# Controlling Metal Ion Fouling in Industrial Water Systems

by

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## Introduction

Industrial water systems problems generally fall into four major areas: (1) precipitation of scale forming salts, (2) deposition of suspended matter, (3) corrosion of metal surfaces, and (4) growth of microbiological organisms. If not properly managed, the potential operating and economic problems include loss of heat transfer efficiency, deterioration of system metallic parts, emergency shutdown, increased energy consumption, and frequent system cleaning. Thus, effective treatment of industrial water systems continues to challenge water treatment technologists.

Greater water conservation has been a driver for operating industrial water systems at higher cycles of concentration thereby increasing the potential for deposit build-up on heat exchanger surfaces. Operating industrial water systems under stressed conditions demands a better understanding of feed and recirculating water chemistry as well as the development of new and innovative scale, deposit, corrosion, and biofouling control agents to handle more challenging operating conditions.

During the past two decades, much work has been done in the area of controlling mineral precipitation and scaling in industrial waters.[1-3] Several reviews have compared the performance of natural and synthetic materials as scale control agents. Previous publications reported the ability of polymers to control the precipitation of several mineral scales (e.g., calcium carbonate, calcium sulfate, calcium phosphate, calcium phosphonate, calcium fluoride, barium sulfate).[4-7] It was recently documented that process variables and water chemistry greatly influence the performance of polymers as calcium phosphate precipitation inhibitors and also as iron oxide dispersants.[8,9] This paper presents new results of an ongoing effort to investigate fouling by metal oxide/hydroxide with particular emphasis on aluminum, iron, manganese, and zinc ions. This paper reviews metal ion solution chemistry followed by the comparative data on the effectiveness of various polymeric and non-polymeric agents as metal ion stabilizers. The goal of this paper is to provide guidance to industrial water technologists seeking to design new formulations for systems where metal ions such as Al, Fe, Mn, and Zn present potential operational problems.

## Metal Ion Solution Chemistry

### Aluminum

Aluminum and iron based compounds (e.g., alum, sodium aluminate, and ferric sulfate) have been used for years as coagulant aids to clarify municipal and industrial waters. These flocculating agents neutralize the charge of turbidity particles in the water and they hydrolyze to form insoluble hydroxide precipitates that entrap additional particles. In most cases, these large particles (or flocs) are removed via settling in a clarifier and are collected as sludge. Occasionally, clarifier upsets cause the metal ion containing flocs to “carry over.”

Aluminum is amphoteric, with $Al^{3+}$ present at low pH values and aluminate anion existing at higher pH values, and exhibits minimum solubility at about pH 6.6. Thus, aluminum is more soluble at higher and lower pH values. Further, if pH adjustment is employed to control calcium carbonate scaling, aluminum hydroxide may precipitate and deposit on heat exchanger and reverse osmosis (RO) membrane surfaces.

In RO applications, acid is used to reduce the pH of feed waters. When feed water pH is lowered, aluminum precipitates from the water. In these instances, troublesome aluminum-based deposits can form within an RO module. If the feed water contains aluminum, any acid addition should be made as far ahead of the media filter as possible so as to avoid aluminum-based fouling. It has recently been observed that aluminum ion, when present at low concentrations, exhibit an antagonistic effect on the performance of calcium phosphate inhibiting polymers.[10]

**Iron**

Among the various dissolved impurities present in natural waters, iron-based compounds present the most serious problems in the efficient operation of industrial water systems. In the reduced state, iron (II) or ferrous ($Fe^{2+}$) ions is very soluble 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 as shown below:

$$Fe^{2+} \longrightarrow Fe^{3+} \qquad (1)$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(0H)_3 + 3H^+ \qquad (2)$$

In addition to 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 by their solubility product constant. The amount of dissolved iron containing compound present in water is dependent on several factors including pH, temperature, total dissolved solids, and type and concentrations of anions.

When ferric (or ferrous) ions precipitate in water, an amorphous or gelatinous solid is usually formed. When the corrosion rate is very low, the iron hydroxide formed may deposit on the heat exchanger surface as a permeable or an impermeable film at the corrosion site. Under severe corrosion conditions, the recirculating water transports iron ions and oxides. Iron oxides that form under these conditions are typically colloidal and form stable suspensions.[11]

In summary, regardless of the source, soluble iron can and does precipitate under certain conditions to form troublesome scale deposits. It is also well documented that soluble iron, particularly ferric ions, interferes with stabilized phosphate treatment programs by forming insoluble ferric phosphate and precipitates of ferric-polymer salts.[1,3,8] Other types of iron-based compounds that can potentially deposit on the heat exchanger surfaces include iron carbonate, iron silicate, iron sulfide, etc. Thus, control of iron-based compounds is of paramount importance in achieving optimum performance from a water treatment program.

**Manganese**

Manganese, like iron and aluminum, also causes serious problems including staining of toilet bowls and sinks, graying of laundry, fouling of heat exchanger and membrane

surfaces, and pitting corrosion. In well waters, manganese fouling and deposition is commonly associated with specific microorganisms. Manganese is usually present below 0.5 ppm in public water supplies. Private water supplies often contain higher manganese levels, mostly in a dissolved form that precipitates as hydroxides on exposure to the oxygen. Results of previous studies have shown that poor control of microorganisms and deposition of manganese oxides can result in well plugging or a loss of water pressure.[12]

In cooling water applications, manganese based foulants have been identified in both once through and recirculating systems. In these cases various factors such as the presence of oxidizing agents (e.g., oxygen, chlorine), pH, temperature, and natural organics appears to influence the precipitation of manganese oxides.[13]

Manganese solution chemistry is very complex. Manganese exists in several oxidation states among which $Mn^{+2}$ and $Mn^{+4}$ are the most important with respect to water problems. $Mn^{+2}$ is soluble and less susceptible to oxidation at pH $\leq$ 7. In alkaline pH conditions, $Mn^{2+}$ readily oxidizes to the less soluble $Mn^{+4}$ (e.g., $MnO_2$). Manganese-based deposits typically encountered in cooling water systems contain $MnO_2$. $Fe^{2+}$ oxidization occurs at a somewhat lower pH than $Mn^{2+}$ oxidization and this is perhaps the reason that Fe and Mn salts are typically encountered together in cooling water applications.

