

Industrial water systems: problems, challenges and solutions for the process industries

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Abstract

Mineral scale deposits such as calcium carbonate and phosphate, calcium oxalate, barium and strontium sulfate, magnesium silicate and others and colloidal inorganic species such as silica present important challenges for process water applications. When silica is left uncontrolled it forms hard and tenacious deposits that are difficult and hazardous to remove. Conventional phosphonate mineral scale inhibitors do not inhibit silica formation and deposition. Chemical cleaning is not free from hazards and requires operational shut-downs. Another challenge is corrosion of critical metal surfaces of industrial equipment. Last but not least, biofouling due to the development of microorganisms. This paper is focused on the presentation of the general scope of these problems and their solutions. More specifically, it concentrates on (a) inhibition of colloidal silica formation, (b) colloidal silica dissolution, and (c) metallic corrosion, in water applications by use of designed chemical approaches. The additives used for silica inhibition were polyaminoamide dendrimers, polyethyloxazoline and polyethyleneimine polymers. For silica dissolution the dissolvers tested were carboxymethyl inulin (CMI), Genesol 40 (a proprietary blend of additives), polyacrylic acid. In principle, silica inhibition is a function of time and inhibitor dosage. Silica dissolution is dependent in a rather unpredictable fashion on the structure of the dissolver, time and dosage. Mild steel corrosion inhibition has been achieved by synergistic use of zinc ions and polyphosphonate anions that create protective films.

Keywords: Water treatment; Scale inhibition; Amorphous silica; Dissolution; Corrosion inhibition; Polymers; Dendrimers

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1. Introduction

Water originating from a variety of natural sources (sea water, brackish water, river/lake water, city water) is a unique “engineering material”. Due to its attractive attributes, especially its high heat capacity, it is the preferred cooling medium for a plethora of “hot” processes. In several areas water scarcity, environmental issues or high costs impose severe limitations on water operators. The only option for reducing the large volumes of “spent” water disposed of to the environment is water recycling and reuse. However, this conceptually simple approach generates a variety of problematic issues that warrant extreme

caution and can evolve into major operational hurdles for the process industries [1]. These are schematically depicted in Fig. 1.

Mineral scale deposits can become major operational problems for poorly treated process waters [1]. These sparingly soluble electrolytes include calcium carbonate and phosphate, calcium oxalate, barium and strontium sulfate, and others and are largely dependent on a plethora of variables, such as water chemistry, temperature, pH, etc. Silica and magnesium silicate are especially troublesome because they can cause catastrophic operational failures in process water systems due to deposit formation. Silica presents a difficult challenge for industrial water systems.

