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Communication

Silica scale inhibition by polyaminoamide STARBURST® dendrimers☆

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Abstract

This paper reports the inhibition efficiency of a family of polyaminoamide (PAMAM) STARBURST® dendrimers in colloidal SiO_2 growth. PAMAMs of various generations (0.5, 1.5, 2.5 with –COOH termini, and 1, and 2 with $–NH_2$ termini) were tested and compared to control samples. Superiority of the dendrimer inhibitors with $–NH_2$ termini (maintaining ~380 ppm soluble SiO_2 after 12 h) versus those with –COOH termini (maintaining ~180 ppm soluble SiO_2 after 12 h) was discovered in solutions containing 500 ppm initial SiO_2. These inhibitors present potential for water treatment applications.

Keywords: Polyaminoamide; Silica scale inhibition; STARBURST® dendrimer; Water treatment; Deposit

Dendrimers are well-defined globular macromolecules constructed around a core unit [1]. Tomalia pioneered the synthesis of polyaminoamide (PAMAM) dendrimers, known as "STARBURST® polymers", Fig. 1 [2]. Their main structural feature is the growth of the dendrimer branches around a central core (in this case an ethylenediamine) via amide chemical linkages. The dendrimer generation number indicates its degree of growth and branching. More specifically, PAMAMs of generations 0.5, 1.5, 2.5 possess –COOH termini, and those of generations 1 and 2 have $–NH_2$ termini.

Fundamental studies, as well as a plethora of applications are at the epicenter of interest [3]. Our research efforts are currently focused on developing new chemistries for scale growth control, as it relates to chemical water treatment [4]. We have studied a novel application of STARBURST® dendrimers as silica (SiO_2) scale growth inhibitors in process industrial waters, and we describe herein our findings.

Silicate ion polymerizes via a condensation polymerization mechanism, at appropriate pH regions [5]. When it occurs in process waters used for cooling purposes, the resulting silica precipitates form a hard and tenacious scale on critical industrial equipment, such as heat exchangers, transfer pipes, etc. Silica removal by dissolution is a challenge [6] and the usual approaches to control it are avoiding supersaturation (leading to water wastage) or pre-treatment (with high equipment costs). Research on chemical inhibitors for SiO_2 is ongoing, but actual applications of inhibition chemistries in the field are rather limited.

Various generations of STARBURST® dendrimers were screened by a SiO_2 supersaturation test.[1] Test solutions of 500 ppm silicate (as SiO_2) were utilized in this study[2]

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[1] Screening tests: *Control*. A 100 mL volume of 500 ppm SiO_2 stock solution in the form of $Na_2SiO_3{\cdot}5H_2O$ is placed in a polyethylene container charged with a teflon-covered magnetic stir bar. The pH of this solution is initially ~11.8 and adjusted to 7.00 ± 0.1 by addition of HCl (the change in the resulting volume is negligible). The beaker is then covered and set aside without stirring. The solution is checked for soluble SiO_2 by the silicomolybdate spectrophotometric method every 2 h for the first 12 h or after 24, 48, 72 h time intervals after the pH reduction. *Inhibitor test*. The procedure above is followed except that before pH adjustment 400 μL of inhibitor a 10,000 ppm stock solution is added to achieve a final inhibitor concentration of 40 ppm. Sampling and timing are the same as the control, except that samples are first filtered through a 0.45 micron syringe filter before testing for soluble SiO_2. Most of the results were reproduced several times with excellent reproducibility, especially those with PAMAM-1 and -2 as inhibitors.

[2] These are considered to be "high stress" conditions with respect to SiO_2 supersaturation. Most untreated industrial cooling systems operate at <200 ppm SiO_2. Use of these "high stress" conditions is necessary in order to differentiate between inhibitor efficiencies.

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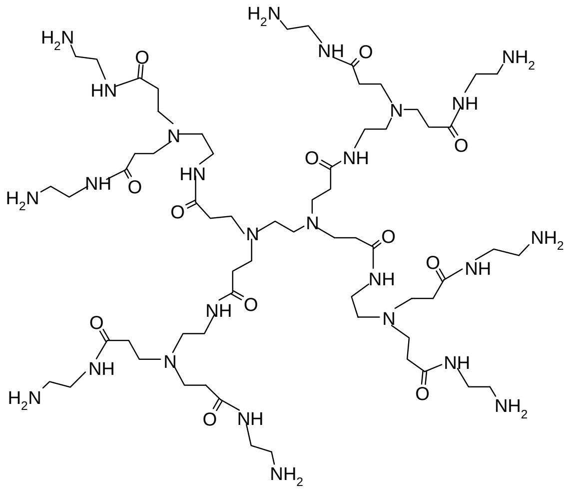

Fig. 1. Schematic structure of PAMAM dendrimer (generation 1, with eight $–NH_2$ surface groups).

and were tested by the silicomolybdate spectrophotometric method (relative error ± 5% [7]) after 24, 48 and 72 h of polymerization time. The results are presented in Fig. 2. This procedure allows determination of "soluble" or "reactive" SiO_2 after supersaturated solutions stand for at least 24 h at a pH appropriate for SiO_2 polymerization and relevant to industrial cooling water applications.