**Zinc**

Corrosion in recirculating cooling water systems is controlled by incorporating one or more of inhibitors in water treatment formulations. Commonly used corrosion inhibitors include chromate, zinc, orthophosphate/polyphosphate, phosphonate, molybdate, and silicate. The levels and/or types of these corrosion inhibitors may vary with various water quality criteria.

Stringent environmental regulations have severely restricted the use of chromate in open recirculating cooling water systems. The phase out of chrome over the last two decades led to the development of several alternative technologies (e.g., stabilized phosphate, high pH / all organic).[14,15] Each of these non-chromate technologies is a viable option under certain operating conditions but they provide limited positive corrosion protection and much less forgiving (require greater control and are more susceptible to upsets) than chromate-based programs.

Chromate/zinc programs were well known for their positive, forgiving corrosion protection. All organic approaches generally contain little or no corrosion inhibitor package and rely heavily on elevated pH and hardness to create a non-corrosive aqueous environment in the cooling system. The mixed phosphate formulation components of stabilized phosphate programs provide a positive corrosion inhibitor that is relatively weak compared to chromate/zinc.

Alkaline zinc programs rely on zinc ions as a cathodic inhibitor and have shown some promise in controlling corrosion. Many effective programs incorporate organic or inorganic phosphates (e.g., phosphonates, phosphate, and polyphosphate) as co-inhibitors. The key to the success of these alkaline zinc programs lies in the selection

and incorporation of an effective polymeric dispersant to control the formation of the corrosion inhibiting film. This film is primarily formed by zinc hydroxide or zinc phosphate precipitation due to the local high pH at the cathode.[16] Successful alkaline zinc programs require that the polymer prevent precipitation of zinc species in the bulk water.

## Fouling Control Methods

The three major approaches for controlling fouling caused by metal ions are precipitation, chelation, and stabilization / dispersion. The following sections detail the advantages and disadvantages of each approach.

### Precipitation

Iron and manganese can be removed by lime or lime-soda softening process at pH $\geq$10 by oxidizing iron to iron hydroxide and oxidizing manganese to manganese hydroxide. Removal of metal hydroxide precipitates is achieved by sludge blow down. Aeration may be employed to supply oxygen to oxidize the iron and manganese before softening.[17]

In situations where the feed water requires no softening, iron and manganese removal is accomplished by using aeration, chemical oxidation, and filtration. For small plants or for waters containing less than 1 ppm of iron or manganese, the removal process may include the addition of potassium permanganate as the primary oxidizing agent followed by a filtration using a bed of anthracite and manganese zeolites or green sand. In this operation, raw water is adjusted to a pH 7.0, potassium permanganate (from a 1 or 2% solution) is continuously added to oxidize the iron and manganese, and the precipitates are removed by filtration.

The use of dithiocarbamates and trithiocarbamates for the removal of heavy metals from aqueous streams has been practiced for several decades. Because of the strong binding properties and the formation of insoluble heavy-metal complexes, both chelating agents have found a wide range of applications. Compared to the precipitation of metals using hydroxides, the minimum solubilities of metal/di- or trithiocarbamates complexes are largely independent of pH and thus can be used effectively across a broad pH range.[18]

### Chelation

Many chemicals both organic and inorganic can chelate metal ions. The chelation properties of several chemicals are discussed below:

**Citric Acid:** Citric acid is an organic acid that has a wide range of industrial uses in metal cleaning and polishing and in water conditioning. The chelating efficiency of citric acid for a number of metal ions is well known and the ranking in terms of decreasing metal-citrate stability constants is:

$$Fe^{3+} >> Zn^{2+} > Ca^{2+} > Cu^{2+} > Mn^{2+} > Fe^{2+}$$

**Gluconic Acid:** Gluconic acid derivatives are important because of their ability to chelate various metal ions especially iron. The chelation ability of gluconate increases

with increasing pH, is more effective at high pH, and preferentially chelates more Fe(III) than Fe(II).

**Sulfamic Acid:** Sulfamic acid is the monoamide of sulfuric acid. The advantages of sulfamic acid have resulted in its wide spread use in acid cleaners. Sulfamic acid is used to remove rust, algae, and hard water scales from air conditioning systems, cooling towers, evaporative condensers, seawater evaporators, and RO systems. Sulfamic acid is also used to clean copper-bottom kettles, steam iron, dish washers, silverware, toilet bowls, bricks and tiles and the processing equipment in the food and dairy, sugar refining, and brewing industries.

**Tartaric Acid:** Tartaric acid is a dibasic hydroxy organic acid capable of sequestering metal ions under certain condition. Tartaric acid is used in some of the same applications as citric and oxalic acids. Its complexing ability makes tartaric acid useful in removing rust, scale, and oxides from metals in finishing operations.

**Polydentate Amino Acid:** Chelants such as the hexadentate ethylenediaminetetra acetic acid (EDTA) and the tetradentate nitrilotriacetic acid (NTA) are known to be strong chelants for metal ions (e.g., $Fe^{3+}$, $Zn^{2+}$, $Ca^{2+}$) and very effective for many applications. However, neither EDTA nor NTA exhibits the threshold effect of phosphorus type derivatives. Therefore, EDTA and NTA are rarely cost-effective in natural waters where hardness values are high.

