Inhibition and Growth Control of Colloidal Silica: Designed Chemical Approaches

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Colloidal silica (SiO_2) is perhaps the most undesirable inorganic deposit formed in process cooling waters, especially on metallic surfaces such as heat exchangers or pipelines. Conventional mineral scale inhibitors do not inhibit its formation. Chemical cleaning is difficult and not free of hazards. Research on silica scale formation and prevention is ongoing and has led to various chemical approaches. This article covers silica fouling and discusses several treatments, with emphasis on those using inhibitors with dendrimeric structure.

Groundwaters in areas such as Texas, New Mexico, Arizona, California, parts of southern Europe, the Pacific Rim, and Latin America contain high silica concentrations (50 to 100 ppm, as colloidal silica [SiO_2]). These levels arise from dissolution of various silicate-containing minerals into the groundwater.

Silica precipitation and deposition occur mostly in evaporative cooling systems, where cation/anion levels gradually increase from partial water evaporation. Silica solubility, which depends on water chemistry and temperature, generally is accepted to be 150 to 180 ppm.[1] Operators must maintain silica at an acceptable level to avoid silica deposits. This requires operation at very low cycles of concentration (which consumes large amounts of water) or use of chemical water treatments that prevent silica scale formation and deposition.

Silica and silicate deposits are particularly difficult to remove once they form. Harsh chemical cleaning or mechanical removal is usually required.[2]

Experimental Details

The methodology described below applies to control solutions (no inhibitor) and test solutions (with inhibitor present). Glass containers are avoided to prevent contamination from silicate ions from the glass. A 500-ppm (as SiO_2) silicate stock solution (100 mL) is placed in a plastic beaker and agitated with a polytetrafluoroethylene-covered magnetic stir bar. The pH of this solution is ~11.5. Gaseous carbon dioxide (CO_2) was bubbled through a fritted glass outlet into the solution. A relatively slow sparging rate is used to avoid large pH drifts. The pH decreased as a result of carbonic acid (H_2CO_3) formation, and the CO_2 sparger is removed when pH reaches 8.5. Because the CO_2 dissolves over time, the pH continues to decrease without the sparger present. Equilibrium pH values are ~7. The beaker contents are placed in a plastic bottle, which is capped and set aside. Solutions are tested for reactive (soluble) silica by the HACH[†] silicomolybdate method after 24-, 48-, and 72-h time intervals. A variety of mineral acids can be used to lower the solution pH. We have successfully

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[†] Trade name.

performed experiments using hydrochloric acid (HCl) for pH adjustments.

Soluble (Reactive) Silica Measurements

The silicomolybdate test measures “soluble,” or “reactive,” silica. It does not measure “colloidal” silica.[3] The term “reactive” represents not only monomeric silica (silicate ion) but also other “oligomeric species” such as dimers, trimers, tetramers, etc. It is not clear where the cutoff is. For practical purposes, the authors assume that the silicomolybdate test results are associated with all forms of reactive silica except colloidal form. The screening and testing procedures are reproduced at least three times, and the relative error is within ±5%.

Approaches to Silica Scale Control

Controlling silica scale can be achieved in several ways, including:

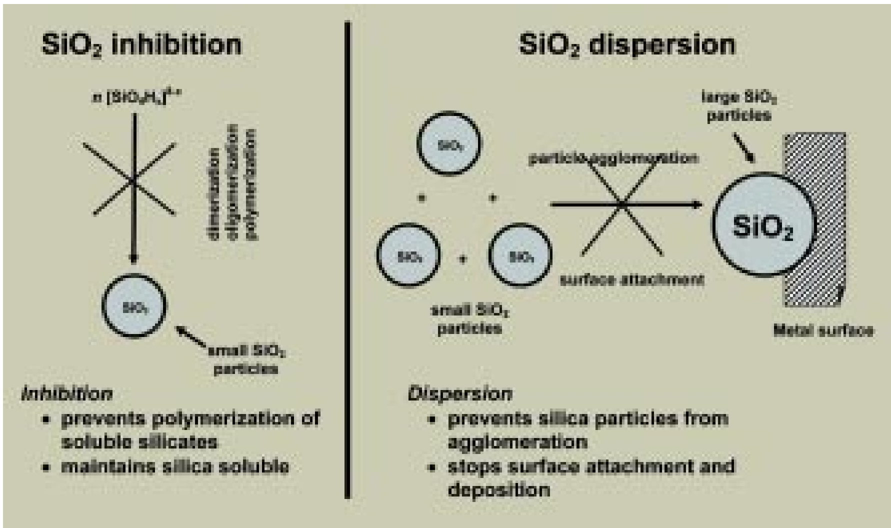
- Operation at low cycles of concentration
- Prevention of other-scale formation
- Pretreatment
- Use of inhibitors or dispersants.

