*Chapter VI*

# Silica Scale Inhibition Relevant to Desalination Technologies: Progress and Recent Developments

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## Abstract

Fouling in industrial waters supporting a number of process industries is a major issue that causes unexpected shutdowns and costly chemical or mechanical cleaning operations. Some deposits, although less common, are exceptionally troublesome. These include silica and magnesium silicate. Accumulation of these deposits greatly diminishes system performance. Scale prevention can be achieved by use of scale inhibitors that are added to any given treatment in minute (parts per million) quantities. Use of environmentally friendly water additives for colloidal silica scale control is a topic of great interest and intense research efforts in our laboratories. Inhibition and dispersion are two generic approaches for preventing silica scale and fouling. Inhibition stops scale-forming precipitates from forming, whereas dispersion keeps scale particles from being attached onto critical surfaces. We have pursued silicate polymerization inhibition by use of cationic and zwitter-ionic macromolecules. These include PAMAM-1, polyaminoamide dendrimer of generation 1; PAMAM-2, polyaminoamide dendrimer of generation 2; PEI, polyethyleneimine; PALAM, polyallylamine; PAMALAM, poly(acrylamide-co-diallyl-dimethylammonium chloride); MAD-co-MEO, statistical polymers with methacrylate ester building units; PPEI, phosphonomethylated polyethyleneimine; CATIN-1280, cationic inulin with average degree of substitution (number of cationic groups per ring) 1.28; PCH, phosphonomethylated chitosan. Based

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on the results reported in this chapter, interesting parallels are drawn between structure and inhibitory activity.

# Introduction

Desalination systems that utilize reverse osmosis membranes for species separation are often plagued by deposition problems that originate from a variety of deposits, organic or inorganic, crystalline or colloidal [1]. 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 material failures and operational shut-downs. Users and operators of industrial and potable water systems 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 every chemical water treatment [2]. Unfortunately, these traditional scale control methods (crystal growth inhibition and crystal modification) applied to crystalline mineral salt precipitates *do not apply to SiO$_2$* because of its amorphous nature. 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 [3-13]. This chapter focuses on use of cationic polymeric additives that inhibit silica scale growth. Silica has been one of the poorly understood problems in the scale prevention technology area. This research is part of our on-going investigations on the design, discovery, application and optimization of scale inhibitors in industrial process waters [4-12].

Chemical additives are used to condition water so the following problems do not occur, or are minimized to an appreciable extent [13]:

a. Scale formation and/or deposition of sparingly soluble salts
b. Corrosion of "critical" metal surfaces
c. Development of biofouling – biofilm colonization

Naturally, chemicals that are added to condition water have various purposes, and thus wildly different physicochemical properties. For example, organophosphonates are used to combat calcium/barium/strontium salt formation and deposition [14]. Control of other types of scales, *eg.* amorphous silica requires a more thoughtful and, at times, "exotic" approach [15]. Colloidal silica presents a problem that has been poorly mitigated and still represents an area of development for inhibitor chemistries.
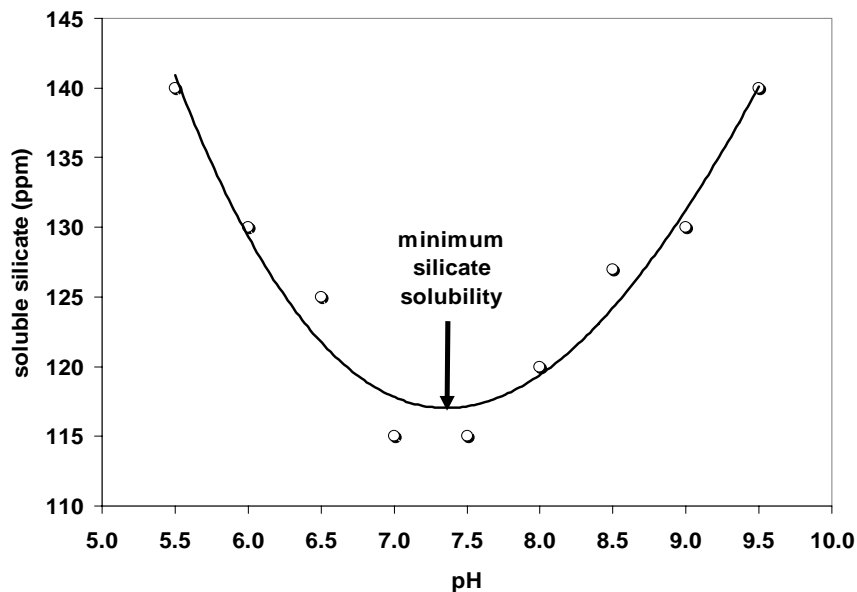
Figure 1. Change in silicate ion solubility according to pH.

