Impact of Heat Treatment on the Performance of Polymers as Ferric Ions Stabilization Agents for Aqueous Systems

The impact of heat treatment on the performance of various polymers as ferric ions stabilization agents in an aqueous system at pH 7.00, 23 °C has been investigated. The polymers evaluated include: (a) homo-polymers of acrylic acid, methacrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid, sulfonated styrene; (b) co-polymers of acrylic acid:2-acrylamido-2-methylpropane sulfonic acid and maleic acid:sulfonated styrene, and (c) ter-polymers of acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:sulfonated styrene, acrylic acid: methacrylic acid:t-butylacrylamide, and acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:t-butylacrylamide. It has been found that all polymers lose performance to a varying degree when exposed to thermal treatment (150 °C, 200 °C, 240 °C, 20 hr). The performance data collected before and after thermal treatment suggest that sulfonated styrene containing co- and ter-polymers are better ferric ions stabilization agents than the co- and ter-polymers containing 2-acrylamido-2-methylpropane sulfonic acid and t-butylacrylamide. In addition, it has been found that heat treatment exhibits positive influence on the performance of homo-polymers of 2-acrylamido-2-methylpropane sulfonic acid. The results have been explained in terms of loss of 2-acrylamido-2-methylpropane sulfonic acid and t-butylacrylamide in the co- and ter-polymers during thermal treatment.

Key words: Ferric ion, stabilization, polymers, thermal stability

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1 Introduction

Among the various dissolved impurities present in natural waters, iron-based compounds present the most serious problems in many domestic and industrial applications. In the reduced state, iron (II) or ferrous (Fe²⁺) ions are very stable and pose no serious problems, especially at low pH values. However, upon contact with air, ferrous ions are oxidized to higher valence state and readily undergo hydrolysis to form insoluble hydroxides. In addition to the feed water, sources that may also contribute to iron fouling include boiler condensate, corrosion products from pumps and pipes, and biological activity (transformation of iron during bacterial processes). The solubility of iron compounds in industrial water systems is determined by their form as well as their solubility product constant. The amount of the dissolved iron containing compounds in water is dependent on several factors including pH, temperature, total dissolved solids, and type and concentrations of anions.

Iron oxide and silica are common foulants in cooling water systems and membrane based desalination processes [1 – 3]. These deposits, in fact, represent one of the major challenges in the efficient operation of such processes. The formation of iron sulfide scale on equipment surfaces has been reported during oil and gas production from formations containing large amounts of hydrogen sulfide [4, 5]. Sulfate-reducing bacteria (Desulfovibrio) are a major source of hydrogen sulfide in natural subsurface water. Iron carbonate or siderite is another type of iron scale which occurs in oil and gas production.

Iron hydroxide formed during corrosion may deposit on the heat exchanger surface as a permeable film at the corrosion site. Iron oxide deposits are porous, hence the problem with steel corrosion. In such instances, sequestrants or dispersants, which are specific in their performance on ferrous and ferric, can prevent the precipitation of iron in the hydroxide and oxide form. Other types of iron-based compounds that can potentially deposit on the heat exchanger surfaces include iron carbonate, iron silicate, iron sulfide, etc. Additionally, it has been reported that soluble metal ions (i.e., Cu, Fe, Zn, Mn) interfere with the performance of calcium carbonate and calcium phosphate scale inhibitors [6, 7]. Commonly used agents to control iron fouling include polyphosphates, organophosphonates, and polyelectrolytes.

