ORIGINAL PAPER

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Green additives to enhance silica dissolution during water treatment

Abstract The effect of various environmentally friendly chemical additives on the dissolution of colloidal silica is systematically studied. These silica scale dissolvers are principally polycarboxylates with one to five –COOH groups, mixed polycarboxylates/phosphonates and aminoacids. Based on these results, an effort is made to link their dissolution performance to structural features in this structure/function study. Presence of additional groups (eg. $-PO_3H_2$, $-NH_2$, or $-OH$) in the dissolver molecule augments the dissolution process.

Keywords Dissolution · Silica · Green additives · Water treatment

Introduction

Water is a universal cooling medium because of its cost-effectiveness and high heat capacity (Zaheer Akhtar 2000). Increasing pressure for water conservation together with environmental concerns have forced operators to limit water discharge and reuse "spent" process water. This water recycling can lead to concentration of dissolved species to a critical point of precipitation/deposition of insoluble mineral salts. Scale formation is a technical challenge for industrial process water operators and a financial burden for all industries that use water to support their operations (Cowan and Weintritt 1976). The chemical nature of scale depends on water chemistry. A phalanx of such deposits is observed in the field and includes alkaline earth metal salts (carbonate(s), sulfate(s) and phosphate(s)), colloidal silica, metal silicates, etc. Scale deposit prevention benefits water operators by minimizing the risk for unexpected production shut-downs. In arid areas with high water costs substantial savings can be gained through water conservation.

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Colloidal silica deposits present one of the most difficult challenges of water treatment and have been referred to as "water treatment's Gordian Knot" (Demadis 2003). Such undesirable deposition problems can be avoided after application of chemical water treatment techniques that commonly involve use of additives as inhibitors. Scale control additives are fed into the water in "parts per million" quantities and enhance saturation limits of sparingly soluble salts. There is active research that embraces design, discovery and application of such additives that are non-toxic and readily biodegradable (Demadis et al. 2005b).

Occasionally, preventive measures for scale control fail due to several reasons including instrument malfunction, pH upsets, incompatibility of treatment additives or human error. At times, system operators are faced with the difficult task of removing hard and tenacious scale deposits from critical equipment surfaces. Silica deposits can be cleaned mechanically by labor-intensive "sandblasting", or chemically with $NH_4 \cdot HF_2$, a process that is not hazard-free. Therefore, an integrated chemical water treatment approach must include contingencies that consider chemical cleaning as a "recovery option" after a scaling event.

Silicate ion polymerizes *via* condensation polymerization at appropriate pH regions. The product of this polymerization event is a silica precipitate, which transforms into a recalcitrant and tenacious deposit on critical industrial equipment. Silica removal by dissolution is a challenge 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 silica is ongoing, but actual applications of inhibition chemistries in the field are rather limited.

Our research is concerned with scale inhibition and dissolution strategies with emphasis on utilization of environmentally benign additives (Demadis et al. 2004a, 2004b, 2005a, 2005b). In this paper we describe the application of several environmentally benign compounds that enhance colloidal silica dissolution, as potential replacements for current silica dissolution approaches, such as $NH_4 \cdot HF_2$, the latter presenting hazard risks and structural materials

damage (*vide infra*). This study also includes other additives for comparison reasons.

Experimental

Materials

All dissolution additives tested herein are from commerical sources and are used as received. All acidic dissolvers were added to the dissolution reaction medium as acids. They all exist in their deprotonated form at the experiment pH (10.0). Model colloidal silica is Aerosil 200 from Degussa (BET surface area 200 ± 25 m^2/g). The choice of Aerosil 200 was based on its high surface area. We opted not to use colloidal silica prepared in our laboratory because Aerosil 200 ensures consistency and it also models satisfactorily colloidal silica formed in real water systems.

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 "parts per million" rather than "milligrams" or "millimole" 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), except in the case of $NH_4 \cdot HF_2$ where final pH was kept to 4.0 (by use of HCl 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 (further details are found in Demadis et al. 2004a, 2004b, 2005a, 2005b). 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). Some representative results are given in the supplementary material. 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.

