Impact of iron oxide (rust) on the performance of calcium phosphate scale inhibitors for industrial water systems

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Abstract
The inhibition of calcium phosphate precipitation by homo- and copolymers containing different functional groups has been examined in aqueous solution. It has been found that polymer performance as calcium phosphate inhibitor depends upon polymer architecture. The influence of iron oxide (Fe₂O₃, rust) on the performance of calcium phosphate inhibitors has also been investigated. Results show that addition of small amount (10 mg to 100 mg) of Fe₂O₃ to the calcium phosphate supersaturated solution exhibits marked antagonistic effect on inhibitor performance. Various mechanism(s) have been proposed to explain the negative impact of Fe₂O₃ on inhibitor performance.

Keywords: calcium phosphate, precipitation, inhibition, polymers, iron oxide (rust).

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 [2]. Effective water treatment formulations must control scale, corrosion, particulate matter, and microbiological growth.

In biological system, examples of calcium containing minerals include dental calculus, calcified plaques of arteriosclerosis, kidney stones, etc. [3]. Calcium phosphate deposits have also been reported during pasteurization of milk and sugar refining processes [4, 5]. In addition, calcium phosphates are widely produced in industry, in such forms as ceramics, nutrient supplements, medicines, dentrifices, and stabilizers for plastic. They are used in solid state chemistry as fluorescent lamp phosphors and play a role in waste water treatment processes.

During the last two decades, the problem of calcium phosphate scaling in industrial water systems has become increasingly important. Higher orthophosphate levels are being encountered in cooling water due to increased water reuse, use of low quality make-up
water, and the use of organic phosphonate as scale and corrosion inhibitors which are degraded to orthophosphate. The increased orthophosphate levels, combined with alkaline operating conditions can lead to the formation of insoluble calcium phosphate scale deposits which are normally attributed to hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP. In cooling water systems however, it is not the HAP which is initially formed, but instead a precursor phase is formed which is widely known as amorphous calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ [6]. Factors influencing the precipitation of calcium phosphate in aqueous system include, pH, temperature, ionic strength, process contaminants [7].

Among the methods used to prevent calcium phosphate precipitation are acidification of water and the use of chemical additives (polymeric and non-polymeric). These methods prevent and/or retard markedly the precipitation and deposition of calcium phosphate scale on the heat exchanger surfaces. The acidification method has the disadvantage of exposing metal surfaces to a corrosive environment while the use of chemical additives seem promising since only very low concentrations are needed to extend the time required for the initiation of scale formation. Also, if the acid addition shuts down, an increase in pH can cause immediate calcium phosphate precipitation. Due to more stringent regulations and from worker safety perspective addition of chemical additives seems to be the only reliable solution to the problem.

Inhibition of calcium phosphate precipitation by polymeric additives has been the subject of intensive research. Chang et al. [8], in their investigation on the evaluation of double-hydrophilic block copolymers reported that these polymers exhibit excellent performance as calcium phosphate inhibitors. Amjad [9] investigated the influence of various homopolymers on the precipitation of calcium phosphates. Results of this study show that at low supersaturation, addition of low concentrations (few parts per million, ppm) of low molecular weight (MW) poly(acrylic acid), PAA, significantly retarded the precipitation of calcium phosphate in aqueous solution. Ohtaka et al. [10] and Amjad et al. [11] in their investigations of the evaluation of homo- and copolymers concluded that both the functional group and the ionic charge of the polymer play important roles in inhibiting precipitation of calcium phosphate.

The influence of suspended matter on the efficacy of polymers as calcium phosphate inhibitors has been reported. Results of this study reveal that addition of clay particles to calcium phosphate supersaturated solutions adversely impact the inhibitory property of polymers because of the adsorption of the polymers on clay particles thereby reducing the available polymer for scale inhibition [12]. Amjad et al. [13] in another study reported that addition of clay to silica supersaturated solution did not exhibit any significant effect on the performance of silica polymerization inhibitors. Recent research in our laboratories has shown that the presence of small amounts (10–100 mg) of iron oxide exhibits negative effect on the performance of calcium sulfate dihydrate and calcium carbonate scale inhibitors [14, 15]. In the present study we try to discover and explore the influence of iron oxide, a commonly encountered corrosion product in industrial water system, on the effectiveness of calcium phosphate scale inhibitors. It is hoped that the data presented in
this paper will enable the water technologists to recognize the impact of suspended matter in selecting the appropriate additives for their formulations.

