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Being “green” in chemical water treatment technologies: issues, challenges and developments

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Abstract

Mineral scale deposits in industrial waters supporting a number of process industries are a major problem 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 laboratory. 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 “green”, environmentally-friendly cationic macromolecules. These utilize inulin as the backbone, which has been chemically modified to introduce quaternary ammonium moieties. Three CATIN polymers (CATIN = cationic inulin) were tested: CATIN-1 (DS = 0.22), CATIN-2 (DS = 0.86), CATIN-3 (DS = 1.28), DS = degree of substitution at dosages 40, 80 and 100 ppm in supersaturated silicate solutions (500 ppm) adjusted to pH 7 for 8 h. Measurements for soluble silicate were performed every hour. After 8 h polymerization time, CATIN-1 achieves stabilization of 275 ppm silicate (~90 ppm above the control), whereas CATIN-2 and CATIN-3 exhibit virtually identical performance, stabilizing ~340 ppm silicate (~150 ppm above the control). Inhibitor dosage increase to 80 ppm does not induce any additional inhibitory performance. Further inhibitor dosage increase to 100 ppm appears to have additional detrimental effects on inhibitory activity. CATIN-1 maintains 247 ppm soluble silicate (only ~50 ppm above the control), CATIN-2 keeps ~300 ppm soluble

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silicate (~100 ppm above the control), and finally CATIN-3 maintains ~270 ppm soluble silicate (~80 ppm above the control). These CATIN additives present promising alternatives to treat silicate-supersaturated process waters.

Keywords: Green chemistry; Environmentally friendly; Scale inhibition; Silica; Additives; Water treatment; Cationic polymers

1. Introduction

“Green chemistry” has become a topic of intense discussion and debate during the last decade [1–4]. The concept of green chemistry has infiltrated to all aspects of chemistry and related technological fields. One important area where green chemistry can potentially find several applications is the use of environmentally acceptable additives for water treatment.

Chemical additives are used to condition water so the following problems do not occur, or are minimized [5]:

- (a) Scale formation-deposition of sparingly soluble salts
- (b) Corrosion of metal surfaces
- (c) Development of biofouling

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 [6]. Control of other types of scales, e.g. silica requires a more thoughtful and at times “exotic” approach [7]. Colloidal silica presents a problem that has been poorly solved and still represents an area of development for inhibitor chemistries.

An important definition of a “green chemical” has been given by Anastas and Warner [1]. They have given a broad definition of green chemistry based on 12 principles that relate to several steps, from chemical synthesis to chemical usage. A green chemical should be synthesized in a safe and energy efficient manner, its toxicity should be minimal, whereas its biodegradation should be optimal. Lastly, its impact to the environment

should be as low as possible.

The OSPAR Commission (Oslo and Paris Commission [8]) is the international body responsible for harmonization of the strategies and legislation in the North-East Atlantic Region. The Commission has stated that every effort should be made to combat eutrophication and achieve a healthy marine environment where eutrophication does not occur by the year 2010. Chemicals are classified differently depending on the particulars of the geographical area. The guidelines set by OSPAR are:

- (a) Biodegradability (>60% in 28 days. If <20%, the chemical is a candidate for substitution)
- (b) Toxicity (LC_{50} or EC_{50} >1 mg/L for inorganic species, LC_{50} or EC_{50} >10 mg/L for organic species)
- (c) Bioaccumulation ($\log_{pow} <3$, pow = partition in octanol/water)

When a chemical fulfils two out of three requirements and its biodegradability is superior to 20% in 28 days it is eligible to be listed on the PLONOR list (pose little or no risk). This emphasizes the biodegradability factor and influences usage of water additives.

In this paper we present results on three inulin-based cationic polymers that are effective silica scale inhibitors. Anionic derivatives of inulin (carboxylate-modified) have been used in the literature to combat $CaCO_3$ crystallization [9,10]. This is the first application of cationic inulins in the water treatment field.