Results and discussion

Silica dissolution is hydrolysis driven (Jendoubi et al. 1997). Enhancement of silica dissolution is directly proportional to pH. However, metallic corrosion of critical system components (heat exchanger tube bundles, piping, etc.) becomes an issue when silica deposit cleaning requires prolonged times and high concentration of OH^- ions.

The acceptable "industry standard" for dissolving silica deposits is ammonium bifluoride, $NH_4 \cdot HF_2$. Although the mechanism of action is not precisely known, formation of water-soluble fluorine-containing "Si compounds" has been invoked (Frenier 2000). This approach, albeit effective, requires meticulous attention to issues such as hazard potential (generation of HF *in situ*) and acid-driven metallic corrosion (since cleanings must be done at low pHs). Therefore, safer, more environmentally friendly ways to remove silica deposits are desirable.

In these experiments stirred suspensions containing colloidal silica and the dissolution additive at various concentrations are vigorously stirred at a fixed pH of 10 and then tested for soluble silica by the silicomolybdate spectrophotometric method after 24, 48 and 72 h of dissolution time. Results are presented in Table 1 and include performance characteristics of $NH_4 \cdot HF_2$ for comparison. The measurement methodology followed for silica is based on the quantification of "soluble" (or "reactive") silica after dissolution experiments are performed for at least 24 h. Colloidal silica is completely unreactive to this test.

After 24 h, in control solutions (no additive present) dissolution proceeds until ~120 ppm silica is solubilized (24%). Silica dissolution continues after 48 and 72 h allowing soluble silica levels to increase to 150 ppm (30%) and 190 ppm (38%), respectively. Presence of 2500 ppm of any additive listed in Table 1 enhances silica dissolution within the first 24 h in a wide range, from 139 ppm (BTC) to 206 (L-histidine). This enhancement is more pronounced after 48 and 72 h of dissolution time. Figure 1 shows the dissolution enhancement in the presence of various additives. The fact that silica 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 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 silica 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 silica (76%) in 24 h. In the cases of oxalic acid, BTC and DL-malate, dosage increase has only a marginal effect on dissolution. Higher dosages of ammonium fluoride have actually a detrimental effect on silica dissolution that is evident particularly in the 10,000 ppm case, allowing only 109 ppm silica to dissolve after 24 h.

Table 1 Effect of various additives on the dissolution of colloidal SiO$_2$

Dissolution additive	Dosage (ppm)	Soluble SiO$_2$ (ppm)		
		24 h	48 h	72 h
Control	0	120	150	190
Acetate	2500	151	219	254
	5000	154	216	199
	7500	175	245	243
	10000	286	367	360
Oxalate	2500	164	220	241
	5000	165	217	205
	7500	198	246	193
	10000	155	219	239
Citrate	2500	142	226	267
	5000	186	228	271
	7500	166	216	253
	10000	380	370	407
BTC[a]	2500	139	202	246
	5000	140	226	228
	7500	146	198	219
	10000	147	210	202
EDTA[b]	2500	305	301	308
	5000	340	345	348
	7500	347	363	391
	10000	341	371	381
DETPA[c]	2500	191	281	275
	5000	237	279	289
	7500	322	340	333
	10000	257	206	271
PBTC[d]	2500	198	267	292
	5000	242	289	309
	7500	274	316	341
	10000	245	314	330
L-histidine	2500	206	259	268
	5000	241	283	282
	7500	249	298	304
	10000	245	283	298
DL-malate	2500	135	235	249
	5000	146	210	205
	7500	147	227	213
	10000	142	191	199
NH$_4$·HF$_2$[e]	0	17	51	10
	2500	506	409	501
	5000	403	455	443
	7500	198	312	400
	10000	87	110	67
L-phenylalanine	2500	202	248	253
	5000	187	246	245
	7500	230	301	282
	10000	231	264	264