EDTA and NTA have been used for polishing treatment in boiler waters and for removal of calcium sulfate, barium sulfate, and calcium hydroxyapatite deposits from the heat exchanger and RO membrane surfaces either by themselves or in conjunction with other chemicals. Although they exhibit excellent chelating properties, EDTA and NTA can be corrosive to steel surfaces especially when used at high concentrations. New chelants have recently been developed with increased specificity for iron by combining the chelating ability of amino acids with the strong iron affinity of hydroxyaromatic groups.[19]

In situations where several ions are present in water and the molar concentration of EDTA is exceeded by the total molar concentration of the metal ions, EDTA complexes metal ions in a specific order. In these cases, EDTA preferentially chelates metal ions, which have the highest metal chelate stability. The chelation stability for various metal-EDTA complexes approximates the following:

$$Na^{+} < Ba^{2+} < Mg^{2+} < Ca^{2+} < Mn^{2+} < Fe^{2+} < Zn^{2+} < Fe^{3+}$$

Thus, EDTA normally complexes more calcium than magnesium and more iron than calcium.

**Phosphonic Acids and Related Derivatives:** Organo phosphonates are a class of compounds that have a phosphonate group on a carbon backbone chain. The most commonly use phosphonates in water treatment are aminotri (methylene phosphonic acid) or AMP; 1-Hydroxyethylidine 1, 1-Diphosphonic Acid or HEDP; and 2-Phosphonobutane 1,2, 4-tricarboxylic acid or PBTC.

Phosphonates are excellent scale control agents and operate best under more alkaline conditions where $CaCO_3$ scale formation becomes a significant problem. However, soluble iron ions can complex and/or precipitate with phosphonates causing them to loose their ability to inhibit corrosion and $CaCO_3$ scale.[19] Certain phosphonates have been used to remove iron oxide deposits and leave a surface that is protected against further corrosion. Phosphonates also function as chelants for controlling metal ions such copper, iron, and zinc.

**Inorganic Polyphosphates**: The inorganic polyphosphates most widely used in industrial water systems for scale prevention are commonly referred to as "condensed phosphates." These inorganic polyphosphates have a repeating P-O-P unit in their structures. Sodium hexametaphosphate also forms complexes with $Fe^{2+}$ and $Mn^{2+}$ and can prevent the deposition of iron and manganese containing salts. Under certain conditions, the condensed polyphosphates have a tendency to hydrolyze and revert back to the orthophosphate. Normally, instead of functioning as a scale inhibitor, orthophosphate precipitates as an insoluble calcium phosphate.

**Polymers:** Polymers have been used extensively in industrial water systems to prevent the precipitation and deposition of scale forming inorganic salts and as dispersants for foulants (e.g., clay, silt, iron oxides). Naturally occurring polymers such as starches, alginates, lignins, tannins, and cellulose derivatives were the earliest dispersants used in industrial water systems

Tannins are a class of compounds that have been investigated for use in on-line removal of iron deposits. These polymers are attractive because they contain hydroxyaromatic constituents that are available to bind to ferric ions. However, the amount of hydroxyaromatic constituents as a percentage of the total polymer is relatively low, and tannins often form insoluble iron complexes.

During the mid 1950s, a search for improved boiler water deposit control agents resulted in the development of entirely new class of additives based on synthetic polymers. The earlier polymers that found widespread use as dispersants were poly(acrylic acid) or P-AA, and poly(maleic acid) or P-MA. Like phosphonates, the performance of polymers, especially P-AA and P-MA, as scale control agents can be adversely affected by soluble iron. The inclusion of monomers containing sulfonate and carboxylate groups generally improves the dispersion of particles of iron oxide.[9]

The term stabilization used in this paper refers to the ability of an additive (polymeric or non-polymeric) to form soluble complexes and/or inhibit metal ion hydrolysis or metal hydroxide precipitation. On the other hand, dispersants function by de-agglomerating the preformed suspended matter (i.e., clay, iron oxide, manganese oxide, etc.). The effectiveness of both metal ion stabilizers and dispersants strongly depends upon polymer molecular weight, charge density, and functional group.

## Performance of Polymeric and Non-Polymeric Agents

A series of experiments were conducted to evaluate the metal ion stabilization properties of several water treatment additives. The preparation of test solutions and the results of performance testing of various polymeric and non-polymeric agents are presented below.

### Metal ion Stabilizing Testing

All solutions were prepared using reagent grade chemicals with deionized, distilled $CO_2$-free water. Metal ion concentrations were determined by atomic absorption spectroscopy. Stock solutions of polymeric and non-polymeric materials were prepared on active solids basis. The synthetic waters shown in Table 1 (see Page 13) are prepared for testing the stabilization of various metal ions.

A known volume of metal ion followed by polymer stock solutions were added to each synthetic water in order to achieve the desired concentrations. The pH of each solution was adjusted to the desired value with dilute NaOH and/or HCl. The solutions were equilibrated at the desired temperature. In the case of manganese, known amounts of chlorine as oxidant was added. At a specified time, solutions were filtered through 0.22-micron filter paper and analyzed by atomic absorption spectroscopy. The performance of stabilization agent was calculated according to the following equation:

$$S = \frac{(M)_{sample} - (M)_{blank}}{(M)_{initial} - (M)_{blank}} \times 100\% \qquad (3)$$

Where:

| | | |
|---|---|---|
| $S$ | = | Stabilization, % |
| $(M)_{sample}$ | = | Metal ion concentration at the end of the experiment, in the presence of additive |
| $(M)_{blank}$ | = | Metal ion concentration in the absence of additive |
| $(M)_{initial}$ | = | Metal ion concentration in the beginning of experiment |

Table 2 lists the products evaluated in this study.

### Aluminum Ion Stabilization

The results of aluminum ion stabilization testing are discussed below.

**Polymer Dosage:** Figure 1 (see Page 14) presents the aluminum ion stabilization by Poly-G [a terpolymer containing acrylic acid (AA), sulfonic acid (SA), and sulfonated styrene (SS)] as a function of polymer dosage and aluminum concentration. Curves I, II, and III show that polymer performance strongly depends upon the concentration of Al ion present in synthetic water. For example, Curve I for 1 ppm Al indicates that 5 ppm polymer is required to achieve >90% stabilization. Comparing Curves I and II shows that increasing the Al concentration by a factor of three (3), necessitates increasing the polymer concentration by a factor of six (6) in order to achieve >90% stabilization. Data presented in Curve III for 4.5 ppm Al shows that in the presence of 40 ppm of Poly-G

results in only ~20% Al stabilization compared to 98% for 3 ppm Al which indicates that polymer performance strongly depends on Al concentration present in aqueous solutions.