The term stabilization used in this paper refers to an ability of an additive (polymeric or non-polymeric) to form soluble complexes and/or inhibit metal ion hydrolysis or metal hydroxide precipitation [8]. In practice, it may be difficult to differentiate between truly soluble and very finely dispersed particles. Under the conditions employed in the pre-
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Mol. Wt</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(acrylic acid)</td>
<td>- (CH₂ - CH₃)ₙ - COOH</td>
<td>2000</td>
<td>H1</td>
</tr>
<tr>
<td>poly(acrylic acid)</td>
<td>- (CH₂ - CH₃)ₙ - COOH</td>
<td>5000</td>
<td>H2</td>
</tr>
<tr>
<td>poly(maleic acid)</td>
<td>- (CH - CH₃)ₙ - COOH</td>
<td>~1000</td>
<td>H3</td>
</tr>
<tr>
<td>poly(methacrylic acid)</td>
<td>- (CH₂ - CH₃)ₙ - COOH</td>
<td>5000</td>
<td>H4</td>
</tr>
<tr>
<td>poly(2-acrylamido-2-methylpropane sulfonic acid)</td>
<td>- (CH₂ - CH₃)ₙ - COOH</td>
<td>~7000</td>
<td>H5</td>
</tr>
<tr>
<td>poly(sulfonated styrene)</td>
<td>- (CH₂ - CH₃)ₙ - COOH</td>
<td>&lt;1500</td>
<td>H6</td>
</tr>
<tr>
<td>poly(acrylic acid : 2-acrylamido-2-methylpropane sulfonic acid : sulfonated styrene)</td>
<td>- (CH₂ - CH₃)ₙ - (CH₂ - CH₃)ₙ - (CH₂ - CH₃)ₙ - COOH</td>
<td>&lt;15000</td>
<td>C1</td>
</tr>
<tr>
<td>poly(acrylic acid : 2-acrylamido-2-methylpropane sulfonic acid : t-butyl acrylamide)</td>
<td>- (CH₂ - CH₃)ₙ - (CH₂ - CH₃)ₙ - (CH₂ - CH₃)ₙ - COOH</td>
<td>&lt;15000</td>
<td>T2</td>
</tr>
<tr>
<td>poly(acrylic acid : methyacrylic acid : t-butyl acrylamide)</td>
<td>- (CH₂ - CH₃)ₙ - (CH₂ - CH₃)ₙ - (CH₂ - CH₃)ₙ - COOH</td>
<td>&lt;15000</td>
<td>T3</td>
</tr>
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</table>

Table 1  Polymers tested
sent work, % stabilization is defined as that concentration of the ionic species which is not removed by filtration through 0.22 µm membrane filter. On the other hand, dispersants function by de-agglomerating the preformed suspended matter (i.e., clay, iron oxide, manganese dioxide). Closely related to dispersion is crystal modification of scale forming salts (i.e., calcium carbonate, calcium sulfate, calcium phosphate). In this process, the morphology of growing crystals is modified and extent of crystal growth is diminished thereby delaying the settling of crystals. The terms chelation, sequestration, and complexation are generally applied to phenomena where ions or complex species are maintained in a soluble form.

During the last two decades a variety of polymers has been developed for domestic and industrial applications [9-11]. For example, in home, institutional, and industrial (HI & I) applications polymers are incorporated in to the formulations to achieve various performance objectives i.e., to prevent precipitation of Ca-surfactant, Ca-polyporphosphate, calcium carbonate; dissolve deposits from hard surfaces; remove clay/soil from fabric; suspend and prevent redeposition of suspended matter on washed fabric/glass. In industrial water treatment, polymers are used to prevent the precipitation of scale forming salts and deposition of unwanted materials on heat exchangers and reverse osmosis membrane surfaces.

Thermal degradation of polymers is a well studied area. However, there is little information available of practical value to water technologists concerned with using low molecular weight polymers. Polymers used in geothermal and boiler water treatment programs should be able to sustain high temperature and pressure environments normally associated with high temperature processes. Denman and Salaltsky [12] briefly examined the thermal stability of a sodium poly(methacrylate) under dry conditions and they found no change to 316 °C. In 1982, Masler presented data on the thermal stability of several homopolymers [i.e., polyacrylic acids (PAA), polymethacrylic acids (PMAA), poly(maleic acid) (PMA)], commonly used in boiler applications [13]. These homopolymers were (before and after thermal stress) (a) characterized by various analytical techniques and (b) evaluated for their performance. It was demonstrated under the conditions employed [pH 10.5, 250 °C, 18 hr] that PAA, PMAA, and PMA all underwent some degradation. In terms of molecular weight loss, PMAA lost slightly less molecular weight than PAA which lost considerably less than PMA. Additionally, PAA and PMAA had minimal performance changes whereas PMA displayed a substantial loss in performance. Several years later, Amjad used a similar test methodology to evaluate the thermal stability of several co-polymers. The results of this study [14] showed that the performance of polymers subjected to thermal stress is affected both by temperature level and exposure time.

Over the last two decades the performance of polymers as scale inhibitors and dispersants has attracted the attention of academic researchers and industrial technologists [15-17]. It has been reported that water chemistry and polymer architecture play important roles in inhibiting the precipitation of scale forming salts and also in dispersing suspended matter under stressed system conditions i.e., high hardness, high alkaline pH, high temperature. In our previous investigations we reported that exposure of polymers to heat treatment has a detrimental effect on polymer performance as calcium phosphate inhibitors [18] and iron oxide dispersants [19]. The focus of the present paper is to study the impact of thermal treatment on the efficacy of polymers as ferric ions stabilizing agents for aqueous systems.