**Experimental**

**Materials**

Reagents grade chemicals and grade A glassware were used. Stock solution of calcium chloride dihydrate and disodium hydrogen phosphate were prepared using distilled water, filtered through 0.22 µm filter paper, and analyzed as described previously [7]. The additives tested were commercial materials and stock solutions of these additives were prepared on a dry weight basis. The desired concentrations of the additives were obtained by dilution. Table 1 lists the compositions, functional group, ionic charge, and acronyms of additives tested. As noted in Table 1, the additives tested as calcium phosphate inhibitors vary significantly both in terms of composition and ionic charge. The iron oxide (Fe₂O₃) used in this study was obtained from Fisher Scientific Company. It was characterized as hematite by X-ray diffraction (JCPDS Phase 33-664, predominantly hematite, with some minor reflections, which do not correspond to any indexed iron oxides). The particle size distribution data as measured by Beckman Coulter Counter (Model LS230) revealed that the majority of Fe₂O₃ particles fall between 20 and 100 µm with the largest volume% at ~50 µm.

**Table 1. Polymers tested.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Functional Group</th>
<th>Ionic Charge*</th>
<th>Molecular Weight</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(acrylic acid)</td>
<td>–COOH</td>
<td>Negative</td>
<td>2k</td>
<td>PAA</td>
</tr>
<tr>
<td>Poly(maleic acid)</td>
<td>–COOH</td>
<td>Negative</td>
<td>&lt;1k</td>
<td>PMA</td>
</tr>
<tr>
<td>Poly(methacrylic acid)</td>
<td>–COOH</td>
<td>Negative</td>
<td>6k</td>
<td>PMAA</td>
</tr>
<tr>
<td>Poly(acrylic acid: hydroxypropyl acrylate)</td>
<td>–COOH –COOR</td>
<td>Negative</td>
<td>10k</td>
<td>PHP</td>
</tr>
<tr>
<td>Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid)</td>
<td>–COOH –SO₃H</td>
<td>Negative</td>
<td>&lt;15k</td>
<td>PSA</td>
</tr>
<tr>
<td>Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:sulfonated styrene)</td>
<td>–COOH –SO₃H</td>
<td>Negative</td>
<td>&lt;15k</td>
<td>PSS</td>
</tr>
<tr>
<td>Poly(maleic acid:sulfonated styrene)</td>
<td>–COOH –SO₃H</td>
<td>Negative</td>
<td>&lt;10k</td>
<td>PMS</td>
</tr>
</tbody>
</table>

*at the pH of working solution.
Calcium phosphate precipitation protocol

The calcium phosphate precipitation experiments were conducted by adding known volume of stock solutions of disodium hydrogen phosphate to known volume of water containing HCO$_3^\text{-}$ / CO$_3^{2-}$ buffer in a 100 mL glass bottle. To this solution was added with continuous stirring a known volume of stock solution of calcium chloride. In experiments involving the additive, a known volume of stock solution of inhibitor was added to the phosphate solution prior to the addition of calcium chloride solution. The pH of the calcium phosphate solutions were adjusted to 8.35±0.05 with dilute sodium hydroxide and experimental solutions were stored in a water bath maintained at 50°C. At known times, the solution was filtered through 0.45 µm filter paper and phosphate concentration was determined by standard spectrophotometric method. Experiments involving the influence of iron oxide were done by adding a known amount of iron oxide to calcium phosphate supersaturated solution and manually mixing the solution for 60 seconds. The experimental conditions employed in the present study include: 110 mg/L Ca, 13.0 mg/L phosphate, pH 8.35, 50°C. The results reported here had good reproducibility (±6%).

