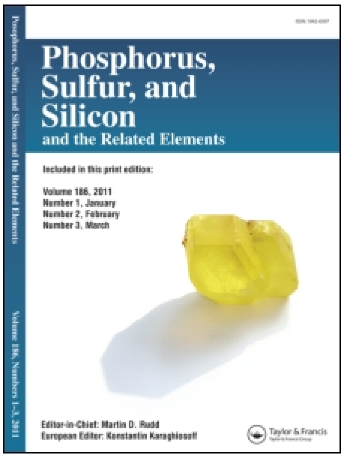

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The Design and Application of Calcium Phosphate Inhibiting Polymers in Industrial Water Systems

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The precipitation of calcium phosphate in the presence of a variety of polymeric additives has been investigated. Included in this work are the key performance properties required by polymers to function as calcium phosphate inhibitor and dispersant, especially under stringent process conditions. The findings from this study helps in the selection of an appropriate polymer for water treatment formulations.

Keywords: calcium phosphate; precipitation; polymeric inhibitors

INTRODUCTION

The importance of calcium phosphates as the major constituents of industrial and pathological mineral deposits has stimulated extensive research on the precipitation and dissolution of these compounds[1]. In cooling, boiler, and desalination applications, the insulating nature of scales on equipment surfaces results in decreased system efficiency and premature equipment failure. In addition to scaling problems, cooling water systems and boilers constructed of carbon steel also experience corrosion problems caused by dissolved oxygen. Effective water treatment formulations must control scale, corrosion, particulate matter, and microbiological growth. Over the years, different inhibitors have been developed to provide corrosion protection[2]. For many years, chromate-based corrosion inhibitors were considered as the standard in the water treatment industry. Unfortunately, chromates are toxic and due to environmental regulations their use has declined considerably in recent years. Among the more acceptable mild steel corrosion inhibitors that have been displacing chromate since the 1960s are molybdates, silicates, polyphosphates/phosphates, phosphonates, and zinc salts. From the perspective of their versatility, cost, and performance, phosphates have become a new performance standard. The key to the successful use of a phosphate based water treatment program lies in the proper selection of a polymeric calcium phosphate inhibitor. The polymer serves a dual purpose in that it controls the thickness of the calcium phosphate film on the metal surface, and prevents precipitation in the recirculating water.

This paper examines the role of various factors such as monomer functionality, composition, and molecular weight in designing an effective calcium phosphate inhibiting polymer. Additionally, the influence of various process variables on the performance of commercial polymers is evaluated.

RESULTS AND DISCUSSION

During the last two decades a wide variety of acrylic acid and maleic acid-based homo- and copolymers have been developed to prevent the precipitation of various sparingly soluble salts. It has been documented that for salts such as CaF_2, $CaSO_4.2H_2O$, $BaSO_4$, etc., homopolymers are effective precipitation inhibitors, but exhibit poor performance for calcium phosphates and phosphonate salts. The ability of these polymers to act as a precipitation inhibitor depends on the polymer composition, ionic charge, and the molecular weight (MW). The polymers which have been developed and/or used as scale control agents fall into following two categories:

Homopolymers: poly(acrylic acid), P-AA; poly(methacrylic acid), P-MAA; poly(maleic acid), P-MA; poly(acrylamide), P-AM.

Copolymers: poly(acrylic acid: vinyl acetate), P-AA:VAC; poly(AA:hydroxylpropyl acrylate), P-AA:HPA; poly(AA: s-acrylamide), P-AA:sAM; poly(AA:sulfonated styrene), P-AA:SS; poly(AA:2-acrylamido-2-methylpropane sulfonic acid), P-AA:SA (GOOD-RITE® K-775*); P-AA:SA:SS (GOOD-RITE® K-798).

Using the pH-stat method[3], many polymers were evaluated for their efficacy as calcium phosphate inhibitors. Figure 1 compares the performance of P-AA, P-MAA, P-SA, P-AM and copolymers in which carboxyl group has been partly replaced by ester, SA, and SS groups. As illustrated in Figure 1, among the homopolymers tested P-AA exhibits good inhibitory activity. It is worth noting that at 5 ppm, terpolymer (P-AA:SA:SS) shows superior performance as a calcium phosphate inhibitor. The

* GOOD-RITE is a registered trademark of The BFGoodrich Company

influence of MW on the performance of P-AA:VAC and P-AA:s-AM copolymers was also investigated. Results illustrated in Figure 2 clearly demonstrate the importance of MW in inhibiting the precipitation of calcium phosphate.