# Silicate Polymerization in Process Waters

The polymerization of silicate ions at pH regions around 7 reaches a maximum, resulting in minimum silica solubility, Figure 1. Therefore, the neutral pH 7 was selected for the inhibition experiments, as a "worst-case scenario". Inhibition protocols that were followed have been reported in detail before [4-12].

Silica precipitation/deposition frequently is encountered in water systems where silicate levels are sufficiently high. Silica solubility in water generally is 150 ppm to 180 ppm, depending on particular water chemistry and temperature [16]. This imposes severe limits on water system operators, leading to (unavoidable) use of chemical water treatment techniques that prevent silica-scale formation and deposition. Silica formation occurs through an $S_N2$-like mechanism that involves attack of a monodeprotonated silicic acid molecule on a fully protonated silicic acid molecule (see Figure 2).

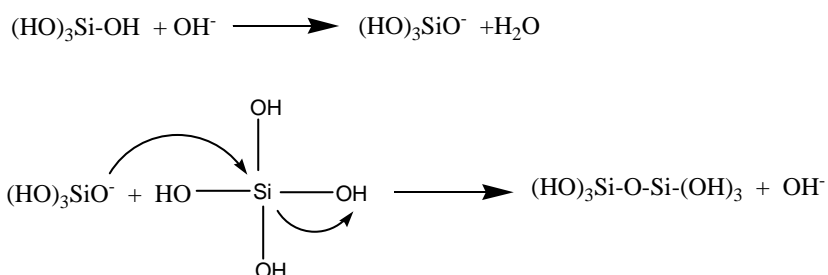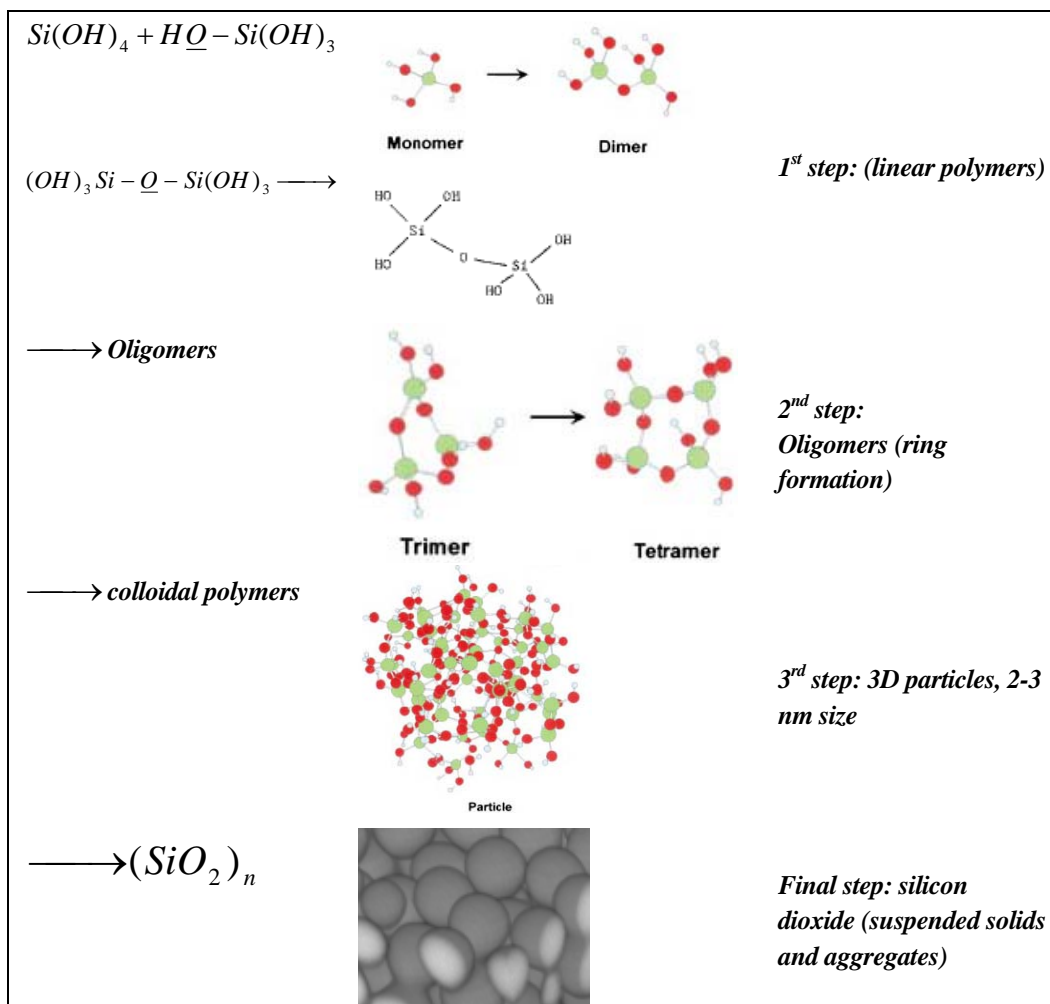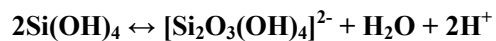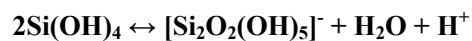$$(HO)_3Si\text{-}OH + OH^- \longrightarrow (HO)_3SiO^- + H_2O$$



