhibitor screening test, soluble silica measurement, silica inhibition and dissolution protocols are reported elsewhere [5]. All reagents used were from commercial sources.

2.1. Control test

100 mL from the 500 ppm SiO_2 stock solution was placed in a plastic beaker which contained a Teflon-covered magnetic stir bar. The pH of this solution was initially ~11.8 and adjusted to 7.00 ± 0.1 by addition of HCl and NaOH (the change in the resulting volume was about 3%). Then the beaker was covered with plastic membrane and set aside without stirring. The solution were checked for the soluble silica by the silicomolybdate method every two hours for the first twelve hours or after 24, 48, 72 h time intervals after the pH reduction.

2.2. Inhibitor test

100 mL portions of the 500 ppm SiO_2 stock solution were placed in plastic containers charged with Teflon-covered magnetic stir bars. In each container different volumes of inhibitor (10,000 ppm stock solution) were added to achieve desirable inhibitor concentration. After that the same procedure for the control test was followed.

2.3. Determination of soluble (reactive) SiO_2

Soluble silica was measured using the silicomolybdate spectrophotometric method [13]. According to this method 2 mL filtered sample, with 0.45 μm syringe filter, from the test solution is diluted to 25 mL in the cell, with light path 1 cm.

1 mL ammonium molybdate stock solution and 0.5 mL 1 + 1 HCl are added to the sample cell, the solution is mixed well and left undisturbed for 10 min. Then 1 mL oxalic acid solution is added and mixed again. The solution is set aside for 2 min. After the second time period the photometer is set at zero absorbance with water. Finally the sample absorbance is measured at 452 nm as "ppm soluble silica". The detectable concentrations range is 0–75.0 ppm. In order to calculate the concentration in the original solution a dilution factor is applied.

The silicomolybdate method is based on the principle that ammonium molybdate reacts with reactive silica and any phoshate present at low pH (about 1.2) and yields heteropoly acids, yellow in color. Oxalic acid is added to destroy the molybdophosphoric acid leaving silicomolybdate intact, and thus eliminating any color interference from phosphates. It must be mentioned that this method measures soluble silica and in this term includes not only the monomer silicate acid but also oligomer species such as dimmers, trimers, tetramers, etc. It is not stated exactly which are the reactive units.

2.4. 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 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, and (c) preliminary experiments (not reported here) showed that the SiO_2 dissolution rates are too slow for any practical experimental set-up. 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 [13]. After each measurement pH is again checked, and in 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). Every dissolution additive is tested for its interference with the silicomolybdate spectrophotometric test. A stock solution (500 ppm) of soluble silica (from sodium silicate) is prepared. To 100 mL of that solution a 10,000 ppm dosage of the cleaning chemical is added. After appropriate dilutions are made, soluble silica is measured and the results are compared to the expected value of 500 ppm. Additives that interfere with the silicomolybdate spectrophotometric test are rejected.

3. Results and discussion

3.1. "Green" additives for scale inhibition

Herein, we report results on the inhibition performance of several environmentally friendly antiscalants. All additives tested are shown in Fig. 1. Some comments are warranted. Polyaminoamide dendrimers (PAMAM's) have been used for several medical applications (e.g. as drug delivery agents). Their backbone is composed of amide bonds rendering them biodegradable. Therefore they are undoubtedly benign molecules. Carboxymethylinulin (CMI) is produced from a chemical reaction with a biopolymer and select reagents. This biopolymer, inulin, is extracted from the roots of the chicory plant. Carboxymethylinulin (CMI) has been investigated in a series of subacute toxicity, genotoxicity and sensitization studies to evaluate its toxicological profile [14]. All studies