The first three approaches are outside the scope of this article. Chemical control of silica scale generally follows two approaches: inhibition and dispersion (Figure 1). Inhibition prevents silica oligomerization or polymerization. As a result, the silica remains soluble and, therefore, reactive. Dispersion prevents particle agglomeration to form larger-size particles and also prevents surface adhesion/attachment.

Silica Scale Inhibition by Dendrimers

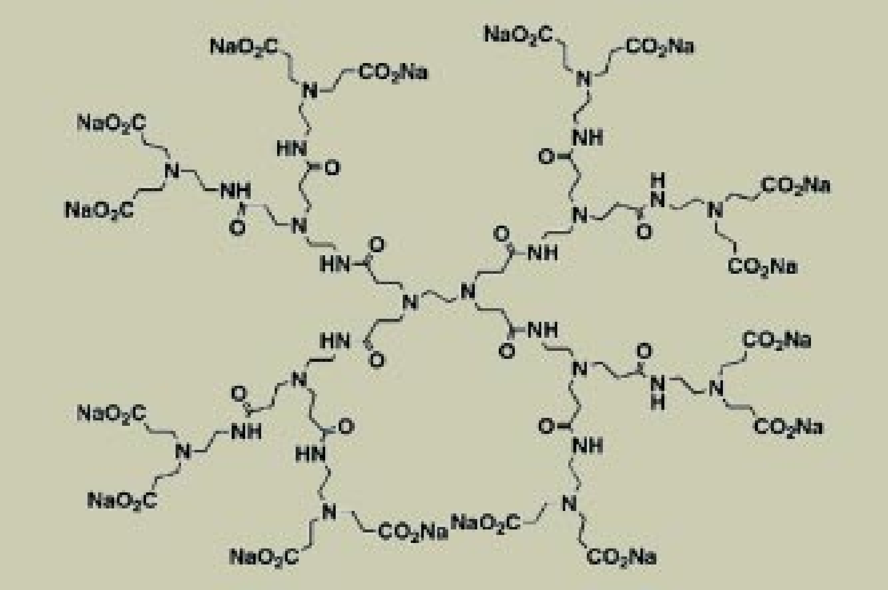
Dendrimers of the polyaminoamide (PAMAM) family were used in this study[4] (Figure 2). These dendrimers are available in generations that indicate the extent of branching. The higher the generation number is, the more extensive the branching is.

FIGURE 1



Chemical approaches to controlling silica scale.

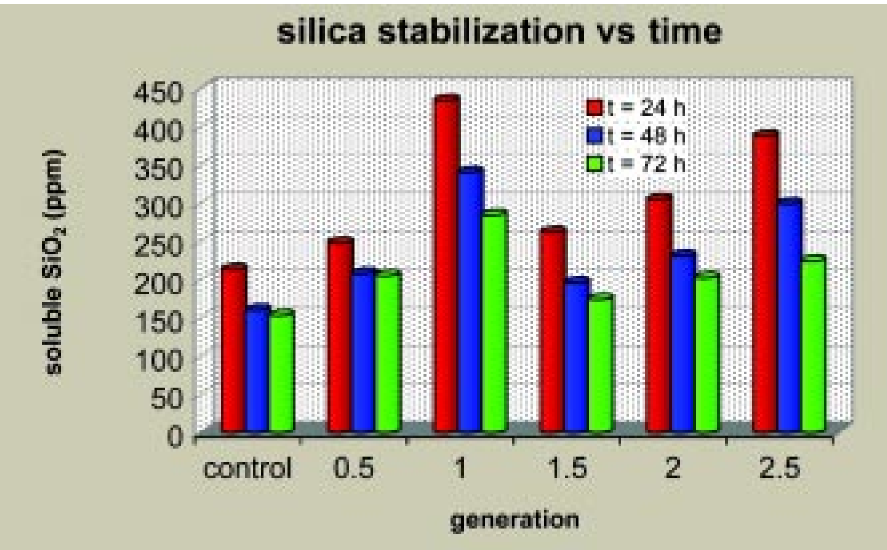
FIGURE 2



Schematic representation of a polyaminoamide dendrimer inhibitor of generation 1.5 (16–COOH terminal groups).

The inhibitors were used at 40 ppm (as actives). After 24 h in control solutions, silica polymerization proceeds until only 213 ppm SiO_2 remain soluble (Table 1, Figure 3). The remaining SiO_2 forms colloidal particles. PAMAM-0.5 gives only marginal inhibition, allowing 248 ppm SiO_2 to remain soluble. PAMAM-1 shows remarkable inhibitory activity in controlling silica polymerization, giving 434 ppm of reactive SiO_2. The inhibition efficiency of the next generation’s PAMAMs appears to be lower. PAMAM-1.5 shows about the same efficiency as PAMAM-0.5 (262 ppm soluble SiO_2). PAMAM-2 and

FIGURE 3



Inhibition of silica polymerization by dendrimers.