[a]BTC: 1,2,3,4-butanetetracarboxylate

[b]EDTA: Ethylenediamine-tetracarboxylate

[c]DETPA: Diethylenetriaminepentaacetate

[d]PBTC: Phosphonobutane-1,2,4-tricarboxylate

[e]Experiment performed at pH 4
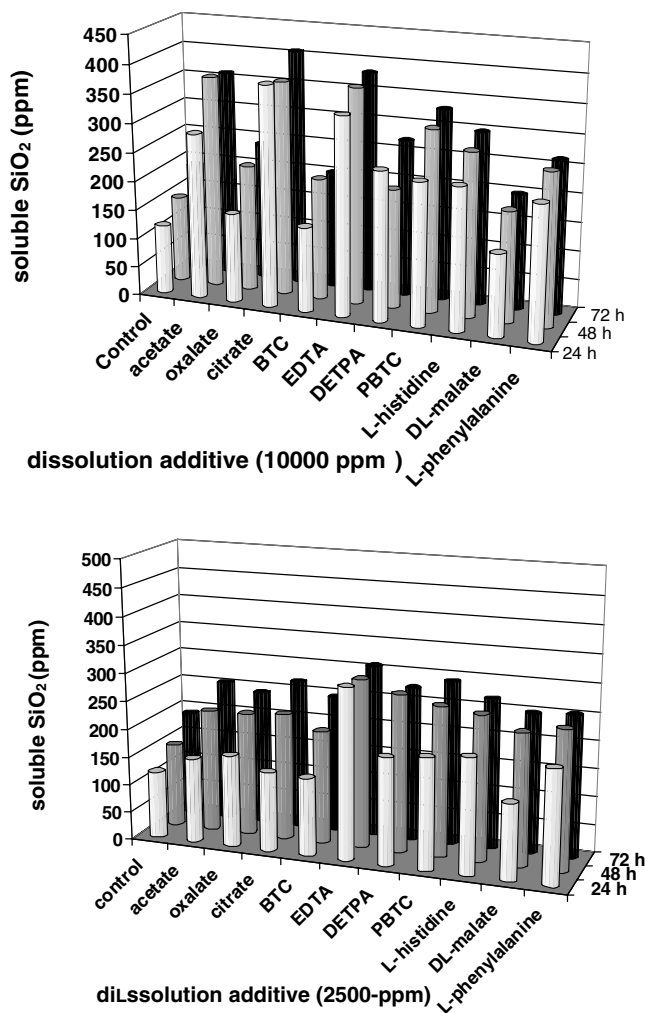
Fig. 1 Dissolution enhancement of colloidal SiO$_2$ in the presence of various additives: 10,000 ppm dosage (*upper*), 2500 ppm dosage (*lower*)

Similar observations are noted for a dosage increase in NH$_4$·HF$_2$.

Silica dissolution is also a factor of time. It is enhanced as dissolution time proceeds. The most dramatic demonstration of this effect is in the case of 10,000 ppm of DETPA that gives 206 ppm soluble silica after 48 h and 271 ppm SiO$_2$ after 72 h, an enhancement of 13%.

The effect of the number of −COOH groups present in the chemical structure of the cleaner molecule can be seen by examining Table 1. 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). EDTA (four −COOH groups) is more efficient that DETPA (five −COOH groups).

The nature of additional groups in the dissolver molecule also appears to be important. When one −COOH group is replaced with a −PO$_3$H$_2$ group in the molecule of BTC the resulting structure, PBTC, appears to exhibit higher dissolution efficiency. 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. Both PBTC and citrate possess three –COOH groups, but differ in that PBTC has an additional –PO$_3$H$_2$ group, whereas citrate a –OH group. This difference allows PBTC to exhibit higher dissolution efficiency than citrate at dosages <7500. However, at 10,000 ppm levels citrate appears more effective.