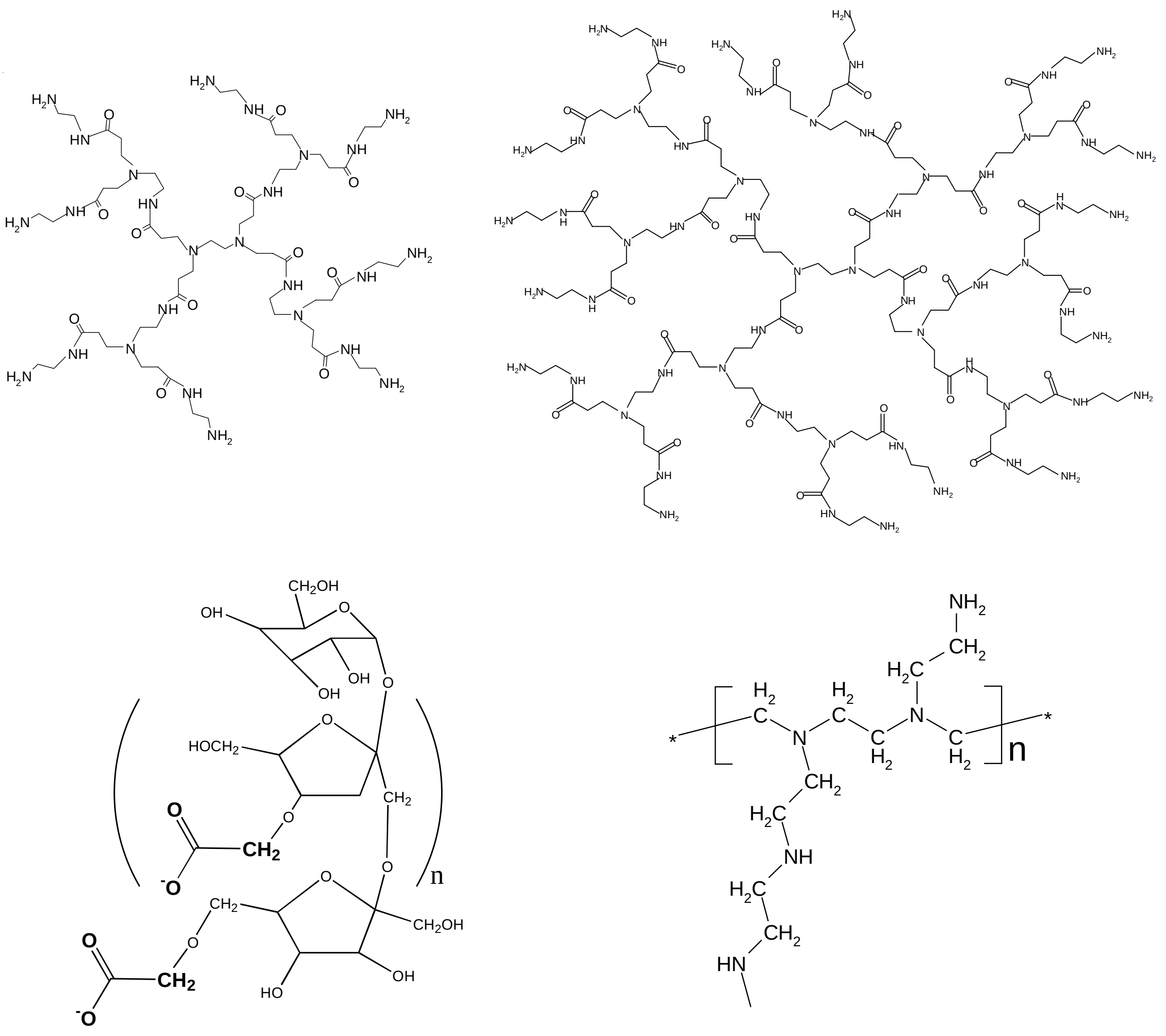

Fig. 1. Schematic structures of PAMAM, Generation 1 (upper left), PAMAM, Generation 2 (upper right), carboxymethylinulin biopolymer (CMI, lower left) and polyethyleneimine (PEI, lower right).

followed accepted testing guidelines as recommended by international regulatory agencies (OECD, EEC and US EPA). No significant toxicological findings were evident. Results of the present toxicity studies with CMI, all conforming to internationally accepted testing standards, show that the toxicological profile of CMI is consistent with other polycarboxylates used in foods. Polyethyleneimine (PEI) is a highly branched cationic polymer that possesses ~25% primary amines, ~50% secondary amines and ~25% tertiary amines. PEI has found several uses in biomedical applications proving its compatibility with biological systems. The PEI used herein was of 70,000 MW. Polyacrylate (MW ~2000) is a well-known non-toxic additive.