Figure 2. Polymerization pathway of silicate to produce silicate dimers and eventually colloidal silica particles (also, see Table 1).

**Table 1. Stepwise formation of colloidal silica particles from soluble silicic acid**

$Si(OH)_4 + H\underline{O} - Si(OH)_3$



Monomer → Dimer

*1st step: (linear polymers)*

$(OH)_3 Si - \underline{O} - Si(OH)_3 \longrightarrow$

$\longrightarrow$ *Oligomers*

Trimer → Tetramer

*2nd step: Oligomers (ring formation)*

$\longrightarrow$ *colloidal polymers*

Particle

*3rd step: 3D particles, 2-3 nm size*

$\longrightarrow (SiO_2)_n$

*Final step: silicon dioxide (suspended solids and aggregates)*

Furthermore, this needs to be put in context with the following silicate equilibria that occur in aqueous systems [16]:

$$Si(OH)_4 \leftrightarrow [SiO(OH)_3]^- + H^+$$

$$Si(OH)_4 \leftrightarrow [SiO_2(OH)_2]^{2-} + 2H^+$$

$$2Si(OH)_4 \leftrightarrow Si_2O(OH)_6 + H_2O$$

$$2Si(OH)_4 \leftrightarrow [Si_2O_2(OH)_5]^- + H_2O + H^+$$

$$2Si(OH)_4 \leftrightarrow [Si_2O_3(OH)_4]^{2-} + H_2O + 2H^+$$

Formation of silica deposits is a complex process that involves a number of steps. These are summarized in the following Table 1.

# Inhibitor Chemistry

Our recent research has shown that "small molecules" are not active in silica scale inhibition. Therefore polymeric additives were sought, that contain some degree of cationic charge. In Figure 3 the schematic structures of inhibitors are shown.

The selected polymers show a variety of structural features. All contain some degree of cationic charge. Some (PAMAM-1, PAMAM-2, PEI, PALAM, PAMALAM and CATIN-1280) possess cationic charge exclusively. Others (MAD-co-MEO, PPEI, PCH) are zwitter-ionic, *ie.* they have cationic and anionic charge on the polymer backbone. Some polymers possess positive charge by virtue of protonated amine groups (PAMAM-1, PAMAM-2, PEI, PALAM), others have a "pure" cationic charge due to a tertiary N group, $-NR_3^+$ (PAMALAM, MAD-co-MEO, CATIN-1280). These additives have been extensively tested with varying dosages. Below, we present silicate stabilization results with 40 ppm dosage for all polymers (Figure 4). It becomes apparent that all polymers show inhibitory activity (higher soluble silicate levels than the "control"). PAMAM-1 and PAMAM-2 (both have their surface amine groups protonated at pH 7) are very effective inhibitors at 40 ppm dosage. Presence of protonated amine groups is not the only necessary condition for good inhibition. Notice that polymers PEI and PALAM (also having their amine groups protonated at pH 7) show rather poor performance. This could be explained by the fact that excessive cationic charge causes the polymeric additive to be entrapped and hence de-activated within the colloidal silica matrix. Polymers that possess a tertiary N group are "medium" performance inhibitors, note PAMALAM and CATIN-1280. From the zwitter-ionic polymers (MAD-co-MEO, PPEI and PCH), MAD-co-MEO and PPEI are very effective inhibitors. In this case, it appears that the negative charge ($-SO_3^-$ for MAD-co-MEO and $-PO_3H^-$ for PPEI) "balances" the positive charge in such a way that the polymer continues to be active, but inhibitor entrapment and deactivation is prevented. For the PCH polymer, perhaps the anionic charge (due to $-PO_3H^-$) is too excessive and the cationic charge (necessary for inhibition) is "neutralized".