The polymer efficacy as a calcium phosphate inhibitor was calculated using the following equation:

\[
\text{Percent Inhibition (}\%I\text{)} = \frac{[(\text{PO}_4^4)\text{c} - (\text{PO}_4^4)\text{f}]}{[(\text{PO}_4^4)\text{i} - (\text{PO}_4^4)\text{f}]} ,
\]

where:

\( (\text{PO}_4^4)\text{c} = \) concentration of phosphate in the filtrate in the presence of inhibitor at known time;
\( (\text{PO}_4^4)\text{i} = \) concentration of phosphate at the beginning of experiment; and
\( (\text{PO}_4^4)\text{f} = \) concentration of phosphate in the filtrate in the absence of inhibitor at 20 hr.

Results and Discussion

During the past two decades, a number of natural or biodegradable and synthetic additives has been developed and is currently being used as component of water treatment formulations. The role of these additives (polymeric and non-polymeric in such formulations is twofold: a) to inhibit the precipitation of scale forming salts such as CaCO$_3$, CaF$_2$, BaSO$_4$, Mg(OH)$_2$, etc., and b) to disperse the suspended matter such as clay, iron oxide, organic debris, etc. In the former case, the additive inhibits the precipitation of scale forming salt, by adsorption onto the scale crystallites and prevents them from further growth. The additives that fall into this category are usually low molecular weight (MW) homopolymers containing carboxyl group (−COOH). Dispersants on the other hand, are copolymers containing different functional groups i.e., −COOH, sulfonic acid (−SO$_3$H); ester (−COOR); s-acrylamide (−CONHR). These polymers function by adsorbing onto particles such as iron oxide, silt, clay, etc., present in recirculating waters and preventing them from settling on the equipment surfaces. In the present investigation we have tested polymers from both categories as calcium phosphate inhibitors.
Performance of polymers

Polymer dosage: By conducting a series of precipitation experiments it is possible to describe the dosage – performance profile relationship for a given polymer as illustrated in Figure 1. As shown the addition of relatively small dosage (i.e., 5.0 ppm) of poly(acrylic acid), PAA, exhibits negligible effect on calcium phosphate precipitation reaction. However, as the PAA dosage is increased from 5.0 to 10.0 ppm, the performance of PAA is substantially improved. For example, solution phosphate concentration in the presence of 10 ppm of PAA at 20 hr is 6.60 compared to 1.95 and 0.45 mg/L obtained in the presence of 5.0 and 0 ppm of PAA, respectively. As shown in Figure 1 increasing the PAA dosage by 50% (i.e., from 10 to 15 ppm) results in ~80% increase in solution phosphate concentration, and at 30 ppm, >90% inhibition is achieved. Figure 2 presents plots of percent calcium phosphate inhibition (%I) at 20 hr as calculated according to Equation 1, as a function of PAA dosage. It is apparent that calcium phosphate inhibition increases with increasing PAA dosage. It is worth noting that similar polymer dosage – performance profile as noted in Figure 2 has been previously reported for CaCO$_3$, CaF$_2$, and BaSO$_4$ scaling systems [16, 17, 18].

Figure 1. Calcium phosphate precipitation as a function of time and in the presence of varying concentration of poly(acrylic acid), PAA.

Polymer composition: The effect of polymer composition on calcium phosphate precipitation was investigated by a series of precipitation experiments conducted under similar experimental conditions in the presence of copolymers of varying compositions. Excellent examples of substitution of –COOH group with other monomers containing different functional groups are presented in Figure 3, in which the %I is plotted for acrylic acid:2-acrylamido-2-methyl propane sulfonic acid, PSA; acrylic acid:2-acrylamido-2-methyl propane sulfonic acid:sulfonated styrene, PSS; acrylic acid:hydroxylpropyl acrylate,
PHA; and maleic acid:sulfonated styrene, PMS. It can be seen that polymers containing 2 or 3 monomers with different functional groups perform better than homopolymers containing –COOH i.e., poly(acrylic acid), PAA; poly(maleic acid), PMA; poly(methacrylic acid), PMAA. It is interesting to point out that whereas copolymers compared to homopolymers show excellent performance as calcium phosphate inhibitors, these homopolymers on the other hand, have been shown to perform better than copolymers for other calcium containing minerals such as CaCO$_3$, CaF$_2$, and BaSO$_4$ [16, 17, 18].