3.2. Dendrimer/polymer combinations as silica antiscalants

We recently reported in detail several aspects of the use of dendrimer additives for silica scale control [4–7, 9–12]. Those findings revealed that the –COOH terminated dendrimers (generations 0.5, 1.5, 2.5) show virtually no activity as inhibitors. In contrast, the –NH_2 terminated analogs (generations 1 and 2) are potent silica scale inhibitors. In spite of the excellent performance of PAMAM 1 and 2 dendrimers as “green” colloidal silica inhibitors, they suffer from a serious drawback: the silicate levels that are not inhibited lead to formation of large colloidal silica particles that entrap the dendrimers, thus depleting the aqueous medium from active inhibitor. Visual observations show that these particles appear as white flocculant precipitates at the bottom of the test vessels. Chemical analysis of these amorphous silica precipitates showed that they are principally composed of silica (> 90%), with the rest being organic material, undoubtedly dendrimer. Presence of dendrimer inside these precipitates was also verified by FT-IR spectroscopy. Formation of silica-PAMAM precipitates occurs due to the combination of anionic SiO_2 particles and cationic PAMAM-1 or 2 dendrimers. To combat this problem, we resorted to utilization of anionic polymer additives. Herein, we describe the effect of carboxymethylinulin biopolymer (CMI) on the performance of the PAMAM-1 and 2 dendrimers. Fig. 2, upper shows results obtained from experiments performed where both PAMAM-1 dendrimer and CMI are present in solution. Fig. 2, lower shows the results from test solutions containing both PAMAM-2 dendrimer and CMI. It should be noted that dendrimets with –COOH terminal groups (generations 0.5, 1.5 and 2.5) were not tested, because their inhibition performance is virtually indistinguishable from the control. When PAMAM 1 is used at 40 ppm levels together with 20 ppm CMI, 408 ppm of soluble SiO_2 are measured within 24 h. This level drops at 381 ppm and 308 ppm after 48 and 72 h, respectively. In general, a drop in soluble silica levels occurs also in control solutions regardless of the presence of inhibitor. Increase of CMI dosage to 40 ppm seems to have no effect on soluble silica. However, increase of CMI dosage to 60 ppm has a detrimen-

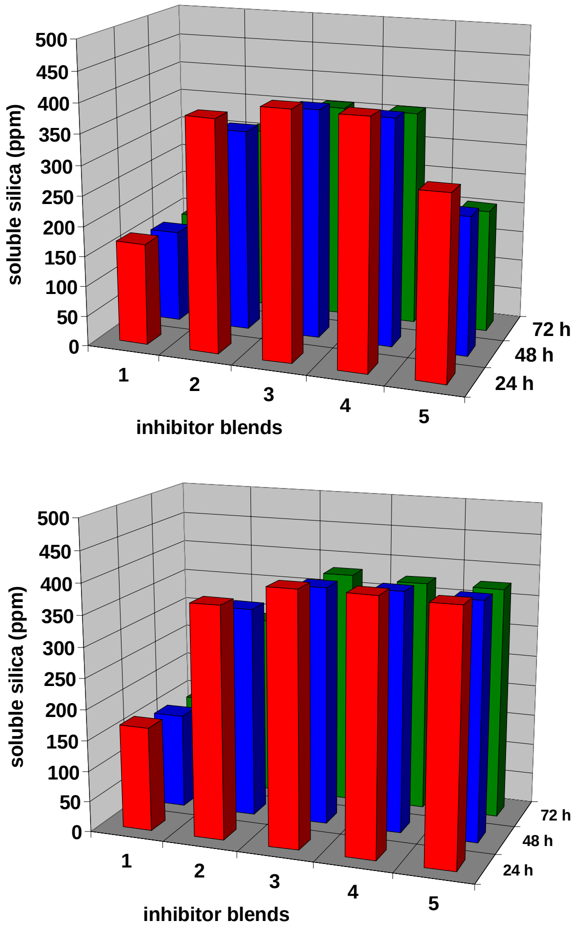

Fig. 2. Effect of inhibitor blend dosage (dendrimer + CMI) on soluble SiO_2. The upper graph refers to PAMAM-1 and the lower graph to PAMAM-2. 1 = control, no additives; 2 = dendrimer (40 ppm) + CMI (0 ppm); 3 = dendrimer (40 ppm) + CMI (20 ppm); 4 = dendrimer (40 ppm) + CMI (40 ppm); 5 = dendrimer (40 ppm) + CMI (60 ppm).

tal effect on maintaining high levels of soluble silica. A level of 301 ppm soluble silica (a drop of ~100 ppm) is observed after of 24 h, compared to 408 ppm when 20 ppm of CMI are present. When PAMAM-2 is used with 20 ppm CMI, 408 ppm soluble SiO_2 are measured after 24 h, 385 ppm after 48 h and 380 ppm after 72 h. It is worth mentioning that soluble SiO_2 levels are higher in solutions containing PAMAM-2 + CMI than those containing PAMAM-1 + CMI (results not shown). Increase of CMI dosage to 40 ppm gives results virtually indistinguishable from those obtained with 20 ppm CMI. Interestingly, a further increase of CMI dosage to 60 ppm does not cause drop in soluble silica levels, as observed with PAMAM-1 and 60 ppm CMI.