When polymer dosage is doubled (an increase from 40 ppm to 80 ppm) a number of interesting features appear in inhibition activity (Figure 5). PAMAM-1 retains its inhibitory activity, in contrast to PAMAM-2, which substantially drops in performance (from 374 to 238 ppm soluble silicate). PEI, PALAM, MAD-co-MEO, PPEI, CATIN-1280 and PCH retain their previous inhibitory activity, with only minor alterations. The only polymer that increases its activity is PAMALAM. Further dosage increase, however, caused no further enhancement (data not shown).

It is now certain that effective silica scale inhibition is dependent on the cationic charge on the polymer backbone, on an insufficiently quantified fashion. We have proven that certain cationic polymers are trapped in the colloidal silica matrix. The FT-IR spectrum shown in Figure 6 demonstrates clearly that PCH is trapped in the silica precipitate.
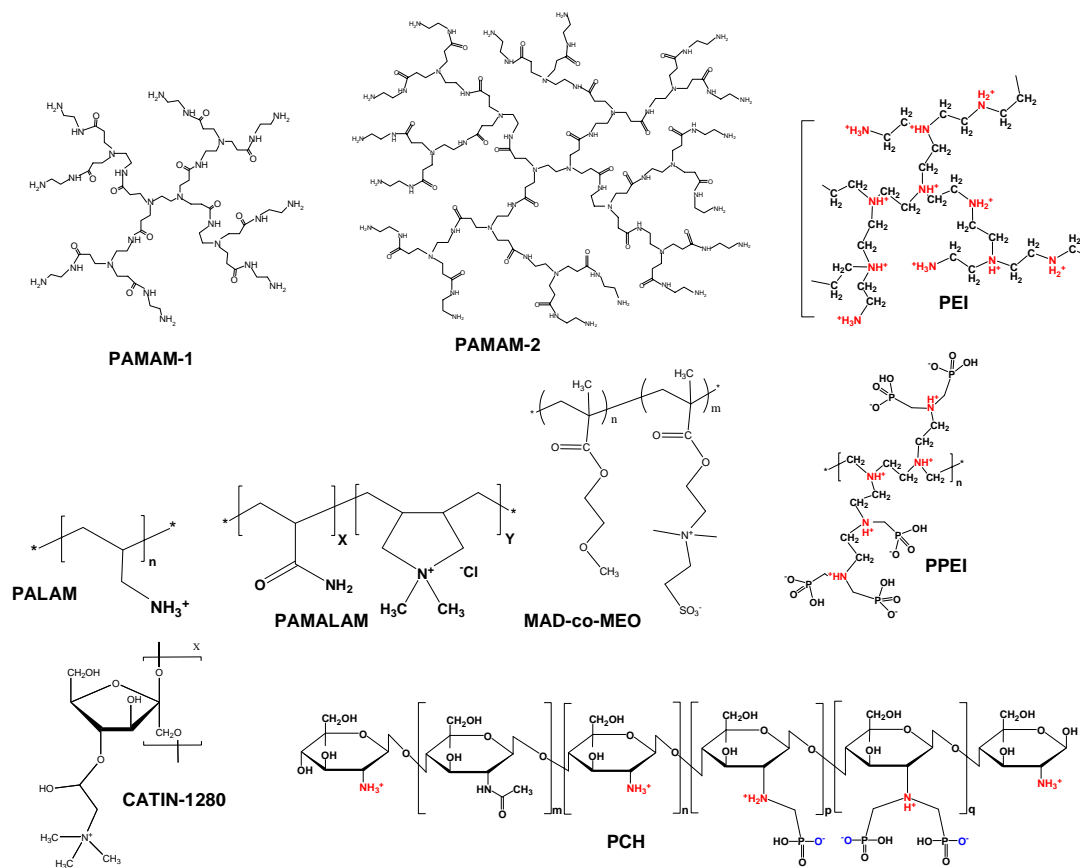
Figure 3. Schematic structures of the polymeric inhibitors. Abbreviations: PAMAM-1, polyaminoamide dendrimer of generation 1; PAMAM-2, polyaminoamide dendrimer of generation 2; PEI, polyethyleneimine (branched); PALAM, polyallylamine; PAMALAM, poly(acrylamide-co-diallyl-dimethylammonium chloride) (x=0.55, y=0.55), MAD-co-MEO, statistical polymers with the building units shown with n=0.63, m=0.37; PPEI, phosphonomethylated PEI; CATIN-1280, cationic inulin with average degree of substitution (number of cationic groups $per$ ring) 1.28; PCH, phosphonomethylated chitosan with m = 0.16, n = 0.37, p = 0.24, q = 0.14.
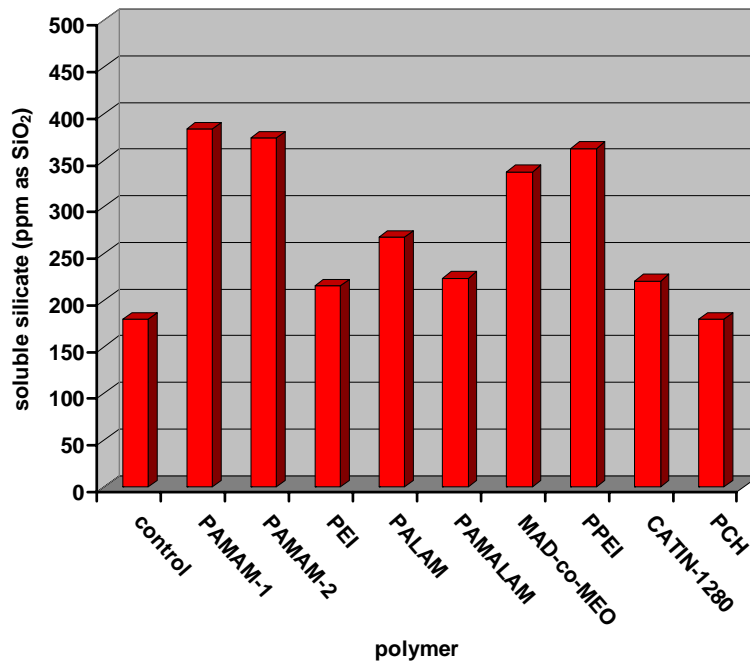
Figure 4. Silicate stabilization (starting silicate level = 500 ppm) in the presence of polymeric additives (at 40 ppm dosage).
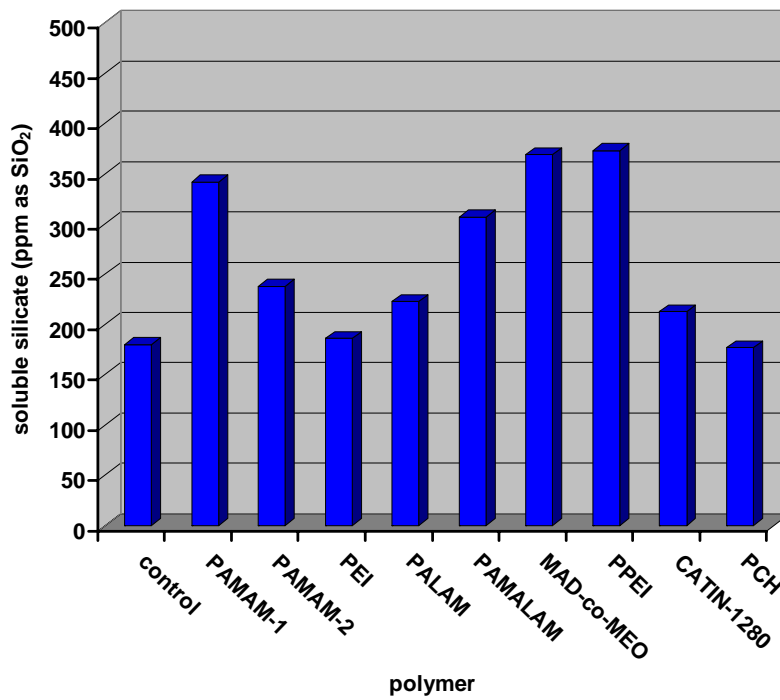