After 24 h, in control solutions silica polymerization proceeds until only 171 ppm SiO_2 remain soluble. The remaining SiO_2 forms colloidal particles. PAMAMs of generations 0.5, 1.5, and 2.5 give only marginal inhibition. The inhibition efficiency of PAMAM-1 and -2 is remarkably higher, giving 384 and 374 ppm of reactive SiO_2, respectively.

Gradual loss of inhibitory activity is observed after 48 and 72 h in all test samples. Soluble SiO_2 in the control solution is eventually stabilized at ~150 ppm.

Based on these results it becomes apparent that the $–NH_2$ terminated PAMAMs (generations 1 and 2) retard colloidal silica growth more effectively than –COOH terminated ones (generations 0.5, 1.5, and 2.5). Their efficiency is comparable and reaches ~300 ppm after 72 h.

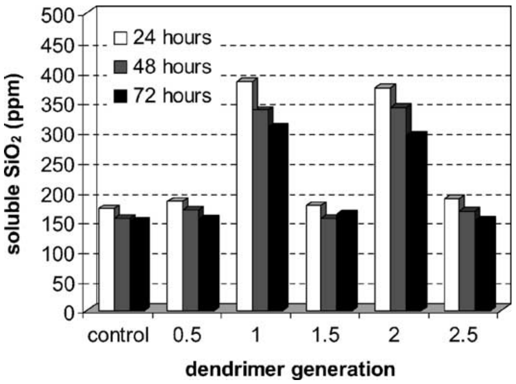

Fig. 2. Colloidal SiO_2 growth inhibition by PAMAM dendrimers at 40 ppm dosage level.

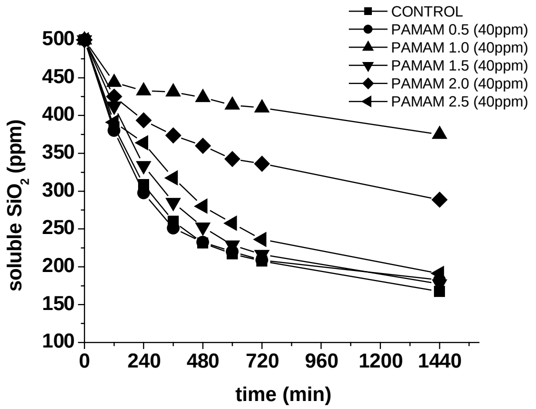

Fig. 3. Solubility enhancement of SiO_2 by PAMAM dendrimers of various generations in the first 12 h.

Results after at least 24 h of polymerization time allowed only marginal differentiation between PAMAM-1 and -2 inhibitors. Therefore, SiO_2 polymerization at the first stages (12 h) was also studied and the results are presented in Fig. 3. PAMAM-1 and -2 still exhibit the highest inhibitory efficiency, however, their relative performance is clearly differentiated, with PAMAM-1 being the most efficient. In solutions containing NH_2-terminated PAMAMs (1 or 2) a flocculant precipitate forms within ~24 h of polymerization that is isolated by filtration, washed thoroughly and dried to remove any remaining free dendrimer. Chemical analysis of the composite (with PAMAM-2) showed that it is mainly SiO_2 (>90%) containing some organic material. It is also amorphous as indicated by XRD. FT-IR spectroscopy shows that the entrapped organic material is PAMAM-2 (the amide ν(C=O) appears at 1645 cm^{-1}) by comparison to an FT-IR spectrum of an authentic PAMAM-2 sample. Silica was identified by several characteristic bands [8], see Supplementary Data).