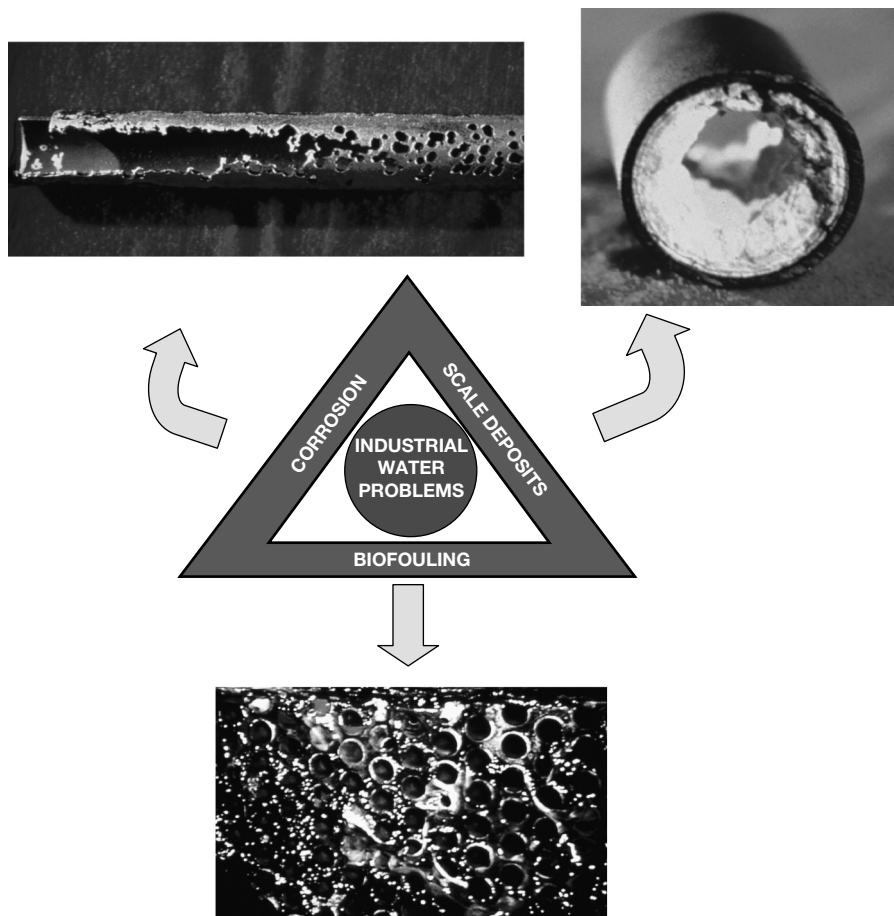


Fig. 1. The three major problems arising from uncontrolled process waters.

When silica is left uncontrolled it forms hard and tenacious deposits that are difficult and hazardous to remove. Conventional phosphonate mineral scale inhibitors do not inhibit silica formation and deposition. Chemical cleaning is not free from hazards and requires operational shut-downs. Another challenge is metallic corrosion. Last but not least, fouling due to microorganism colonies completes the widely accepted industrial water triangle (shown in Fig. 1).

Deposits cause a drastic reduction in heat transfer rates in equipment such as boilers, steam generators, evaporators, distillation units, heat exchangers, cooling tower fill, engine jackets, etc. [2]. Boiler tube failures caused by overheating, increased fuel consumption, and reduced efficiency of equipment [3,4]. Equipment failure from corrosion as a result of under deposit corrosion can significantly add to this cost. Biofouling can directly contribute to corrosion in addition to constituting a complex matrix for sparingly soluble salt deposition [5]. Deposit formed in the pipes can also have a significant economic effect on various processes such as oil production, mining, water supply, and disposal pipes [6]. Pulp/paper mills suffer significant production loss caused by both inorganic and organic deposits. This paper continues our research efforts in the discovery, design and application of antiscalant and anticorrosion additives that have mild environmental impact. These chemicals are also known as “green additives” and their purpose is to mitigate corrosion and deposition problems in process industrial waters. In light of increasing environmental concerns and restrictions for discharge of process water coming from industrial water systems, this research acquires significant interest.

2. Experimental protocols

Detailed procedures for some of the instruments used, reagents, solution preparation, inhibitor

screening test, soluble silica measurements and corrosion experiments are reported in other publications originated from our group [7–16]. The additives used, PAMAM-1 and 2 (Aldrich), Dequest PB-11615 (CMI, Solutia), Genesol 40 (Genesys) a proprietary blend of additives, polyacrylic acid (PAA MW 2000, Polysciences), polyethyleneimine (PEI MW 70000, Polysciences) and Aquazol (Polymer Chemistry Innovations) were from commercial sources. Colloidal silica (Aerosil 200) BET surface area $200 \pm 25 \text{ m}^2/\text{g}$ was from Degussa. Schematic structures for the additives used in this study are shown in Fig. 2. The notation Aquazol-XX (XX = 5, 50, 200, 500) indicated the molecular weight of the polymer in kilodaltons (kD). Soluble silica was measured by an established spectrophotometric method [17]. For the corrosion experiments a protocol issued by the National Association of Corrosion Engineers (NACE International) was used [18].

3. Results and discussion

This paper is focused on the presentation of the general scope of the problems arising in principle in industrial cooling waters and their possible mitigation by chemical approaches. More specifically, it concentrates on (a) inhibition of colloidal silica formation, (b) colloidal silica dissolution, and (c) metallic corrosion, in water applications by use of designed chemical approaches. The additives used for silica inhibition were polyaminoamide dendrimers and polyethyleneimine. For silica dissolution polymeric additives such as polyacrylic acid, Genesol 40 (a proprietary blend of additives) and CMI (Dequest PB-11615) were used. In principle, silica inhibition is a function of time and inhibitor dosage. Silica dissolution is dependent (in a rather unpredictable fashion) on the structure of the dissolver, time and dosage. Metal corrosion inhibition has been achieved by synergistic use of zinc ions and polyphosphonate anions that create protective films.