2 Experimental

The polymers used in this study were commercial and/or experimental polymers and their structures are shown in Table 1. The polymers tested fall into the following three categories: (a) homopolymers of acrylic, methacrylic, maleic, and 2-acrylamido-2-methylpropane sulfonic acid, sulfonated styrene, (b) co-polymers of acrylic acid/maleic and sulfonic acid containing monomers, and (c) ter-polymers of acrylic acid, methacrylic acid, sulfonic acid containing monomers or s-acrylamide.

2.1 Sample preparation

A solution of polymer was prepared containing 10% polymer (as active solids) at pH 10.5 using sodium hydroxide to neutralize the polymer. Sodium sulfite was added as an oxygen scavenger. A known amount of polymer solution was retained for characterization and performance testing. The balance was charged to a stainless steel tube. The headspace was purged with nitrogen followed by tightening the fittings. The tube was then placed in the oven maintained at the required temperature (either 150 °C, 200 °C, or 240 °C). After 20 hr, tubes were removed from the oven, cooled to room temperature, and solution transferred to vials for characterization and performance testing.

2.2 Ferric ions stabilization

A known amount of Fe³⁺ as Fe(NO₃)₃ was added to a known volume of synthetic tap water containing varying amounts of iron stabilizing stock solution in a 125 ml glass bottle. The synthetic tap water was prepared by mixing standard solutions of calcium chloride, magnesium chloride, sodium sulfate, sodium chloride, and sodium bicarbonate. The synthetic water composition was 100 mg/l Ca²⁺, 30 mg/l Mg²⁺, 314 mg/l Na⁺, 200 mg/l SO₄²⁻, 571 mg/l Cl⁻, and 60 mg/l HCO₃⁻. After the addition of Fe³⁺ solution to the synthetic water, the pH of the solution was adjusted to 7.00 with dilute sodium hydroxide. After pH adjustment the experimental solutions were stored in a water bath maintained at 23 °C without stirring. At 2 hr the solutions were filtered through 0.22 µm membrane filter and the filtrate analyzed for iron by Inductively Coupled Plasma – Optical Emission Spectroscopy. The experimental set-up used in the present investigation is shown in Fig. 1.

The polymer performance for iron ions stabilization was calculated according to the following equation:

\[
S = \frac{[\text{Fe}]_{\text{sample}} - [\text{Fe}]_{\text{blank}}}{[\text{Fe}]_{\text{sample}}} \times 100 \%
\]

Where:

- \([\text{Fe}]_{\text{sample}}\) = Fe concentration in the presence of stabilizing agent at 2 hr
- \([\text{Fe}]_{\text{blank}}\) = Fe concentration in the absence of stabilizing agent at 2 hr
- \([\text{Fe}]_{\text{initial}}\) = Fe concentration in the beginning of experiment

Under the conditions employed in the present work, % stabilization is defined as that concentration of the ionic species which is not removed by filtration through 0.22 µm membrane filter.
3 Results and discussion

Using the experimental procedure outlined above a series of ferric ions stabilization experiments were carried out at 23°C, pH 7.00 or 8.50 and in the presence of varying concentrations of polymers of different compositions and molecular weights.

3.1 Homo- co-, and ter-polymers

In laundry, hard surface cleaners, and industrial water treatment formulations various types of additives are used to achieve a variety of benefits (e.g., hardness ions complexation, soil removal and suspension, fabric color protection, scale inhibition, corrosion prevention, dispersancy, etc.). Some commonly used additives include citric acid, polyphosphates, organophosphonates, homo-polymers of acrylic acid, maleic acids, and acrylic acid/maleic acid-based co- and ter-polymers. Numerous studies on the influence of polymer composition have shown that both the monomer unit ratio and the type of the functional group in the polymer play key roles on the inhibitory activity of the polymer in terms of preventing the precipitation of scale forming salts [20–22].

3.1.1 Polymer dosage and composition

To understand the effect of polymer concentration in stabilizing Fe\textsuperscript{3+} ions, a series of experiments were carried out in the presence varying dosages of homo-, co, and ter-polymers. The stabilization data presented in Fig. 2 show that performance of polymer as iron stabilizing agent strongly depends on polymer concentration. As illustrated homo-polymer of acrylic acid, P-AA, (H1) exhibits poor performance at low polymer concentration. For example, % S values obtained in the presence of 5 ppm and 10 ppm are 4% and 25%, respectively. As noted in Fig. 2, increasing polymer concentration from 10 ppm to 25 ppm, results in ~3.5 fold increase in % S values.