Inhibition of silica scale growth is poorly understood. The inhibitor disrupts polymerization by influencing nucleophilic attack of silicate ions among themselves (an S_{N2}-like mechanism). Orthoborate ion, for example, inhibits silica growth by forming borosilicates that possess much higher supersaturation indices than SiO_2 (*vide infra*). In the case of PAMAMs, it is apparent that NH_2-terminated analogs (most likely in a $–NH_3^+$ form in pH ranges examined) associate with negatively charged silicate ions or small silica oligomers, and thus prevent further particle growth. PAMAMs with –COOH terminus apparently cannot function in a similar manner due to charge repulsions between the deprotonated surface carboxylate groups and the silicate ions or SiO_2 oligomers. The marginal efficiency of the –COOH terminated PAMAMs within the first 12 h may be related to possible stabilization of soluble SiO_2 within the dendrimer internal voids. This hypothesis is reminiscent of a similar type of stabilization of metallic Cu nanoclusters within PAMAMs internal space [9]. At present the current test for measuring soluble SiO_2 is inefficient

Table 1
Comparison of PAMAMs to various anionic inhibitors in maintaining soluble SiO_2

Inhibitor[a]/dosage (ppm)	End-groups[b] (number)	Reactive SiO_2 (ppm, 24 h)
Control	–	171
PAMAM-0.5/40	–COOH (8)	183
PAMAM-1/40	$–NH_2$ (8)	384
PAMAM-1.5/40	–COOH (16)	176
PAMAM-2/40	$–NH_2$ (16)	374
PAMAM-2.5/40	–COOH (32)	187
HEDP/54	$–PO_3H_2$ (2), –OH (1)	180
AMP/54	$–PO_3H_2$ (3)	176
PBTC/54	–COOH (3), $–PO_3H_2$ (1)	169
PAA/100	–COOH (several)	164
HMDTMP/50	$–PO_3H_2$ (4)	169
DETMP/50	$–PO_3H_2$ (5)	171

[a] AMP, amino-tris-(methylenephosphonate); HEDP, 1-hydroxy-ethylidene-1,1-diphosphonate; PBTC, 2-phosphono-butane-1,2,4-tri-carboxylate; PAA, polyacrylate (MW ∼ 2000 Da), HMDTMP, hexamethylene-*N*,*N*′,*N*′,*N*′-diamine tetramethylenephosphonate; DETMP, diethylene triaminepenta (methylenephosphonate).

[b] These groups are partially deprotonated at the test pH.

in differentiating SiO_2 “outside” the dendrimer from that “inside” it.

Arguments based on charge alone cannot explain the inhibition performance of PAMAM-1 and -2. Experiments performed in which cationic molecules, such as NH_4^+ and $(CH_3CH_2)_4N^+$, are added in amounts that could generate in solution the same positive charge as either PAMAM-1 or -2. Neither molecule exhibits any degree of inhibition.

Growth of crystalline scale deposits is controlled by use of phosphonate inhibitors [10] or polyacrylate polymers and derivatives [10,11]. Mineral scale inhibitors achieve inhibition by stereospecific adsorption onto crystallographic planes of a growing nucleus after a nucleation event, resulting into “poisoning” further growth and crystallite agglomeration. The amorphous nature of SiO_2 scale in process waters renders effectiveness of “classical” mineral scale inhibitors questionable. This was confirmed in inhibition tests performed with several phosphonates and anionic polymers (Table 1). Orthoborate, claimed to be a SiO_2 inhibitor, is also ineffective at 40 ppm dosage levels [12].

The purpose of this work is to identify and exploit novel dendrimer chemistries as effective SiO_2 scale growth inhibitors in process waters. The principle findings are summarized as follows. (1) PAMAM dendrimers with $–NH_2$ termini are more effective inhibitors of SiO_2 scale growth than the –COOH terminated analogs. (2) Their structure (generation number and nature of termini) affects inhibitory activity. PAMAM-1 is more effective than PAMAM-2. (3) NH_2-terminated PAMAMs also act as SiO_2 aggregators forming SiO_2–PAMAM composites. This inhibitor entrapment within the SiO_2 matrix may explain loss of efficiency over time. (4) Inhibitory activity of NH_2-terminated PAMAMs may be related to their cationic nature, but also to specific topologies of the $–NH_2$ groups.

Colloidal SiO_2 having precise structure, particle size and porosity is of great interest both from a fundamental and applications perspective [13]. One such example is the preparation of amorphous silica materials from tetraethylorthosilicate (TEOS) by use of dendrimer templates with structures similar to those of PAMAMs [14]. Inhibition of SiO_2 may be desirable in some applications, whereas in others controlled formation is the goal.

Utilization of molecules with precise molecular topologies, such as STARBURST® dendrimers, may prove useful in such applications. Recently, the effect of –COOH terminated PAMAMs on the crystallization of $CaCO_3$ was reported [15].

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