TABLE 1

SOLUBLE SILICA AFTER 24 H

Generation	Soluble Silica in Bulk (ppm)	Filtered Soluble Silica (ppm)	End-Group	Number of End Groups
Control (no inhibitor)	213	213	—	—
0.5	248	177	–COOH	8
1	434	329	$–NH_2$	8
1.5	262	215	–COOH	16
2	305	257	$–NH_2$	16
2.5	388	335	–COOH	32

PAMAM-2.5 give values of 305 and 388 ppm soluble SiO_2, respectively.

SiO_2 polymerization continues after 48 h (Figure 3). In control solutions, soluble SiO_2 levels drop to 160 ppm (loss of 53 ppm). Inhibition efficiencies of all PAMAM dendrimers drop as well. PAMAM-0.5 retains 208 ppm soluble SiO_2 (loss of 40 ppm). PAMAM-1 solubilizes 340 ppm a loss of 94 ppm soluble SiO_2. Gradual loss of inhibitory activity is observed in results with PAMAM-1.5, 2, and 2.5, giving 196, 231, and 299 ppm, respectively.

Loss of inhibition performance continues to drop after 72 h. Soluble SiO_2 in the control solution appears to be stabilized at ~150 ppm. PAMAM-0.5 allows 205 ppm of SiO_2 to remain soluble (a drop of only 3 ppm from the 48-h measurement). PAMAM-1 keeps 284 ppm silica soluble, whereas PAMAM-1.5, 2, and 2.5 give 174, 202, and 224 ppm soluble silica, respectively. Solutions containing any of the PAMAM dendrimers exhibited higher levels of soluble SiO_2 than those containing no inhibitor after 72 h of polymerization time.

Silica Scale Formation and Deposition

Silica scale growth is a complex process involving numerous equilibria.[5] In evaporative cooling water systems (where the pH of interest is 7 to 9.5), colloidal silica usually is favored at a pH of <8.5; in contrast, magnesium silicate ($3MgSiO_3·5H_2O$) scale forms at a pH of more than 8.5.[6] There is no clear cutoff, and silica and magnesium silicate usually form in random mixtures. Silica exhibits normal solubility characteristics, which increase proportionally to temperature. In contrast, magnesium silicate exhibits inverse solubility.

Formation of colloidal silica actually results from silicate ion polymerization,[7] contrasting with crystalline scales—such as calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), etc.—which are products of cation-anion association. When silicate ions polymerize, they form primarily crosslinked polymeric chains, oligomeric structures, etc. The resulting amorphous silica scale is a complex, multicomponent product mixture.

Dissolved silica principally precipitates out of solution in three ways: by surface deposition, in living organisms, and through bulk precipitation. In surface deposition, forms of the silicate ion condense with any solid surface possessing –OH groups. If the surface contains M-OH moieties (M = metal), this reaction is enhanced further. Such pronounced silica deposition phenomena in the water treatment industry are observed on metallic surfaces that have suffered severe corrosion—the surface is covered with metal oxides/hydroxides. Once the receptive surface is covered with silica scale, additional silica is deposited on an already formed silica film. Silica in living organisms is called "biogenic" and appears in certain microorganisms that have the ability to deposit silica from highly undersaturated solutions. Bulk precipitation allows silicate ions to polymerize and form small colloidal silica particles. The particles grow and agglomerate, forming larger silica particles (Figure 1).

The precise mechanism of silica formation is not well understood. Any interference with the condensation reaction may lead to silica scale growth inhibition. A relevant example is silica inhibition by orthoborate. Orthoborate reacts with silicate ions to form borosilicates, which are more water-soluble than silica/metal silicates.[8] PAMAMs seem to have a deleterious effect on the silica condensation reaction—most likely at its earlier stages where the reaction products are oligomeric silicates. These silicates most likely allow small silica particles to be "stored" within the dendrimer internal void spaces, thus preventing silica precipitation (Figure 4).

The silica levels tested in this study represent a high-stress situation with regard to silica supersaturation. No real system is known to operate at such high levels. The dendrimer inhibitors lose their inhibitory activity after 72 h and allow the formation of silica precipitates—a result of co-precipitation and entrapment within the silica matrix. The reaction was verified by infrared spectroscopy (data not shown), which proved the presence of dendrimer in the deposit.