**Figure 2.** Plot of calcium phosphate inhibition (%$I$) as a function of varying concentration of PAA.

**Figure 3.** Plots of % inhibition in the presence of 10 ppm of various homo- and copolymers at 20 hr.
Effect of filter size on polymer performance: It is generally agreed that both, dispersion (or de-agglomeration) of suspended particles and scale inhibition processes are believed to play an important role in the success of the phosphate-based treatment program for cooling water system. Although many factors play a role in determining the rate of scale formation, one key aspect is maintaining the size of the particulates below a certain minimum [19]. According to Stoke’s law, the settling rate of spherical particles is proportional to the square of its diameter in quite solution. Particles with less 0.1 µm diameter will settle at about 1/20th the rate of 0.45 µm particles, if no secondary effects are operative. In addition, rapid growth of particles can occur after a certain critical diameter is reached [20]. Polymeric inhibitors serve to limit particle size, thereby controlling additional growth. To study the impact of polymeric scale inhibitors on the growth of calcium phosphate particles, a series of experiments were carried out in which different filter paper size was used to filter the solutions. As indicated in Table 2, PSS performs the best at minimizing particle growth.

Table 2. Particle size effects on the performance of calcium phosphate inhibitors.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% Inhibition 0.10 µm</th>
<th>% Inhibition 0.22 µm</th>
<th>% Inhibition 0.45 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA</td>
<td>19</td>
<td>28</td>
<td>44</td>
</tr>
<tr>
<td>PHPSA</td>
<td>32</td>
<td>55</td>
<td>72</td>
</tr>
<tr>
<td>PSS</td>
<td>61</td>
<td>80</td>
<td>97</td>
</tr>
</tbody>
</table>

Influence of iron oxide on polymers performance

Feed water used in many industrial processes comes from various sources such as rivers, ponds, lakes, and contains a variety of soluble and insoluble impurities (or suspended particles). Typical suspended particles include, metal oxides/hydroxides, clay, silt, metal carbonates, algae, bacteria, and viruses. It is generally known that higher concentrations of suspended particles not only lead to high turbidity but also provide high surface area for adsorption of dissolved species including tannins, fulvic acid, humic acid, and additives used to control scale formations.

Effect of Mixing Time: In order to understand the influence of mixing time after the addition of Fe₂O₃ to the calcium phosphate supersaturated solutions, several precipitation experiments were carried out in the presence of 10 ppm of PSS, and 10 mg of Fe₂O₃. Results presented in Figure 4 show that mixing time exhibits marked negative effect on the performance of PSS. For example, %I values obtained at 20 hr, after no mixing (0 min), 0.50 min and 1.0 min are 76%, 58%, and 34% respectively, compared to 98% obtained at 20 hr in the absence of iron oxide. It is interesting to note that increasing the mixing time by three fold i.e., from 1 in to 3 min does not show any significant impact (i.e., 34% to 30%) on the performance of PSS, suggesting that mixing time plays an important role in the adsorption of PSS on iron oxide particles and/or removal of PSS from the calcium phosphate supersaturated solution.
Figure 4. Effect of mixing time on the performance of 10 ppm copolymer (PSS) in the presence of 100 mg iron oxide.