**Polymer Composition:** The effect of polymeric materials to maximize stabilization of aluminum is strongly dependent upon the polymer's chemical composition. Figure 2 (see Page 14) illustrates that little improvement in Al stabilization was obtained with Poly-C (when AA (acrylic acid) was partly substituted with VAc (vinyl acetate)). Moderate increases in Al stabilization was obtained with Poly-D [AA:carbitol acrylate (CA)] and Poly-E [AA: hydroxypropylacrylate (HPA)] polymers. The addition of Poly-F (AA:SA) to the Al solution shows improvement over other polymers. The observed improved performance of Poly-F suggests that the nature of the co-monomer (SA is strongly acidic whereas CA and HPA are neutral) plays an important role in the overall performance of the polymer. Figure 2 also shows that Poly-G exhibits excellent performance as an Al stabilization agent. From a practical viewpoint, if aluminum is encountered in industrial water systems, incorporating a high performance aluminum-stabilizing polymer in the water treatment program will ensure better overall performance.

**Non-Polymeric Materials**: Figure 3 (see Page 14) shows the performance for a variety of non-polymeric materials known to form soluble complexes with metal ions. The data show that that all phosphorus containing materials tested (i.e., SHMP, AMP, HEDP, and PBTC) with the exception of SHMP exhibit excellent stabilizing ability. In the case of hydroxyl and carboxyl containing materials such as citric acid (CA), oxalic acid (OxA), and sodium gluconate, the data presented in Figure 3 show that citric acid exhibits the best performance. It is interesting to note that sodium fluoride is about five (5) times more effective in stabilizing Al than the organophosphonates. The observed excellent performance for NaF may be attributed to the formation of a much stronger soluble Al-F complex.

**Iron Ion Stabilization**

The effectiveness of inhibitors as iron ion stabilizers was evaluated by carrying out a series of precipitation experiments using various inhibitors as several concentrations. Figure 4 (see Page 14) shows the '% Fe Stabilization' vs. inhibitor concentration profiles for various products. It is evident that Poly-A shows very little stabilizing activity (<10%). However, as AA content is replaced with SA and SS, the stabilizing power of the polymer increases dramatically and excellent performance is obtained for Poly-G (AA:SA:SS terpolymer). It is noteworthy that HEDP, which shows good stabilizing power for iron, has also been shown to be an effective stabilizing agent for Al (see Figure 3).

In order to better understand the performance profile of various inhibitors, additional experiments were performed with homopolymers, copolymers, and chelating agents under high iron concentrations (i.e., 2.5 ppm). Among the polymers evaluated were homopolymers such as Poly-A and Poly-B, and acrylic acid based copolymers in which carboxyl group has been substituted with other groups of varying chain length and ionic charge. Figure 5 (see Page 15) shows iron stabilization data obtained in the presence of 4.0 ppm of various products. As illustrated, homopolymers of acrylic acid and maleic

acid exhibit poor performance. The iron stabilizing data for copolymers suggest that polymers containing neutral co-monomers (i.e., vinyl acetate and hydroxypropylacrylate) are relatively poor performers compared to polymers comprised of acidic monomers (i.e., containing carboxylic or sulfonic acid groups). For example, the '% Fe Stabilization' values obtained for Poly-C, Poly-E, Poly-F, and Poly-G were 12%, 66%, 75%, and 94%, respectively.

The observed ranking in copolymer performance may be attributed to the increased size of co-monomer. Thus, for these polymers, both anionic character and the monomer size play important roles in influencing the stabilizing power of the polymer. It should be noted that the performance trend observed for copolymers in stabilizing iron (III) is consistent with earlier reports on these polymers regarding their influence in preventing the precipitation of calcium phosphate and dispersing iron oxide in aqueous solutions.[4]

Figure 5 also shows iron stabilizing data for non-polymeric materials [i.e., citric acid (CA), ascorbic acid (AsA), and sodium hexametaphosphate (SHMP)]. As illustrated, SHMP and AsA exhibit poor performance compared to CA. It is noteworthy that these non-polymeric materials are not only poor iron stabilizing agents compared to copolymers, but also show poor performance as iron oxide dispersants and scale control agents.

**Manganese Ion Stabilization**

The use of polymeric and non-polymeric materials to stabilize Mn(II) in aqueous solutions was evaluated by carrying out a series of precipitation experiments. Oxidation of Mn(II) to Mn(IV) was achieved by the addition of a sodium oxychloride solution. Figure 6 (see Page 15) shows the Mn stabilization data for various products. As illustrated, all products gave good to excellent (45 to 95%) results or stabilization values. Interestingly, terpolymer Poly-G outperforms all the products evaluated. It is noteworthy that SHMP, which is relatively ineffective as an aluminum and iron stabilization agent, exhibits good stabilizing power toward manganese ions. Figure 7 (see Page 16) shows the comparative performance of various products. As illustrated, Poly-G is an effective Mn ion stabilizer (the darker the brown color, the more manganese hydroxide precipitated from solution).

**Zinc Ion Stabilization**

Figure 8 (see Page 16) illustrates '% Zn Stabilization' vs. inhibitor concentration profiles for various products under standard test conditions. It is evident that addition of low concentrations of polymer has a marked effect on the stabilizing ability of the polymer. Figure 8 shows that Poly-A provides the poorest performance among the polymers studied. The next polymer in terms of increasing effectiveness is Poly-F in which part of acrylic acid has been substituted with monomer containing sulfonic acid. Terpolymer Poly-G (AA:SA:SS) exhibits the best performance indicating that the polymer composition plays an important role in improving the effectiveness of the polymer for stabilizing zinc ions under stressed conditions. It should be pointed out that SHMP, a well-known calcium carbonate inhibitor, shows the worst performance.