The Effect of Cations

Operating industrial water at a high pH is not necessarily a solution for combating silica scale. One must take into account the presence of magnesium (Mg^{2+}) and other scaling ions such as calcium (Ca^{2+}). A pH adjustment to >8.5 might cause massive precipitation of magnesium silicate if high levels of Mg^{2+} are present or calcium carbonates or phosphates if high levels of these ions are overlooked[9] (Figure 5).

Silica precipitation also can be aggravated by the presence of metal ions such as iron or aluminum and their hydroxides.[10] Corroded steel surfaces are prone to silica fouling as the oxides/hydroxides act as deposition matrices for either soluble or colloidal silica deposits.

Polyvalent metal ions present in feedwater can adsorb onto colloidal silica particles and accelerate particle agglomeration and eventual precipitation and fouling. The adverse effect of these ions on silica precipitation emphasizes the importance of silica inhibition rather than dispersion. Dispersion of colloidal silica is challenging at higher cycles, where concentrations of metal ions such as calcium and magnesium are very high. The situation worsens in the presence of iron or aluminum. The presence of cations, such as Ca and Mg, does not significantly affect silica polymerization—unless operational pH favors formation of Mg silicate.

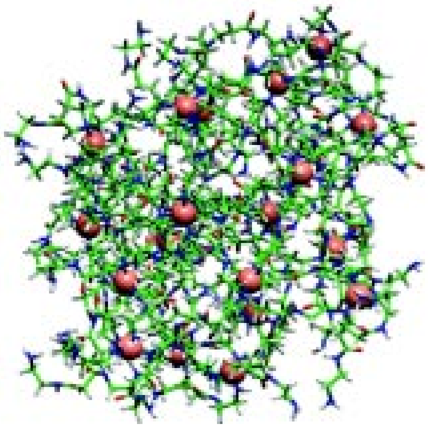
Conclusions/Perspectives

Silica scale severely impedes heat transfer; is tenacious, costly, and potentially hazardous to remove; and is extremely prone to co-precipitation with other scales. It often limits the ability to achieve high cycles of concentration.

The amorphous character of silica deposits precludes the use of conventional crystal modification technologies. Molecules such as phosphonates that are effective crystalline scale threshold inhibitors provide virtually no direct benefit in inhibiting silica scale formation.

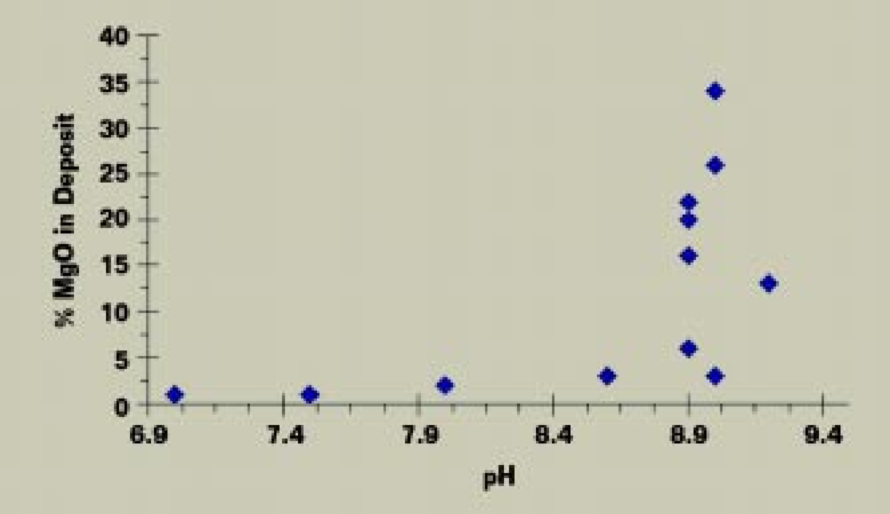
Resolving the silica problem is a difficult task.[11] No single solution will ensure a water system free of silica deposits. Several factors, unique to the individual system, must be taken into account: a) water chemistry (presence of other scaling ions), b) nature of the silica (colloidal or reactive), c) target cycles of concentration, d) feasibility of mechanical silica removal through filtration and softening, and e) capital costs for chemicals and/or equipment. A chemical approach is necessary most of the time. Randomly testing inhibitors for silica scale growth is certain to be a useless exercise. The discovery process must include careful design of the inhibitor molecule, even at the early stages of the research and development process.

FIGURE 4



Computer-generated image of possible stabilization of small colloidal silica particles within the dendrimer core. (Reproduced from http://www.dendritech.com.)

FIGURE 5



Effect of pH on magnesium silicate precipitation and deposition.

In this article, the authors have explored the ability of a family of dendrimers to inhibit and stabilize silica and examined their potential as storage vesicles of small colloidal silica particles. Although the cost of these molecules is still prohibitive for cooling water applications, further exploration might open new possibilities for field applications.

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