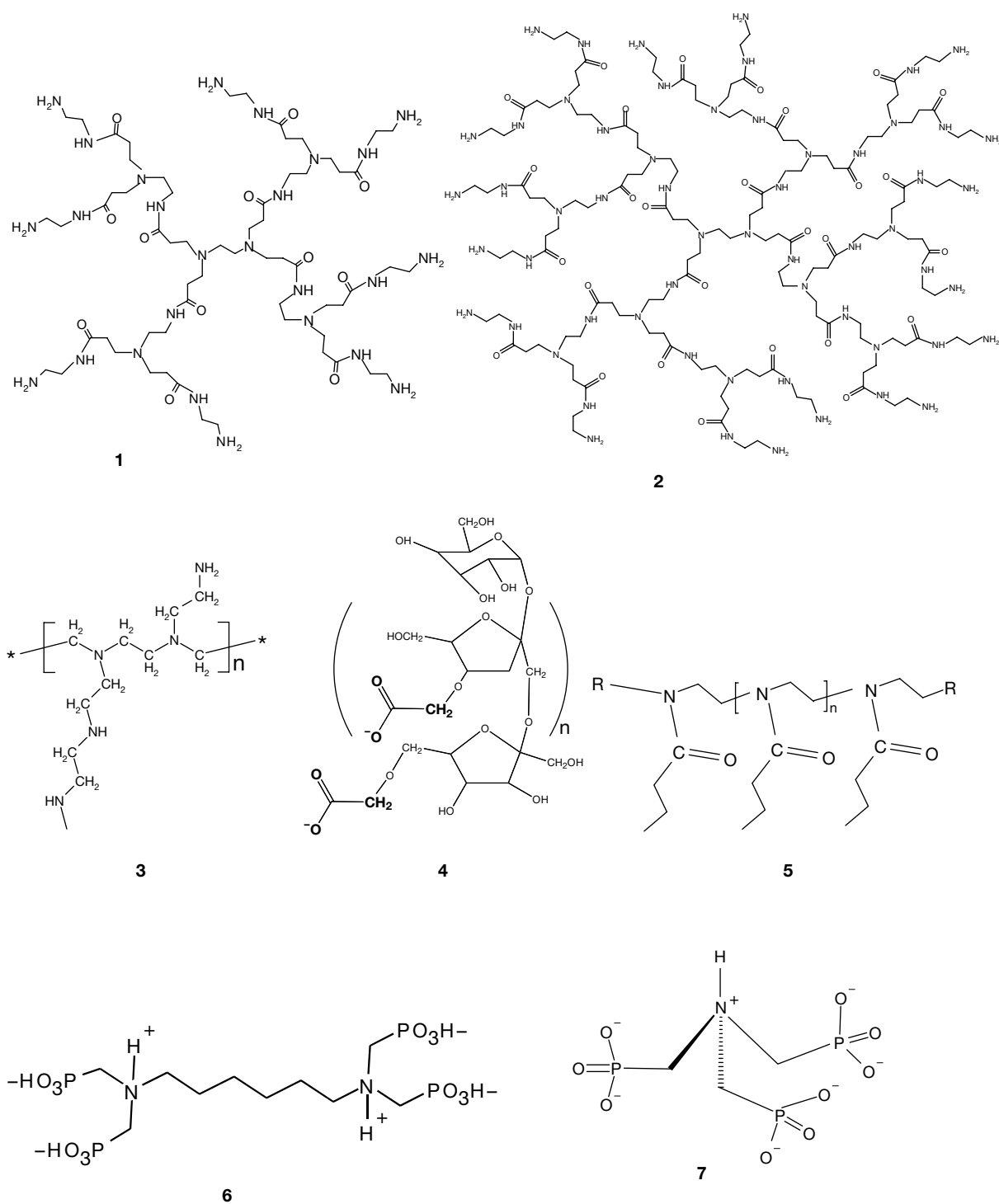


Fig. 2. Schematic structures of the additives used in this study: PAMAM-1 (1), PAMAM-2 (2), PEI (3), CMI (4), Aquazol (5), HDTMP (6) and AMP (7).

3.1. Silica scale inhibition

In Fig. 3 inhibition results are presented at 40 ppm additive. Soluble silica is measured every 24 h for a total period of 72 h.

Based on the results presented in Fig. 3 it is obvious that all additives tested show silica levels higher than the control (no additives present). All Aquazol polymers show rather low inhibitory activity maintaining ~200 ppm soluble silica at 24 h. At longer times (>24 h) silicate polymerization continues even in the presence of Aquazol additives to reach eventually control levels. There is virtually no dependence of inhibitory power on molecular weight. Additional results (not shown here) indicate that dosage increase improves inhibition efficiency.