Effect of iron oxide concentration on polymers performance: To understand the impact of iron oxide concentration on the performance of a polymer, a series of precipitation experiments was carried out in the presence of 10 ppm of PSS and varying amounts of Fe$_2$O$_3$. Figure 5 presents phosphate concentration as a function of time for experiments carried out in the absence of PSS and in the presence of varying amounts of Fe$_2$O$_3$. It can be seen that in the presence of 0 ppm PSS, the addition of 25 or 100 mg Fe$_2$O$_3$ to the calcium phosphate supersaturated solutions does not exhibit any significant effect on the rate of calcium phosphate precipitation in the absence of PSS (curves A, B, C). Figure 5 also presents phosphate concentration as a function of time collected for experiments conducted in the presence of 10 ppm PSS and 0 mg and 100 mg of Fe$_2$O$_3$. It is apparent from the data that in the absence of Fe$_2$O$_3$, calcium phosphate precipitation is completely inhibited for at least 20 hr. However, as shown in Figure 5 addition of 100 mg Fe$_2$O$_3$ to the calcium phosphate supersaturated solution containing 10 ppm PSS exhibits marked negative impact on the performance of PSS. For example, solution phosphate concentration obtained at 20 hr in the absence of Fe$_2$O$_3$ and 10 ppm of PSS are 12.4 mg/L (curve D) compared to 4.85 mg/L (curve E) obtained in the presence of Fe$_2$O$_3$, a decrease of ~60% in phosphate concentration. The observed decrease (from 12.8 to 4.85 mg/L) in phosphate concentration in the presence of Fe$_2$O$_3$ may be attributed to the depletion of PSS via adsorption on Fe$_2$O$_3$ particles, thus resulting in poor performance of PSS.

To overcome the negative impact of Fe$_2$O$_3$ on the performance of PSS, a series of precipitation experiments were conducted at constant supersaturation and in the presence of 100 mg Fe$_2$O$_3$ and varying dosages of PSS. Results of these experiments are presented in Figure 6. It is evident that in the absence and presence of 100 mg Fe$_2$O$_3$, calcium phosphate inhibition increases with increasing PSS concentrations. It is also worth noting that to achieve similar %I value (i.e., >90%) it would require ~9.0 and ~25 ppm PSS in the
absence and presence of Fe$_2$O$_3$, respectively. Thus, to overcome the antagonistic influence of Fe$_2$O$_3$ on the performance of inhibitor, additional amount, almost by \(~2.8\)x of PSS is required to inhibit calcium phosphate inhibition. It is also worth mentioning that in calcium sulfate dihydrate scaling system, to achieve \(>85\)% inhibition, it required \(~2.5\)x the amount of inhibitor \(i.e.,\) poly(acrylic acid) in the presence of Fe$_2$O$_3$ [14].

**Figure 5.** Plots of phosphate concentrations as a function of time in the presence and absence of PSS and iron oxide (curve \(A\), no polymer, no iron oxide; curve \(B\), no polymer, 25 mg iron oxide; curve \(C\), no polymer, 100 mg iron oxide; curve \(D\), 10 ppm of polymer (PSS), no iron oxide; curve \(E\), 10 ppm of PSS, 100 mg iron oxide).

**Figure 6.** Plots of % inhibition at 20 hr in the presence of 10 ppm PSS and 0 and 100 mg iron oxide.
It is known that whereas homopolymers containing the \(-\text{COOH}\) group are effective inhibitors for various scales \textit{i.e.}, \(\text{CaF}_2\), \(\text{CaCO}_3\), and \(\text{BaSO}_4\) [16, 17, 18], copolymers containing \(-\text{COOH}\) and other functional groups such as \(-\text{COOR}, -\text{SO}_3\text{H}, -\text{CONR}_1\text{R}_2\), etc., are excellent inhibitors for calcium phosphate and are also effective dispersants for iron oxide [7, 21]. In order to investigate the influence of \(\text{Fe}_2\text{O}_3\) on the performance of homo-, co-, and terpolymers, several experiments were carried out in the presence of 10 ppm of polymers and 100 mg of \(\text{Fe}_2\text{O}_3\). The polymers tested include: PAA, PMA, PSA, PSS, PMS, and PHP. Results obtained in the presence of 10 ppm of polymers and 100 mg \(\text{Fe}_2\text{O}_3\), are presented in Figure 7. It can be seen that under similar experimental conditions all polymers lose their inhibition efficacy by \(\sim\)80\%. The decreased \(\%I\) values obtained in the presence of \(\text{Fe}_2\text{O}_3\) reflect the depletion of polymer concentration in calcium phosphate supersaturated solutions \textit{via} adsorption onto \(\text{Fe}_2\text{O}_3\) particles.