Figure 5. Silicate stabilization (starting silicate level = 500 ppm) in the presence of polymeric additives (at 80 ppm dosage).
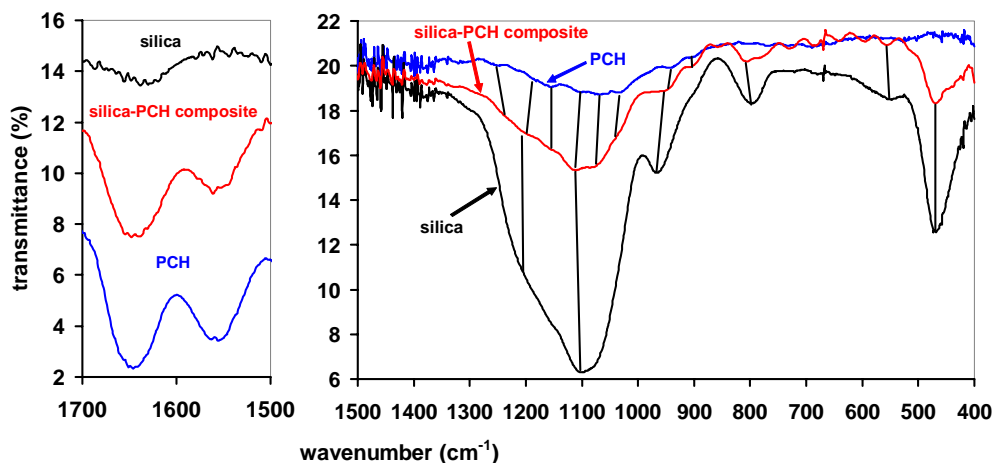
Figure 6. PCH entrapment within the colloidal SiO$_2$ matrix, as demonstrated by FT-IR spectroscopy.

It is apparent that inhibitor dosage increase has detrimental effects on inhibitory activity. This has been observed before for other cationic inhibitors [7,10]. It can be explained upon examination of the possible silica inhibition mechanism. Experimental results from our group have supported the premise that anionic molecules (either monomeric or polymeric) have no effect on silicate polymerization [7]. In contrast, cationic polymeric molecules are effective silica scale inhibitors [5-12]. When silicate polymerization takes place in the presence of a cationic polymeric additive, there are a number of competing reactions taking place concurrently:

a. Polymerization of silicate anions. This occurs through an S$_N$2-like mechanism that involves attack of a monodeprotonated silicic acid molecule on a fully protonated silicic acid molecule. This pathway generates at first short-lived silicate dimers, which in turn continue to polymerize in a random way to eventually yield colloidal silica particles (see Table 1).

b. Silicate ion stabilization by the cationic additive. This is the actual inhibition step and occurs presumably through cation-anion and/or hydrogen bonding interactions.

c. Flocculation between the polycationic inhibitor and the negatively charged colloidal silica particles (at pH 7) that are formed by the uninhibited silicate polymerization (Figure 7).