The influence of solution pH on corrosion rate as well scaling tendency has been investigated. It is well known that high alkalinity generally reduces corrosion rates.

However, an increase in solution pH can increase calcium phosphate and calcium carbonate scaling potentials, thus requiring incorporation of high performance scale inhibitor in the formulations.

The role of solution pH on the performance of stabilizing agents was studied. Figure 9 (see Page 17) indicates that the precipitation of zinc increases with increasing solution pH from 7.5 to 9.0. At pH 7.5, essentially no precipitation of zinc is observed in the presence and absence of stabilization agent. Curve I in Figure 9 shows that in the absence of a stabilization agent and at pH 9.0, more than 95% zinc is precipitated. Figure 9 (curves II, III, IV, and V) shows the residual zinc concentrations in the presence of 4.5 ppm of various stabilization agents. The data clearly indicate that the terpolymer (Poly-G) is a superior stabilization agent.

## *Summary*

Industrial water systems frequently experience operational problems due to equipment fouling; the most common cause of increased operational costs. This paper has provides an overview of fouling caused by metal ions (i.e., aluminum, iron, manganese, and zinc). It has been shown that to control the formation of aluminum, iron, manganese, and zinc based foulants, the water treatment technologist needs a much higher level of performance than the SHMP or homopolymers such as poly(acrylic acid) and poly(maleic acid). Thus, to control metal ion fouling, the incorporation of an effective polymer (e.g., Poly-G) into the water treatment program can ensure better overall system performance.

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**Table 1 - Synthetic Waters Prepared for Metal Ion Stabilization Testing**

| Parameter | Synthetic Water | | | |
|---|---|---|---|---|
| | Aluminum | Iron | Manganese | Zinc |
| Ca (ppm) | 60 | 300 | | 60 |
| Mg (ppm) | 30 | 300 | | 20 |
| Cl (ppm) | 194 | 2170 | 10 | 172 |
| Na (ppm) | | 1120 | | 202 |
| $SO_4$ (ppm) | | 700 | | 200 |
| $HCO_3$ (ppm) | | 153 | | 36 |
| Al (ppm) | 1, 3, or 4.5 | | | |
| $Fe^{3+}$ (ppm) | | 1.0 or 2.5 | | |
| Mn (ppm) | | | 3 | |
| Zn (ppm) | | | | 6 |
| pH | 6.6 | 7.0 | 7.5 | 7.5, 8.0, 8.5, or 9.0 |
| Temperature (°C) | 22 | 22 | 40 | 30 |
| Time (hr) | 3 | 2 | 3 | 20 |

**Table 2 - Products Evaluated in This Study**

| Product | Acronym |
|---|---|
| Poly(acrylic acid) | Poly-A |
| Poly(maleic acid) | Poly-B |
| Poly(acrylic acid: vinyl acetate) | Poly-C |
| Poly(acrylic acid: carbitol acrylate) | Poly-D |
| Poly(acrylic acid: hydroxylpropyl acrylate | Poly-E |
| Poly(acrylic acid: 2-acrylamido-2-methyl propane sulfonic acid) | Poly-F |
| Poly(acrylic acid: 2-acrylamido-2-methyl propane sulfonic acid: sulfonated styrene) | Poly-G |
| Citric acid | CA |
| Ascorbic acid | AsA |
| Oxalic acid | OxA |
| Sodium hexametaphosphate | SHMP |
| Aminotris(methylene phosphonic acid) | AMP |
| 1-hydroxyethylidine 1,1-diphosphonic acid | HEDP |
| 2-phosphonobutane 1,2,4-tricarboxylic acid | PBTC |
| Sodium fluoride | NaF |
| Sodium gluconate | NaGl |

Note: Poly-A, Poly-F, and Poly-G are Carbosperse™ (formerly Good-Rite) K-7028, K775, and K-798 polymers, respectively supplied by Lubrizol Advanced Materials, Inc. (formerly BFGoodrich Performance Materials).