![Figure 7. Effect of iron oxide on the performance of various homo- and copolymers at 20 hr, 10 ppm polymer.](image)

**Proposed mechanism(s) for performance loss of polymers by \(\text{Fe}_2\text{O}_3\)**

The marked antagonistic effect by \(\text{Fe}_2\text{O}_3\) on the performance of various polymeric additives may be attributed to one or more of the following mechanisms:

\(a\) Interactions of \(\text{Fe(III)}\)-hydroxo complexes with additives: It is likely that \(\text{Fe(III)}\)
hydroxo complexes (\textit{i.e.}, \(\text{Fe(OH)}^{2+}\), \(\text{Fe(OH)}^{+}\), \(\text{Fe}_2\text{(OH)}^{4+}\), etc., formed in the aqueous solution interact with anionic additive molecules, thus resulting in decreased solution concentration of the additive.

\(b\) Effect of \(\text{Fe(III)}\) ions: It has been reported [22, 23] that the presence of low concentrations (\(\sim 1\) to 3 mg/L) of \(\text{Fe(III)}\) ions exhibits inhibitory effect on calcium phosphate precipitation from supersaturated solutions. In precipitation experiments involving \(\text{Fe}_2\text{O}_3\), the \(\text{Fe(III)}\) concentration in the filtrate at 20 hr was found to be \(\sim 0.02 \text{ mg/L}\). To check if \(\text{Fe(III)}\) shows any effect (synergistic or antagonist) on the
performance of additive, calcium phosphate precipitation experiments were carried out in the presence of 10 ppm of PSS and 0.02 and 0.1 mg/L of Fe(III). Results of these experiments show that Fe(III) under the conditions employed did not exhibit any significant influence on the performance of PSS.

c) Interactions of Fe(III) with anionic inhibitors: The formation of insoluble salts of –COOH containing polymers with metal ions such as Ca, Mg, Ba, etc., has been reported [24]. It is possible that trace levels of Fe(III) generated in experiments involving Fe₂O₃ in CaCO₃ supersaturated solutions may form insoluble salt with anionic polymers, thus reducing polymer concentration in solution.

d) Removal of Additives via Adsorption on Fe₂O₃: The influence of homo-, co-, and terpolymers as dispersants for suspended matter (i.e., iron oxide, clay, calcium phosphate, etc.) has been investigated [21]. Results of these studies reveal acrylic acid and maleic acid based homo- and copolymers disperse suspended matter to a varying degree. In general, co- and terpolymers are better dispersants than homopolymers. The fact that additive performance is affected by the amount of Fe₂O₃ present in the supersaturated solution suggest that additive concentration in solution is depleted via adsorption onto Fe₂O₃ particles thus effectively decreases the solution concentration of the additive.

Based on the data presented in the present study, it is likely that one or more of the proposed mechanism(s) is responsible for the marked decrease in additive performance as CaCO₃ inhibitor. Studies are currently underway to better understand the additive performance loss and the results of these studies will be presented in future papers.

Summary

The results presented in this paper support the following conclusions on the effect of iron oxide in inhibiting calcium phosphate by polymers with varying composition and containing different functional groups:

- Carboxyl group containing homopolymers i.e., poly(acrylic acid), poly(maleic acid), poly(methacrylic acid) show poor performance as calcium phosphate inhibitors.
- Based on the data presented, the order of polymer performance in terms of decreasing performance is: copolymers > homopolymers.
- Inhibition of calcium phosphate precipitation increases with increasing polymer concentration.
- Addition of iron oxide particles to calcium phosphate supersaturated markedly reduces polymer performance as calcium phosphate inhibitor.
- Data presented in this study further reveal that the negative influence shown by the addition of Fe₂O₃ to calcium phosphate supersaturated solution can be overcome by increasing the inhibitor concentration.
Acknowledgement

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References

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