Growth of crystalline scale deposits is controlled by use of phosphonate inhibitors, or polyacrylate polymers and derivatives (Agnihotri et al. 1999). Inhibition is believed to occur through stereospecific adsorption of inhibitor molecules onto crystallographic planes of a growing nucleus, resulting into "poisoning" further growth and crystallite agglomeration. The amorphous nature of silica scale in process waters renders effectiveness of "classical" mineral scale inhibitors questionable (Demadis and Neofotistou 2004a, 2004b). Control of silica scale can be achieved either by preventive approaches or dissolution techniques in the aftermath of scale deposition. Dissolution methods for silica scale are much less developed that those for "traditional" scales such as calcium carbonates and sulfates, barium and strontium sulfate, etc. that commonly involve use of chelants for metal ion abstraction through surface complexation (Wang et al. 2000). Therefore, available techniques for silica scale dissolution must complement preventive approaches.

The precise mechanism of colloidal silica dissolution is poorly understood. It is catalyzed by hydroxyl ions, therefore it is reasonable to assume that OH$^-$ ions attack the surface tetrahedral Si centers belonging to deprotonated silanol groups ($\equiv$Si–O$^-$). Inner Si centers are unreactive because they are well imbedded within the silica particle core. Once OH$^-$ forms a Si–OH bond with surface Si, the Si–O network that connects surface Si atoms with internal Si centers starts to collapse, thus exposing additional Si sites that become susceptible to attack. Additives containing chemical groups that are strongly anionic, such as –COO$^-$ and –PO$_3$$^{2-}$, may react with Si centers in the amorphous network of SiO$_2$ in a similar fashion as OH$^-$. Formation of silicate esters may be a possibility and such dissolution pathways will be investigated.

In order to verify that the initial stage of silica dissolution is surface complexation by the dissolution additive onto the amorphous silica surface, we devised an inhibition experiment. Colloidal silica was first reacted with a cationic polymer, polyethyleneimine, PEI, (MW 10,000 Da, containing primary, secondary, and tertiary amine groups in approximately 25/50/25 ratio). Attachment of cationic polymers onto silica surfaces is well established (Patwardhan and Clarson 2002; Patwardhan and Clarson 2003). Coverage of the silica surface by the cationic polymer would be expected to block and inhibit surface complexation by the dissolution additive. The dissolution protocol described in "Experimental" was followed. Indeed, silica dissolution (no dissolvers present) dropped to ∼7% efficiency in 24 h, in the presence of 500 ppm PEI, compared to 24% with no PEI present. Even in the presence of PBTC (2500 ppm) dissolution only reached 69 ppm silica within 24 h (14%

efficiency), compared to 198 ppm (40%) for uninhibited silica. Higher PBTC dosages did not show any beneficial effect in increasing soluble silica levels. It appears that blockage of the silica surface by cationic polymers is an irreversible process and is not alleviated by dosage increase of the dissolution additive (in this case PBTC).

Conclusion

The purpose of this work is to identify and exploit novel, green dissolution technologies for silica deposits in process waters. The principle findings are summarized below: (1) anionic additives that possess at least one –COOH group are effective silica scale dissolvers at >2500 ppm dosage levels. (2) Their chemical structure affects dissolution performance. (3) Dosage increase improves performance only in some cases. (4) Presence of additional groups (eg. –PO$_3$H$_2$, –NH$_2$, or –OH) in the dissolver molecule augments the dissolution process. (5) The first step of silica dissolution is surface complexation. It can be dramatically inhibited by appropriate cationic reagents. Lastly, it should be noted that dissolution experiments performed at pH 9.0 revealed significantly lower dissolution efficiencies by all additives (results not shown here).

Colloidal silica deposits present a challenge for a plethora of industrial water applications including heat exchangers, reverse osmosis membranes, piping etc. (Frenier 2000). Dissolution of such silica deposits by chemical cleaning presents a number of issues that relate to performance and environmental compliance. Green dissolution approaches should be further developed and such environmentally benign chemical technologies are an on-going effort in our laboratories (Demadis 2005a and Demadis et al. 2005b).

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