**Figure 1 -Aluminum Ion Stabilization in the Presence of Varying Concentrations of Aluminum Ion and Poly-G at pH 6.6.**

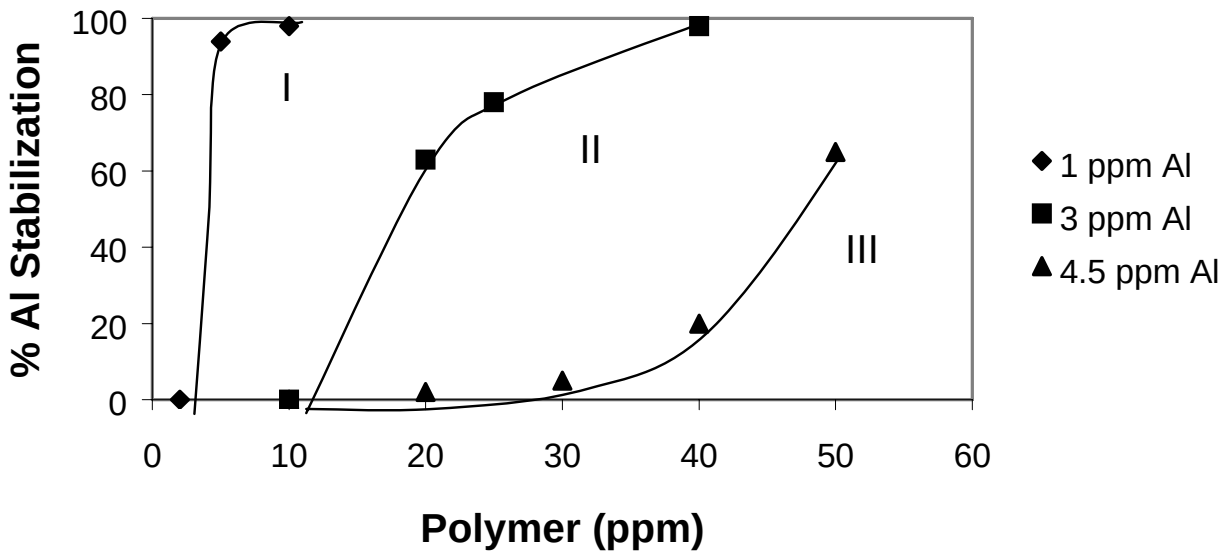



**Figure 2 - Aluminum Ion Stabilization by Polymers of Varying Composition (3 ppm Al, 20 ppm Polymer, pH 6.6).**

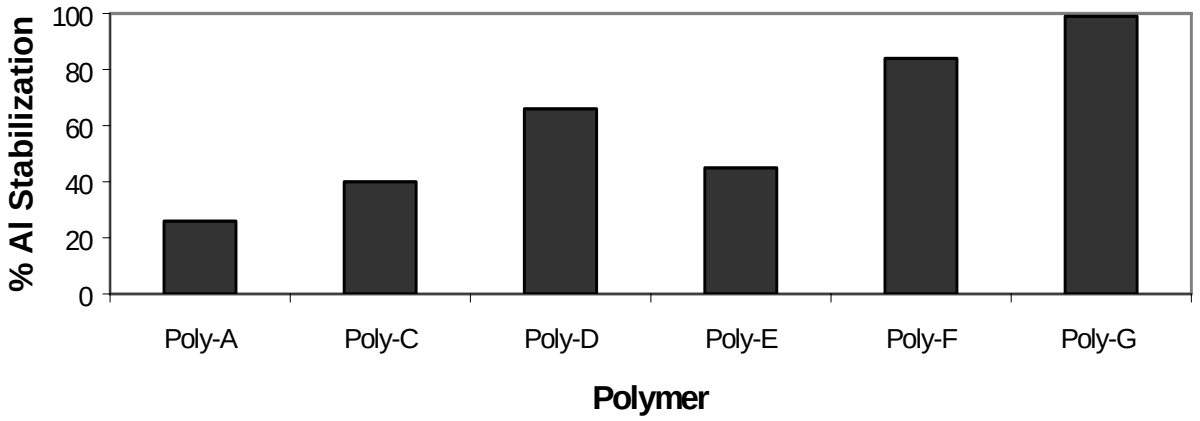


**Figure 3 - Aluminum Ion Stabilization by Non-Polymeric Product (3 ppm Al, 20 ppm Product, pH 6.6)**

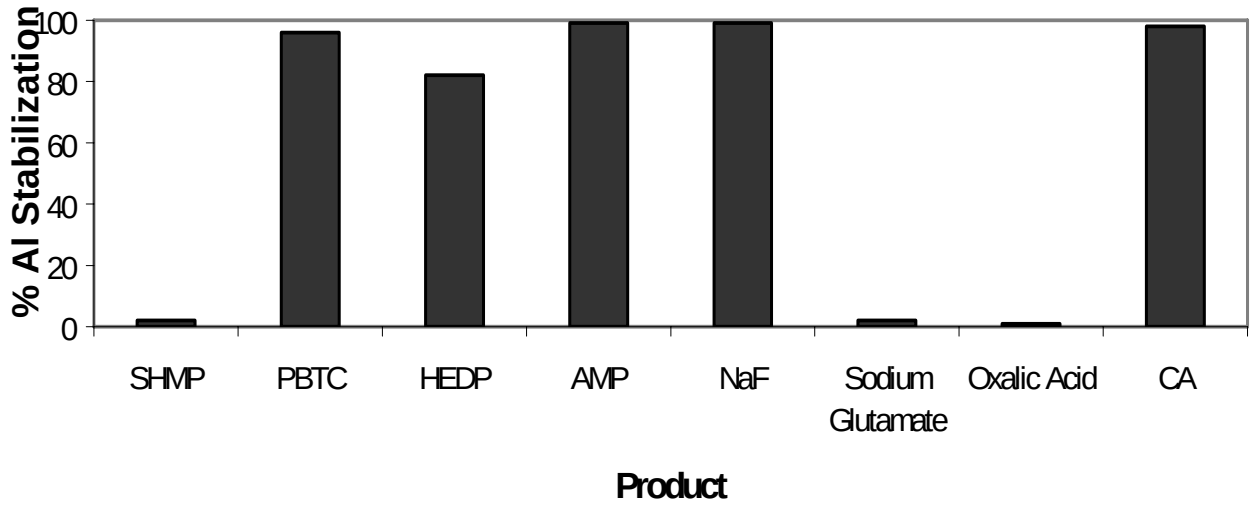