Both dendrimers PAMAM-1 and 2 show significant inhibition in silicate polymerization allowing ~380 ppm to remain soluble at 24 h. Even after 72 polymerization time ~300 ppm (with PAMAM-1) and ~290 ppm (with PAMAM-2) silica remain soluble. Apparently, both dendrimer additives are more efficient inhibitors than the Aquazol additives, in maintaining both higher soluble silica levels and inhibiting polymerization for a longer time period.

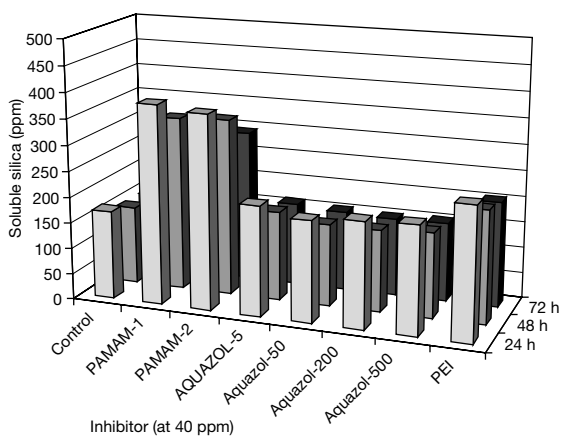


Fig. 3. Comparative inhibitive effect of additives on silica formation at 40 ppm dosage.

The superior performance of cationic PAMAM-1 and PAMAM-2 dendrimers in SiO_2 polymerization inhibition, prompted us to seek other, alternative and more cost-effective polymers as inhibitors. We tested the effect of polyethyleneimine (PEI) on silicate polymerization inhibition. The initial results are presented in Fig. 4.

It appears that a dosage of 10 ppm is the optimum. Increase of PEI dosage seems to have an adverse effect on inhibitory activity, which seems like a paradox. This can be explained on examination of the PEI chemical structure. PEI is a highly branched *cationic* polymer that possesses ~25% primary amines, ~50% secondary amines and ~25% tertiary amines. These groups are protonated at the pH of the inhibition experiment (7.0), therefore rendering the polymer positively charged. Its cationic charge strongly interacts with the negative charge of colloidal silica particles generating PEI- SiO_2 precipitates. These entrap and deactivate the inhibitor. This situation can be alleviated by addition of anionic polyelectrolytes and these results will be published at a later time [19].

3.2. Silica scale dissolution

Dissolution of colloidal silica is hydrolysis driven. Addition of OH^- ions can dissolve silica at high pH regions [20]. However, metallic

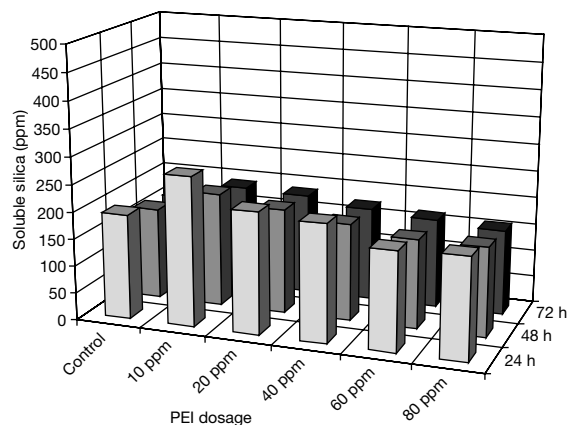


Fig. 4. Effect of PEI dosage on solubility of silica.

corrosion of critical system components becomes an issue when silica deposit cleaning requires prolonged times and high concentration of OH^- ions. The acceptable “industry standard” for removing silica deposits is ammonium bifluoride, NH_4HF_2 . Although the precise mechanism of action is not known, formation of soluble fluorine-containing Si compounds has been invoked [21]. This approach is not free of problems such as hazard potential and acid-driven metallic corrosion (since cleanings must be done at low pH’s). Therefore, safer, more environmentally sound methods to remove silica deposits are sought.