2. Experimental

The additives used in this study are shown in Fig. 1. Experimental details about inhibition pro-

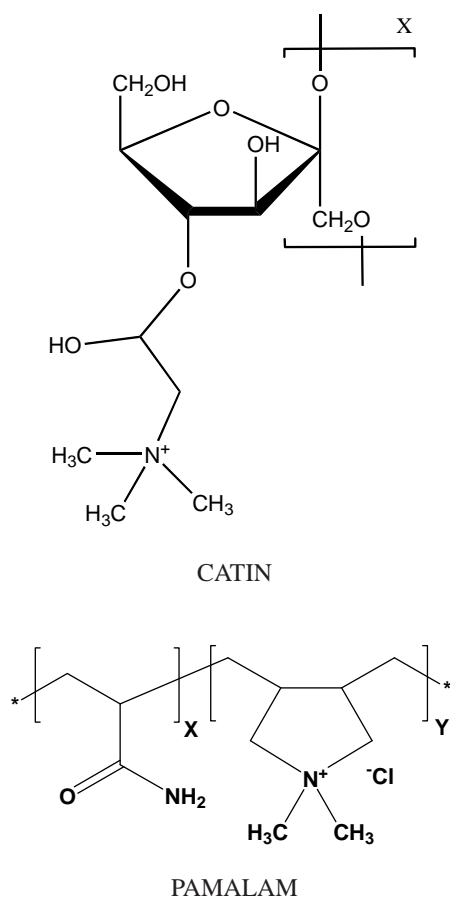


Fig. 1. Schematic structures of CATIN (upper) and PAMALAM (lower).

protocols used herein are described in detail elsewhere [11]. The CATIN polymers were supplied by Cosun (Breda, the Netherlands). Polymer details: CATIN-1 (DS = 0.22), CATIN-2 (DS = 0.86), CATIN-3 (DS = 1.28), DS = degree of substitution. Degree of substitution is defined as the average number of cationic groups per monomeric unit.

3. Results and discussion

The polymerization of silicate ions at pH regions around 7 reaches a maximum, resulting in

a reduced solubility for silica (Fig. 2). Therefore we selected the neutral pH 7 for the inhibition experiments, as a “worst-case scenario”. The inhibitors CATINs and PAMALAM were selected because they possess a quaternary ammonium cationic charge that is not affected by pH in their building units.

In this paper we present inhibition results during the first 8 h of silicate polymerization time. Various inhibitor dosages were tested (10, 20, 40, 80 and 100 ppm). Lower inhibitor dosages (10–20 ppm) are not capable of effectively inhibiting silicate polymerization (results not shown herein). Fig. 3 demonstrates the inhibition efficiency of the three CATIN polymers at 40 ppm dosage. After 8 h polymerization time, CATIN-1 achieves stabilization of 275 ppm silicate (~90 ppm above the control), whereas CATIN-2 and CATIN-3 exhibit virtually identical performance, stabilizing ~340 ppm silicate (~150 ppm above the control). Inhibitor dosage increase to 80 ppm does not induce any additional inhibitory performance (Fig. 4). More specifically, CATIN-2 stabilizes ~330 ppm silicate (~140 ppm above the control), and CATIN-3 maintains ~280 ppm soluble silicate (~90 ppm above the control). Further inhibitor dosage increase to 100 ppm appears to have additional detrimental effects on inhibitory activity (Fig. 5). CATIN-1 maintains 247 ppm soluble silicate (only ~50 ppm above the control), CATIN-2 keeps ~300 ppm soluble silicate (~100 ppm above the control), and finally CATIN-3 maintains ~270 ppm soluble silicate (~80 ppm above the control).

For comparison, we present inhibition results obtained with PAMALAM as silica growth inhibitor (Figs. 4 and 5). When 80 ppm PAMALAM are added in 500 ppm silicate solutions 385 ppm soluble silicate are measured after 8 h (~200 ppm above the control). When PAMALAM dosage is increased to 100 ppm, 325 ppm soluble silicates are measured after 8 h (~130 ppm above the control). It appears that PAMALAM is a moderately more effective inhibitor of silica growth than all the CATIN polymeric additives.

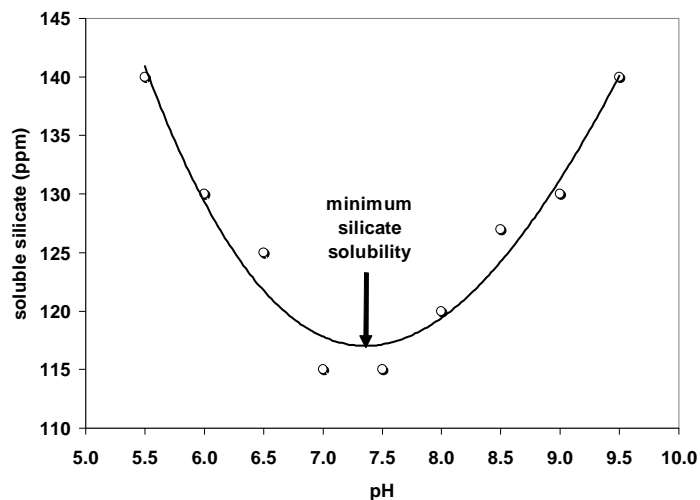


Fig. 2. Change in silicate ion solubility according to pH.