**Figure 4 - Iron Ion Stabilization as a Function of Product Dosage (1 ppm Fe, pH 7.0)**

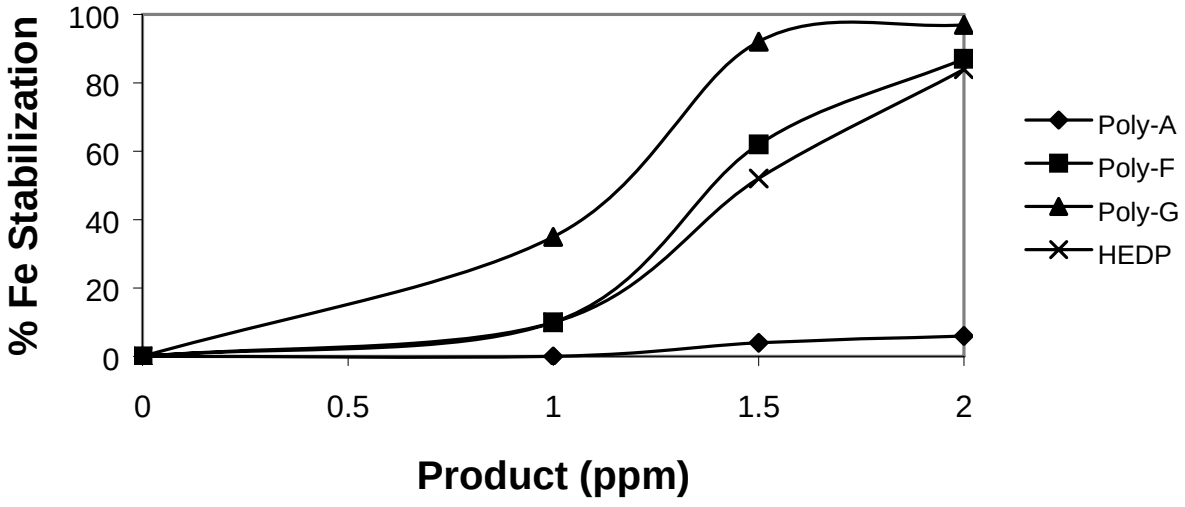


**Figure 5 -Iron Stabilization by Polymeric and Non-Polymeric Product (2.5 ppm Fe, 4.0 ppm Product, pH 7.0)**

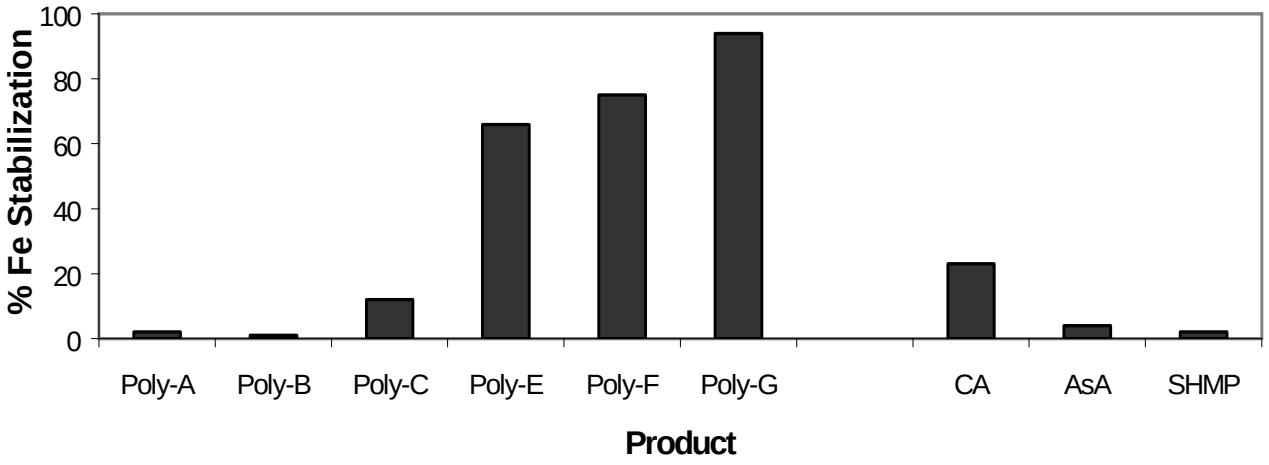



**Figure 6 - Manganese Stabilization by Various Products 3 ppm Mn, 10 ppm Cl, pH 7.5, 40°C, 2 ppm Product)**

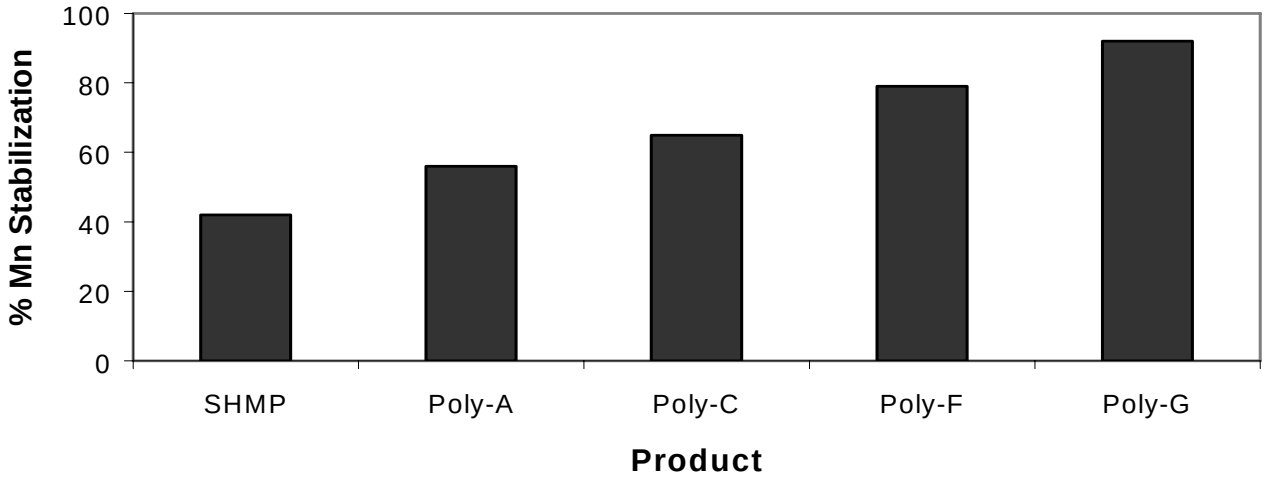