Industrial water systems operating on surface water also experience fouling of heat exchangers by the deposition of suspended matter. The development of high MW cationic polymers such as diallydimethyl ammonium chloride, DMAC, has overcome the problems associated with the application of metal flocculants used historically. Although DMAC is very effective at low dosages, this polymer has been known to "carry over" and could interfere with the performance of anionic polymers. Results obtained in the presence of 1.0 ppm of DMAC and 10 ppm calcium phosphate inhibiting polymer are illustrated in Figure 3. As shown, the terpolymer (P-AA:SA:SS) exhibits better tolerance to DMAC than the copolymers P-MA:SS and P-AA:SA.

Another factor in determining calcium phosphate precipitation is the presence of soluble iron in make-up water as it can lead to deposit formation in industrial water systems. Ferrous (Fe^{2+}) ion is not a significant problem as long as it remains soluble. A mixture of iron oxide and hydroxide can precipitate at typical cooling system pH values. The inhibition data for various polymers in the presence of 0, 1.0, and 2.5 ppm iron (III) is illustrated in Figure 4 and shows the superior tolerance to iron (III) of the terpolymer over several copolymers. From a practical point of view, if iron is encountered in recirculating cooling water systems, incorporation of high performance calcium phosphate inhibiting polymer in the formulation will ensure better overall performance of the system.

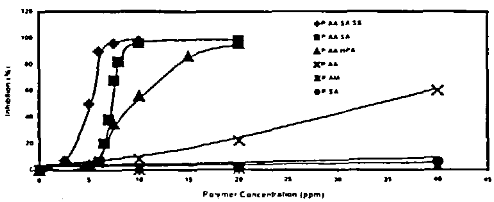

FIGURE 1 Calcium phosphate precipitation in the presence of polymer. Conditions: 140 mg/L Ca^{2+}, 9 mg/L PO_4^{3-}, pH 8.5, 50°C, 20 h.

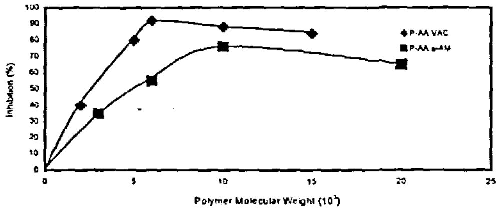

FIGURE 2 Calcium phosphate precipitation in the presence of P-AA:VAC and P-AA-sAM. Conditions: 140 mg/L Ca^{2+}, 9 mg/L PO_4^{3-}, pH 8.5, 50°C, 20 h.

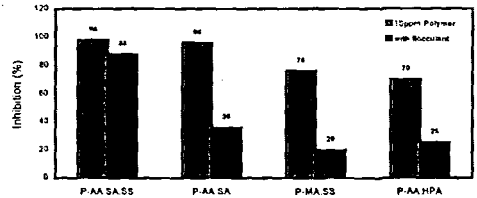

FIGURE 3 Calcium phosphate inhibition by copolymers in the presence of cationic flocculant. Conditions: 140 mg/L Ca^{2+}, 9 mg/L PO_4^{3-}, pH 8.5, 50°C, 20 h.

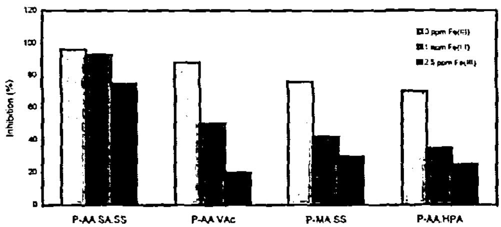

FIGURE 4 Calcium phosphate inhibition by copolymers in the presence of Iron (III). Conditions: 140 mg/L Ca^{2+}, 9 mg/L PO_4^{3-}, pH 8.5, 50°C, 20 h.

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