3.3. Polyethyleneimine/polymer combinations as silica antiscalants

Combinations of cationic PEI and polyacrylate (PAA) polymer of ~2000 molecular weight also mitigate silica inhibition (Fig. 3). Only the 20 ppm PEI dosage was tested in combination with 20, 40 and 60 ppm PAA dosages. Based on previous results (not shown here) the 20 ppm PEI dosage showed the best inhibition results. It appears that all PAA dosages increase soluble silica within the first 24 h. Afterwards there is a gradual drop to the control levels. Optimum silica inhibition performance is achieved with the PEI (20 ppm) + PAA (20 ppm) blend, allowing nearly 400 ppm silica to remain soluble.

3.4. Dissolution of colloidal silica

The solubility of SiO_2 increases as pH increases. Therefore, high pH regions are desirable for SiO_2 scale dissolution. However, SiO_2 chemical cleanings have to be performed at pH regions that do not compromise system integrity and personnel safety. In the experiments reported herein a pH of 10.00 was selected. Various “green” additives were tested. Acetic, oxalic and citric acids, L-histidine and L-phenylalanine were tested as silica scale dissolvers. These additives present potential replacements for ammonium bifluoride, $NH_4F{\cdot}HF$, the current “industrial standard”. Hazards associated with generating HF *in situ*, as well as the low pH of the dissolution process and the resulting high metallic corrosion rates during cleaning, are some of the reasons that alternative, safer and more effective chemical approaches are sought for SiO_2/silicate deposit dissolution. Results are presented in Fig. 4. After 24 h, in control solutions (no additive present) dissolution proceeds until ~120 ppm SiO_2 is solubilized (24%). SiO_2 dissolution continues after 48 and 72 h allowing soluble SiO_2 levels to increase to 150 ppm (30%) and 190 ppm (38%), respectively. Presence of 2500 ppm of any additive shown in Fig. 4 enhances SiO_2 dissolution within the first 24 h in a wide range, from 164 ppm (oxalate) to 206 (L-histidine). This enhancement is more pronounced after 48 and 72 h of dissolution time. The fact that SiO_2 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

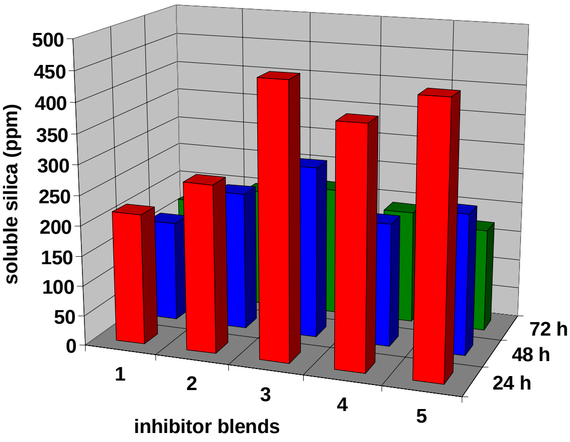

Fig. 3. Effect of inhibitor blend dosage (PEI + PAA) on soluble SiO_2. 1 = control, no additives; 2 = PEI (20 ppm) + PAA (0 ppm); 3 = PEI (20 ppm) + PAA (20 ppm); 4 = PEI (20 ppm) + PAA (40 ppm); 5 = PEI (20 ppm) + PAA (60 ppm).

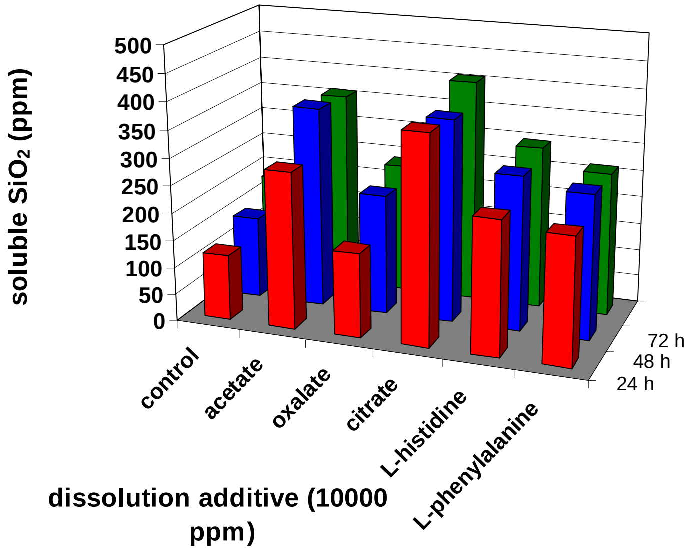

Fig. 4. Dissolution enhancement of colloidal SiO_2 in the presence of various additives.