The influence of molecular weight and functional groups on polymer performance was investigated in the presence 20 ppm of homo-polymers and the results are presented in Fig. 3. It is evident that performance of homo-polymers strongly depends on polymer molecular weight (MW) and functional group. For example, % S values obtained in the presence of 2,000 and 5,000 MW P-AAs are 90% and 64%, respectively. It should be noted that MW dependence observed in the present study is consistent with earlier investigations on the evaluations of P-AAs of varying MW as precipitation inhibitors for calcium sulfate dihydrate, barium sulfate, and calcium phosphate [23–25]. Fig. 3 also presents stabilization data for poly(maleic acid), P-MA, MW 1,000 and homo-polymers containing sulfonic acid group (i.e., H5, H6). The poor performance shown by H3 (containing two –COOH groups attached to adjacent carbon atoms), H5 and H6 may be attributed to polymer MW (~1000 for H3) and/or poor interaction of Fe\textsuperscript{3+} with SO\textsubscript{3}H group (H5, H6). It is worth noting that in earlier study on the evaluation of homo-polymers containing different functional groups, H3 and H5 have been found to be ineffective calcium phosphate inhibitors. Binbuga et al. [26] studied the interaction of Fe\textsuperscript{3+} with sulfonated morin. The chelation data of this study reveal that the chelation of Fe\textsuperscript{3+} with sulfonated morin is through the 3-hydroxy-4-keto group and not with the sulfonated group. The results obtained with sulfonated morin is consistent with our findings that the lignosulfonate, a natural product containing phenolic and sulfonate groups, is an effective Fe\textsuperscript{3+} stabilization agent [27].

The impact of substituting the carboxyl group with other groups of varying chain length and ionic charge (i.e., sulfonated styrene, SS; 2-acrylamido-2-methylpropane sulfonic acid, SA) show that co-polymers compared to homo-polymers exhibit different behaviors in terms of stabilizing Fe\textsuperscript{3+} in aqueous solutions. For example, substituting acrylic acid with sulfonic acid containing monomer (i.e., 2-acrylamido-2-methylpropane sulfonic acid, SA) markedly improves the stabilizing ability of co-polymer (C1). As illustrated in
Fig. 4, % S values obtained in the presence of 10 ppm of C1 (AA:SA) and H2 are 84% and 4%, respectively. Similar improvement in stabilization value was observed for co-polymer of maleic acid: sulfonated styrene, MA: SS (C2). It is worth noting that whereas homo-polymers of acrylic acid (H1), maleic acid (H3), and sulfonic acids containing polymers (H5, H6) show poor performance, incorporation of SA in poly(acrylic acid), H2, or SS in poly(maleic acid), H3, significantly improves the performance of co-polymers (C1, C2). It is interesting to note that the excellent performance shown by co-polymers over homo-polymers in the present study is consistent with the results of earlier study on the evaluation of homo- and co-polymers as calcium phosphate inhibitors [6]. This suggests that polymer architecture plays an important role in imparting inhibitory property to the co-polymers. Fig. 5 shows the performance comparison of homo- (H1), co- (C1), and ter-polymer (T1, AA:SA:SS). It is evident that substituting part of AA with two sulfonic acid monomers in poly(acrylic acid) results in marked improvement in the performance of the ter-polymer. For example, % stabilization values at 7.5 ppm polymer concentration obtained for homo-polymer (H1) and co-polymer (C1) are 6% and 42% respectively, compared to 98% obtained for ter-polymer (T1) thus suggesting that incorporation of two sulfonic acid monomers in T1 play important roles in ter-polymer performance.

3.2 Effect of solution pH

It is generally accepted that increasing the re-circulating water pH has a two-fold effect on system performance: (a) it tends to decrease the rates of metal corrosion, and (b) it increases the scaling tendency by increasing the supersaturation of scale forming salts. It is well recognized for polymeric inhibitors such as poly(acrylic acid) and acrylic acid and/or maleic acid based co- and ter-polymers that the degree of de-protonation explains the observed improvement in polymer performance as the solution pH is increases from 4.5 to 9.0 [22]. Fig. 6 shows the iron stabilization data for three structurally different but commonly used polymers namely: homo-polymer (H1), co-polymer (C1), and ter-polymer (T1). As illustrated solution pH in the 7.00 to 8.50 range influences to varying degree the stabilization power of these polymers for Fe3+ ions. It is evident from the data presented in Fig. 6 that for homo-, co-, and ter-polymers tested, the stabilization values decrease by a factor of 1.5 to 2 as the pH is increased from 7.00 to 8.50. The observed decrease in polymer performance may be attributed to increased iron hydroxide and calcium carbonate supersaturation and the presence of various forms of iron hydroxides at pH 8.50. It is interesting to note that similar trend in polymers performance was noted in an earlier study on the interactions of hardness ions with polymeric scale inhibitors [28].