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 Figs. 5–7 for polymeric additives Genesol 40, Dequest PB-11615, and polyacrylate, respectively. Similar experiments were performed in the presence of non-polymeric additives and the results have been published [11,14,16]. Genesol 40 shows a dosage dependence in dissolving colloidal silica. The maximum performance,

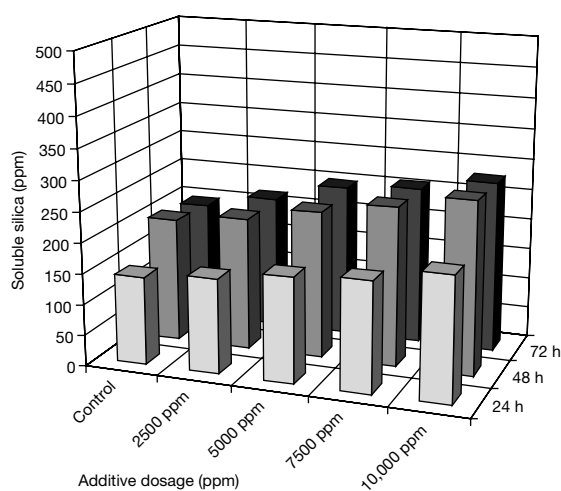


Fig. 5. Dissolution enhancement of colloidal silica in the presence of Genesol 40.

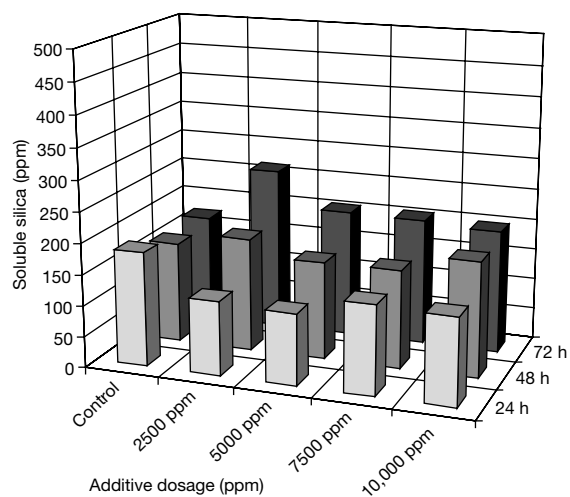


Fig. 6. Dissolution enhancement of colloidal silica in the presence of Dequest PB-11615.

~280 ppm, is reached at 10,000 ppm dosage at 72 h dissolution time (Fig. 5). Carboxymethyl inulin (Dequest PB-11615) is a poor silica dissolver, except at the dosage of 2500 ppm after 72 h dissolution time, solubilizing ~260 ppm silica (Fig. 6). Polyacrylic acid dissolves silica only marginally, with the best performance shown at 5000 ppm dosage after 72 h at ~130 ppm soluble

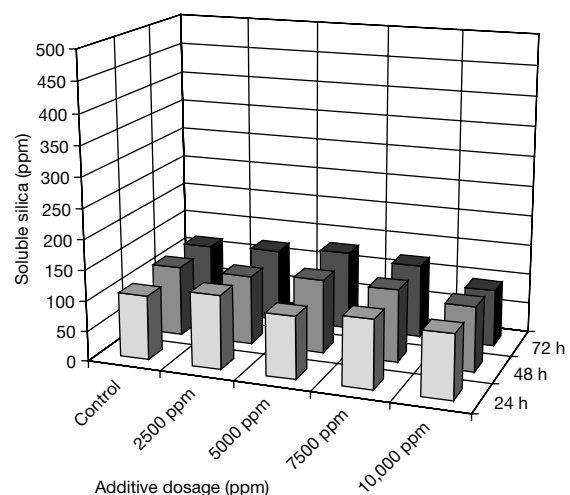


Fig. 7. Dissolution enhancement of colloidal silica in the presence of polyacrylate (MW 2000).

silica (Fig.7). Based on these results, it appears that polymeric additives show a markedly reduced silica dissolution efficiency compared to other “small molecule” additives, such as 2-phosphobutane-1,2,4-tricarboxylic acid, citric acid, L-histidine, and others [11,14,16].

3.3. Inhibition of metallic corrosion

Synergistic combinations of 1:1 molar ratio Zn^{2+} and AMP are reported to exhibit superior inhibition performance than either Zn^{2+} or AMP alone [22–26]. However, no mention is made regarding the identity of the inhibitor species involved in corrosion inhibition. Therefore, a corrosion experiment was designed in order to verify the literature results and prove that the protective material acting as a corrosion barrier is an organic–inorganic hybrid composed of Zn and AMP. A synergistic combination of Zn^{2+} and AMP in a 1:1 ratio offers excellent corrosion protection for carbon steel (see Fig. 8).