**Figure 7 - Manganese Stabilization by Various Products**

**Control** **SHMP** **Poly-A** **Poly-G**

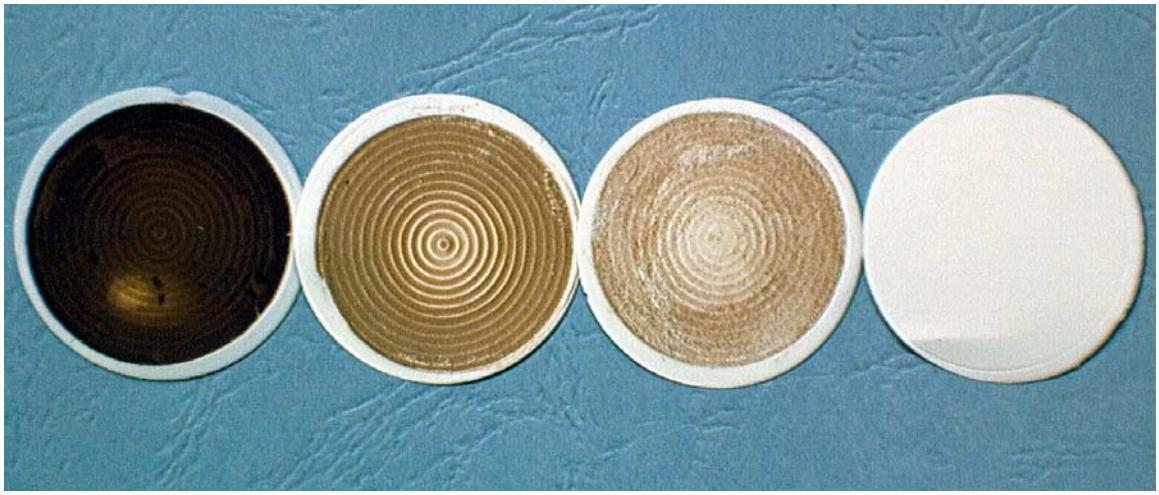


**Figure 8 - Zinc Stabilization by Various Products as a Function of Product Concentration (6 ppm Zn, pH 8.5)**

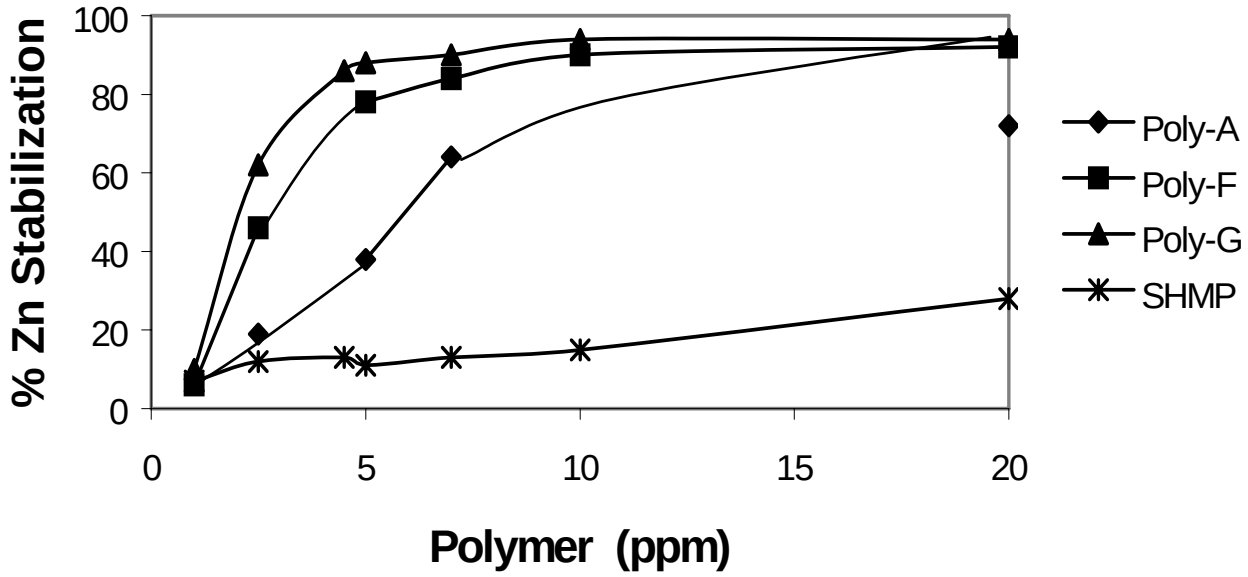
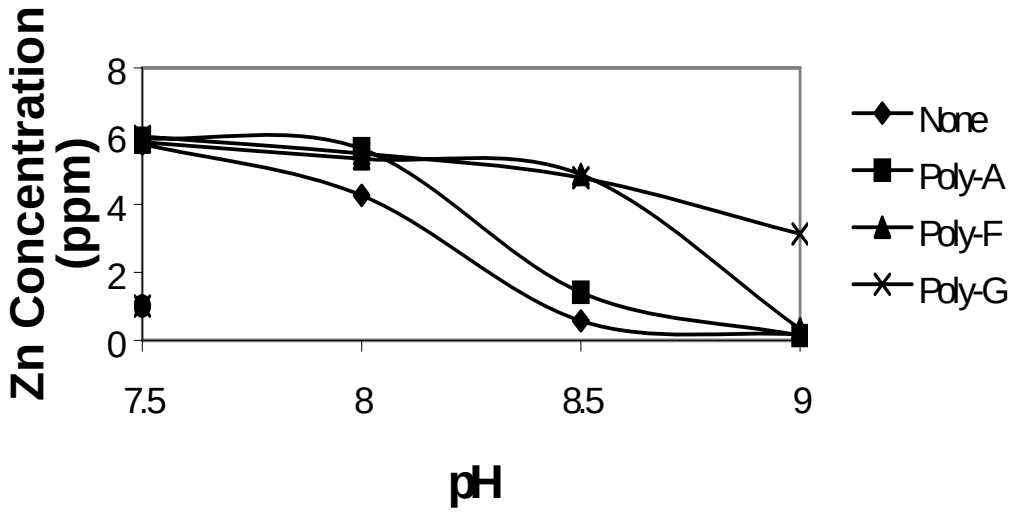


**Figure 9 - Zinc Stabilization by Various Polymers as a Function of Solution pH (6 ppm Zn, 4.5 ppm Polymer)**

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