appears to have an effect in only some cases. For example, in the case of acetic acid, dosage increase to 10,000 ppm results into SiO_2 dissolution enhancement that reaches 286 ppm (57 %) in 24 h 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 SiO_2 (76%) in 24 h. In the cases of oxalic acid dosage increase has only a marginal effect on dissolution. As shown in Fig. 4, SiO_2 dissolution is also a factor of time. It is enhanced as dissolution time proceeds. The effect of the number of –COOH groups present in the chemical structure of the cleaner molecule can be seen by examining Fig. 4. Increase in the number of –COOH groups does not have an obvious effect in dissolution efficiency. For example, acetate (one –COOH group) at 10,000 ppm dosage is more active than oxalate (two –COOH groups). The nature of additional groups in the dissolver molecule also appears to be important. L-histidine and L-phenylalanine (one $–NH_2$ group at α-position to a –COOH group) are more active particularly in lower dosages than acetate that does not possess such structural features.

Based on the good results obtained with the two aminoacids and also their chemical structure, we propose a possible mechanism for the dissolution of colloidal silica by such zwitterions. This pathway is shown in Fig. 5. One can envision that the first silica-aminoacid interaction is an electrostatic association between the negatively charged silica particle and the cationic “ammonium” moiety of the aminoacid. The positioning of the aminoacid is such that the deprotonated and negatively charged carboxylate group can “swing” and attach a surface Si center, thus enhancing the cleavage of a surface Si-O bond. This function is in a way “mimicking” the action of HO^- anions in the hydrolysis of the Si-O-Si network.

4. Conclusions

The present paper is part of our continuing research efforts to identify and exploit novel chemistries as effective mineral scale growth in-

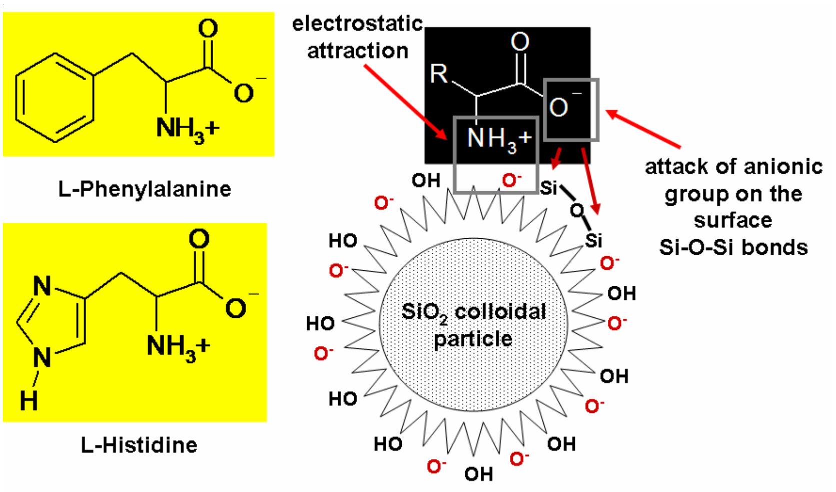

Fig. 5. Possible mechanism of dissolution enhancement of colloidal SiO_2 in the presence of aminoacid additives.

hibitors in process waters [4–12,15]. Herein, the emphasis is given on inhibitors that have no, or mild environmental impact. PAMAM-1 and 2 dendrimers as well as PEI combined with anionic polymers, such as CMI and PAA, seem to have a significant inhibitory effect on SiO_2 formation, most likely at its earlier stages where the reaction products are oligomeric silicates. CMI and PAA assist the inhibitory action of PAMAM-1 and 2 and PEI by alleviating formation of insoluble SiO_2-PAMAM precipitates. This most likely occurs by partial neutralization of the positive charge that exists in $–NH_3^+$ surface groups. However, increase of anionic polymer dosage above a certain threshold has a detrimental effect on the activity of the cationic inhibitors. In that case the polymer's negative charge "overwhelms" the cationic charge of the inhibitor and poisons its inhibition ability. Notably, the activity of PAMAM-2 dendimer does not seem to be as sensitive to CMI "overdosing" because it probably maintain some partial cationic character. Colloidal SiO_2 dissolution is a difficult task when applied to deposits in process water systems. Alternative chemistries sought herein involve polycarboxylates and aminoacids. These show variable activities. Colloidal SiO_2 dissolution is catalyzed by hydroxyl ions. However, their function is assisted by the presence of additives in a fashion that is not entirely clear. The details of such a dissolution mechanism are currently under investigation in our laboratory.

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