Although differentiation between the “control” and “Zn-AMP” protected specimens is evident within the first hours, the corrosion experiment is left to proceed over a 3-day period. Based on mass loss measurements the corrosion rate for the “control” sample is 2.5 mm/year, whereas for the Zn-AMP protected sample 0.9 mm/year, a substantial reduction in corrosion rate. The

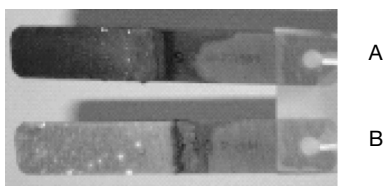


Fig. 8. Corrosion inhibition by Zn-AMP. The upper specimen (A) is the control, no inhibitor present; the lower specimen (B) is with Zn^{2+} /AMP combination present, both in 1 mM. Corrosion inhibition is dramatically demonstrated at pH 3.0. Formation of Zn-AMP can be clearly seen on the steel specimen as a thin white layer, with additional material accumulated at certain locations, appearing as white spots.

filming material is collected and subjected to FT-IR, XRF and EDS studies. These show that the inhibiting film is a material containing Zn (from added Zn^{2+}) and P (from added AMP) in an approximately 1:3 ratio. Fe was also present apparently originating from the steel specimen. FT-IR showed multiple bands associated with the phosphonate groups that closely resemble those of an authentically prepared Zn-AMP material [9]. For comparison, EDS and XRF spectra of a “protected” and an “unprotected” region show presence of Zn and P in the former, but complete absence in the latter.

A combination of Zn^{2+} and HDTMP in a 1:1 ratio offers excellent corrosion protection for carbon steel (Fig. 9). Although differentiation between the “control” and “Zn-HDTMP” protected specimens is profound within the first hours, the corrosion experiment is left to proceed over a 3-day period. Based on mass loss measurements the corrosion rate for the “control” sample is 7.28 mm/year, whereas for the Zn-HDTMP protected sample 2.11 mm/year, a ~170% reduction in corrosion rate. The filming material was collected and subjected to FT-IR, XRF and EDS studies. These show that the corrosion inhibiting film is a material containing Zn^{2+} (from externally added Zn^{2+}) and P (from added HDTMP) in an approximate 1:4 ratio. Fe was also present apparently originating from the carbon steel specimen. FT-IR of the filming material showed multiple bands associated with the phosphonate groups in the 950–1200 cm^{-1} region that closely



Fig. 9. The anticorrosive effect of Zn-HDTMP films on carbon steel. The upper specimen is the “control” (A), no inhibitor present. Corrosion inhibition in the lower specimen (B) by a 1 mM Zn^{2+} /HDTMP synergistic combination is dramatically demonstrated.

resemble those of the authentically prepared Zn-HDTMP material. For comparison, EDS and XRF spectra of a “protected” and an “unprotected” region show presence of Zn and P in the former, but complete absence in the latter.

An ideal phosphonate corrosion inhibitor of the “complexing type” is required to possess the following significant features: (a) it must be capable of generating metal-phosphonate thin films on the surface to be protected; (b) it should not form very soluble metal complexes, because these will not eventually “deposit” onto the metal surface, but will remain soluble in the bulk; (c) it should not form sparingly soluble metal complexes because these may never reach the metal surface to achieve inhibition, but may generate undesirable deposits in the bulk or on other critical system surfaces; (d) its metal complexes generated by controlled deposition on the metal surface must create dense thin films with robust structure. If the anticorrosion film is non-uniform or porous, then uneven oxygen permeation may create sites for localized attack, leading to pitting of the metal surface.

Lastly, the ability of a metal-phosphonate corrosion inhibitor to adhere onto the metal surface plays a vital role in corrosion efficacy. Bulk precipitation of a metal-phosphonate complex will lead to loss of active inhibitor to precipitation, leading to insufficient levels for thin film formation. Surface adherence of the inhibitor films is a property that cannot be precisely predicted. However, it is a necessary condition for acceptable inhibition. In addition, the metal-phosphonate protective layer has to be robust and uniform.

4. Epilogue

Industrial water treatment has been greatly impacted by various governmental regulatory authorities depending on the geographic location. Tighter water discharge limits have resulted in higher water reuse. In addition to make up water cost or even pumping and discharge cost, the water prior to discharge must be treated to meet

very stringent quality requirements. The environmental regulations also control the scale and corrosion inhibitors for their ill effect to air or water. In this paper, an attempt was made to investigate possible chemical solutions to various water treatment problems [27]. This approach represents part of recent efforts in our laboratories [7–16, 28–33] to provide environmentally friendly approaches in order to control major operational problems in industrial water systems.

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