Cationic inhibitor is trapped within the colloidal silica matrix, based on reaction (c). This is demonstrated by the appearance of a light flocculent precipitates (or stable dispersions at times). Inhibitor entrapment causes its depletion from solution and its deactivation. Therefore, only a portion of the inhibitor is available to continue inhibition at much lower levels than initially added to the polymerization medium. Thus, soluble silicate levels continue to decrease because eventually there is not sufficient inhibitor to perform inhibition. Inhibitor entrapment is directly proportional to cationic charge density. For example, PEI (polyethyleneimine) a branched cationic polymer with high positive charge density causes rapid formation of composite precipitates with colloidal silica [17].
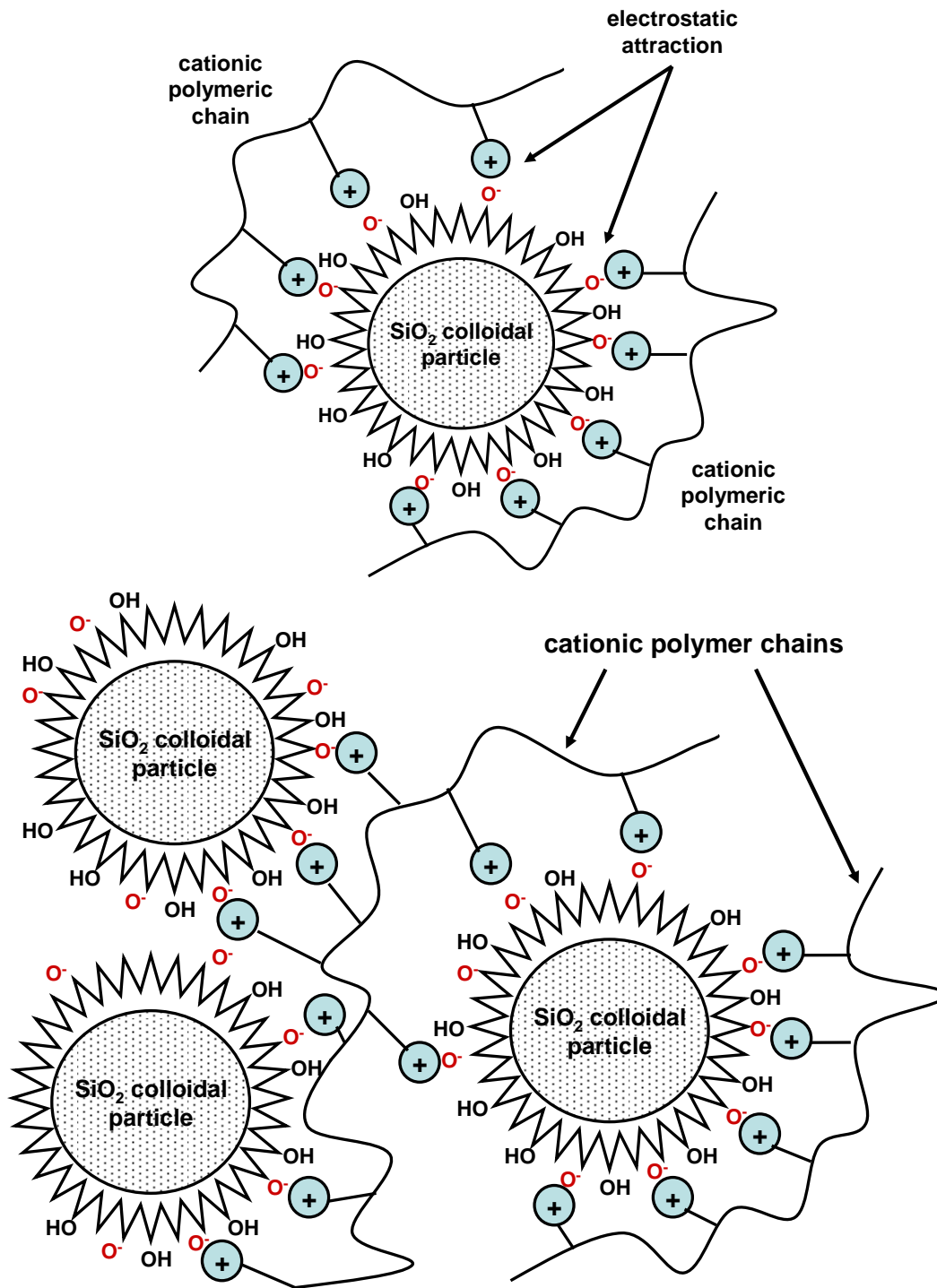
Figure 7. Schematic representations of colloidal silica-polycation flocculation. Upper: polymer attachment on a single silica nanoparticle. Lower: polymer bridging neighboring silica nanoparticles.

# Conclusions/Perspectives

Desalination is the "art" of desalting water for potable uses. It is now widely recognized that formation of sparingly soluble salts and deposits on desalination equipment (eg. RO membranes) is a profound (both technologically and economically) problem. Its mitigation by chemical means is of utmost importance for proper system operation. In this chapter we presented some results on how silica scale can be mitigated by the use of polymeric additives. The principal findings are summarized below:

(1) Cationic polymers show inhibitory activity in silicate polymerization.
(2) Their inhibitory performance is dosage dependent, but inhibitor dosage increase does not predictably result in performance improvement.
(3) Cationic charge on the polymer backbone, although necessary for inhibition, can cause inhibitor entrapment within the colloidal silica matrix because of polycation (polymer)-polyanion (silica) interactions.
(4) Effective silica inhibition is based on a delicate balance of cationic-anionic charges on the polymer backbone.

Research on inhibitor chemistries is intense and lately focused on additives that are not only efficient and cost-effective, but also environmentally friendly. With governments and environmental groups becoming increasingly aware of the positive impact that can be brought on the environment by use of safe, non-toxic and green inhibitors, intense research in this field is a "one-way street".

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