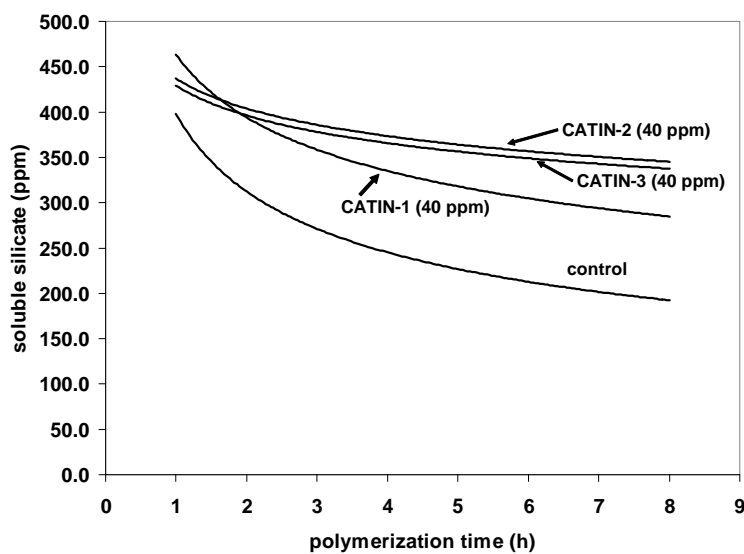


Fig. 3. Enhancement of silicate ion solubility in the presence of cationic polymeric inhibitors in 40 ppm dosages.

It is apparent that inhibitor dosage increase has detrimental effects on inhibitory activity. This has been observed before for other cationic inhibitors [12]. 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 [13]. In contrast, cationic polymeric molecules (not monomeric) are effective silica scale inhibitors [14]. When silicate polymerization takes place in the presence of a cationic polymeric ad-

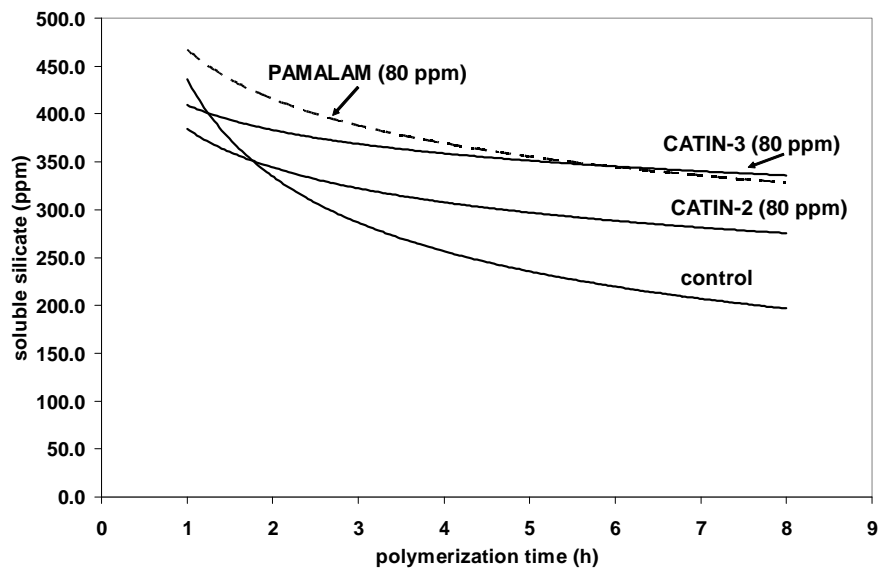


Fig. 4. Enhancement of silicate ion solubility in the presence of cationic polymeric inhibitors in 80 ppm dosages.