3.3 Effect of heat treatment on polymer performance

3.3.1 Homo-, co- and ter-polymers

The performance data on various homo-polymers of acrylic acid (H1) and 2-acrylamido-2-methylpropane sulfonic acid (H5) are shown in Fig. 7. It is evident that exposure of heat treatment shows small but measurable effect on the performance of poly(acrylic acid). For example, % S value obtained in the presence of 25 ppm of H2 exposed to 200 °C is 85% compared to 92% obtained for non-heat treated H1. Regarding H5, the heat treatment has an opposite effect on the performance of polymer i.e., performance increases as the H5 is subjected to heat treatment. For example, % S value obtained in the presence of 25 ppm for heat treated (200 °C, 20 hr) H5 is 32% compared to 4% obtained for non-heat treated PSA. The improved performance observed for heat treated H5 may be attributed to the conversion of 2-acrylamido-2-methylpropane sulfonic acid to P-AA. It is worth noting that similar improved performance of heat treated H5 was also observed in our earlier study on the inhibition of calcium carbonate from aqueous solution [29].

The impact of temperature on the thermal stability of co- and ter-polymers was investigated at 200 °C. Fig. 7 shows a comparison of the acrylic acid:2-acrylamido-2-methylpropane sulfonic acid (C1) and maleic acid:sulfonated styrene (C2) co-polymers. The stabilization data indicate that thermal stability (as determined by retention of performance following thermal treatment) of C2 is better than the C1. The data presented in Fig. 7 clearly demonstrate the excellent thermal stability of sulfonated styrene (SS) containing co-polymer (C2). The performance of ter-polymers as iron stabilization additives before and after thermal treatment is illustrated in Fig. 7. Although two (i.e., AA and SA) of the three monomers used to manufacture these acrylate ter-polymers (T1, T2) are the same, the functionality of third monomer (sulfonated styrene) plays a key role in explaining the performance difference between two ter-polymers. Fig. 7 also shows the stabilization data for the ter-polymer of ac-
The influence of temperature on the thermal stability of ter-polymers was also investigated at 150 °C, 200 °C and 240 °C. Fig. 8 shows a comparison of the ter-polymers that have the same baseline performance before heat treatment. However, as the polymers are exposed to 150 °C, 200 °C, and 240 °C a marked decrease in iron stabilization is observed. For example, % stabilization values for T1 and T2 without heat treatment are 98% and 94% compared to 88% and 66%, respectively after heat treatment (150 °C, 20 hr). As noted in Fig. 8, increasing solution temperature from 150 °C to 200 °C resulted in a significant decrease in performance for each of the ter-polymers. It is worth noting that at 240 °C, T1 lost only ~50% performance compared to ~90% performance lost observed for T2. The data presented in Fig. 8 clearly show that T1 is more tolerant to heat treatment than T2. It is worth noting that results obtained on the performance of polymers investigated in the present study are in agreement with our earlier investigations on the evaluation of these polymers as iron oxide dispersants and calcium phosphate inhibitors [14, 19].

4 Summary

The conclusions from this study appear below:

1) Homo-polymers of acrylic acid, methacrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid, and sulfonated styrene show poor performance as ferric ion stabilization agents.

2) Compared to homo-polymers, co- and ter-polymers containing sulfonic acid and non-ionic groups exhibit excellent performance as ferric ion stabilization agents.

3) Increasing solution pH from 7.00 to 8.50 decreased the performance of homo-, co-, and ter-polymers.

4) Thermal treatment of polymers (10% polymer solutions stored for 20 hr at pH 10.5, either 150 °C, 200 °C or 240 °C, in the absence of oxygen) has a pronounced and varied effect on a polymer's performance in stabilizing ferric ions as follows:
   a) Carboxylic-based (acrylic and maleic) homo-polymers experienced essentially no performance loss < 15%.
   b) Sulfonic acid containing homo-polymers on exposure to heat treatment results in improved polymer performance presumably due to the formation of poly(acrylic acid).
   c) A co-polymer containing both acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (C1) resulted in essentially complete degradation of the second monomer and performed like a homo-poly(acrylic acid). Under similar experimental conditions a co-polymer of maleic acid and sulfonated styrene show relatively good thermal stability.

d) Ter-polymers experience varying degrees of performance loss depending upon the degree of thermal stress and polymer composition. However, among the two (3) ter-polymers (both of which containing carboxylic, t-butylacrylamide, and SA groups), T1 (containing S$) is more stable than T2 and T3 (containing a t-butylacrylamide group).

References


Received: 17. 10. 2007
Revised: 13. 01. 2008

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