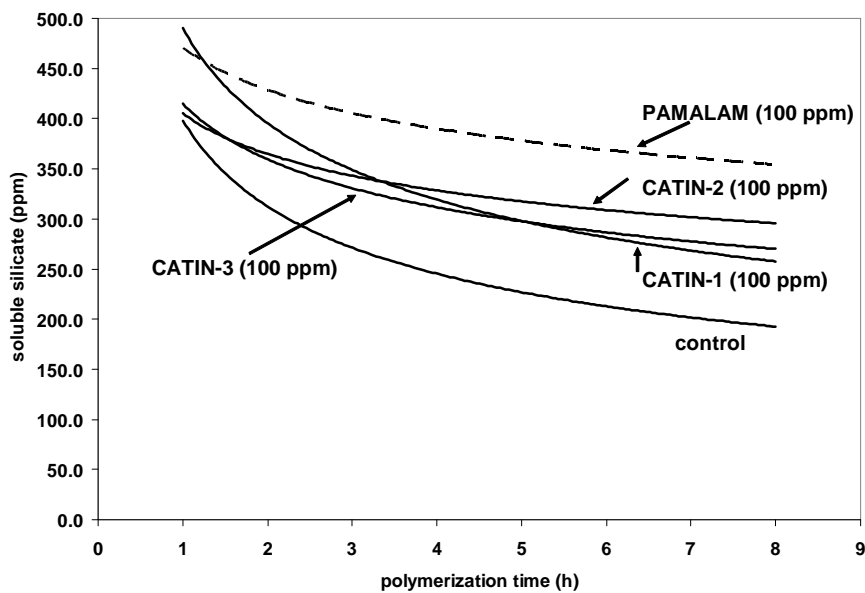


Fig. 5. Enhancement of silicate ion solubility in the presence of cationic polymeric inhibitors in 100 ppm dosages.

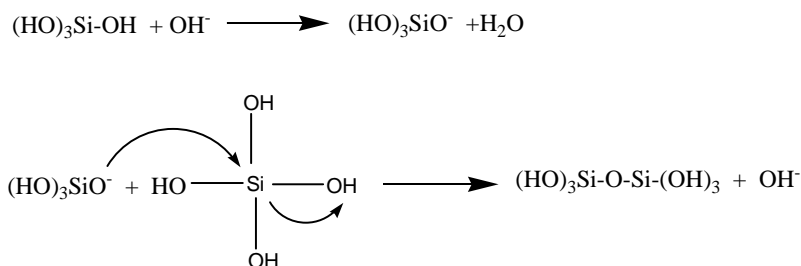


Fig. 6. Polymerization pathway of silicate to produce silicate dimmers and eventually colloidal silica particles.

ditive, there are a number of competing reactions taking place cocurrently:

- Polymerization of silicate anions. This occurs through an $\text{S}_{\text{N}}2$ -like mechanism that involves attack of a monodeprotonated silicic acid molecule on a fully protonated silicic acid molecule (see Fig. 6). 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.
- Silicate ion stabilization by the cationic additive. This is the actual inhibition step and occurs presumably through cation-anion interactions (Fig. 7).
- Flocculation between the polycationic inhibitor and the negatively charged colloidal silica particles (at pH 7) that are formed by the uninhibited silicate polymerization.

Cationic inhibitor is trapped within the colloidal silica matrix, based on reaction (c). This is demonstrated by the appearance of a light flocculent precipitate (or dispersion at times). Inhibitor entrapment caused 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 the inhibition. Inhibitor entrapment is directly proportional

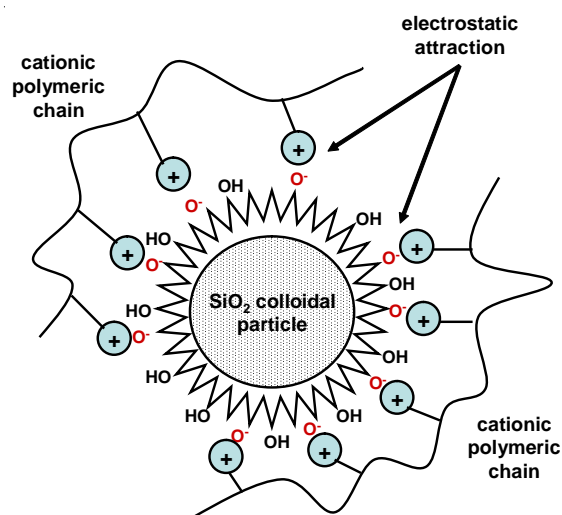


Fig. 7. Schematic representation of colloidal silica-polycation flocculation.

to cationic charge density. For example, PEI (polyethyleneimine) a branched cationic polymer with high positive charge density creates composite precipitates with colloidal silica rapidly [15].

We have designed experiments to resolve this problematic issue. They involve addition of a polyanionic polymer that acts as a positive charge “neutralizer”. Such results will be reported at a later date.

4. Conclusions

The following are the principle findings of this study:

- (1) CATIN polymers show inhibitory activity in silicate polymerization.
- (2) Their inhibitory performance is dosage dependent, but inhibitor dosage increase does not result in performance improvement.
- (3) Cationic charge density on the CATIN backbone correlates with inhibitory activity. CATINs with higher degree of substitution exhibit higher inhibitory performance.
- (4) 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.

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