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The Use of Polymers to Improve Control of Calcium Carbonate Scaling In High Stressed Cooling Water Systems*—Part I

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Introduction

Phosphonates and polyphosphates are used in water treatment processes for a variety of reasons. Most importantly, phosphonates and polyphosphate inhibit the formation of scale forming salts and control low carbon steel corrosion. Scale inhibition is prevented in a "sub-stoichiometric" manner as phosphorus containing compounds adsorb onto crystal growth sites of sub-microscopic crystallites, thereby interfering with crystal growth and altering the crystal morphology. Phosphonates are used to sequester metal ions such as copper, manganese, iron, and zinc. Additionally, these phosphorus containing compounds also exhibit some dispersancy activity for suspended matter such as clay, silt, and calcium carbonate. Although there are many phosphonates available, the three most commonly used phosphonates in industrial water treatment applications are shown in Table 1 below.

Table 1. Phosphonates Commonly Used in Industrial Water Treatment Applications

Chemical Name	Acronym	Molecular Weight
Aminotris(methylenephosphonic acid)	AMP	299
1-Hydroxyethylidine 1,1-diphosphonic acid	HEDP	206
2-Phosphonobutane 1,2,4-tricarboxylic acid	PBTC	270

Ashcraft[1] in his study on the performance of AMP, HEDP, and PBTC in the presence of soluble iron showed that PBTC to be superior to AMP and HEDP in the presence of high calcium ion presumably due to the greater solubility of Ca-PBTC salt. The precipitation of calcium phosphonate salts can:

- Directly cause heat exchanger fouling, and
- Indirectly cause severe calcium carbonate scaling due to the decrease in phosphonate concentrations.

Smyk, et al.[2] in their investigation on the influence of various polymers on the precipitation of calcium phosphonate showed that acrylic acid based terpolymers perform better than homopolymers of acrylic acid and maleic acid. Amjad[3] in another study showed that various factors (i.e., solution hardness, pH, temperature) greatly influence the precipitation of calcium phosphonate salts. Currently, many cooling systems are operated at high cycles of concentration due to water conservation and wastewater discharge regulations. However, these practices increase scaling tendency in recirculating water and necessitate the use of high performance scale and deposit control additives to prevent the deposition of unwanted materials on heat exchanger and other equipment surfaces.

The use of polymers as scale inhibitors and dispersants in industrial applications is well known to water technologists. It is generally agreed that polymers when present at low concentrations greatly inhibit the precipitation of scale forming salts (i.e., calcium carbonate, calcium sulfate, calcium phosphate, barium sulfate).[4-6] The incorporation of polymers in water treatment formulations also enables the water technologist in stabilizing metal ions (i.e., Fe, Mn, Cu) in recirculating cooling water systems.[7]

In the present study, we have investigated the tolerance of phosphonates with calcium ions under several different water chemistries (i.e., calcium ion concentration, pH, temperature). The ability of polymers to extend tolerance of phosphonates with calcium ions has also been explored. The object of this article is to provide the water technologist with data that helps facilitate the selection of deposit control polymers (DCPs) that prevent the precipitation of calcium phosphonate salt under high stressed conditions.

Experimental

Phosphonate Tolerance (Turbidity Test)

Phosphonates tolerance towards calcium ions was measured by turbidity monitoring. The test set-up used a constant temperature water bath, pH meter, and a Brinkmann PC 800 Colorimeter with 420 nm filter (for transmittance measurements).

A known volume of stock calcium chloride solution was added to glass bottles containing known volume of deionized/distilled water to obtain a final concentration of calcium ion (250, 500, or 750 mg/L as Ca^{2+}). To these calcium solutions were added varying amounts of polymer stock solutions to yield required (1 to 100 mg/L) of polymer in solutions. The bottles were capped and equilibrated at the required temperature for 30 minutes. Subsequently, phosphonate stock solution (to yield 10 to 50 mg/L) was added. The total volume of final solution was kept constant (i.e., 100 mL). The pH levels of these solutions were adjusted to pH 9.0 with dilute NaOH and/or HCl solution. At a known time (typically 45 minutes) transmittance readings were taken using a fiber-optic probe.

When the concentration of phosphonate in the experimental solution exceeded the solubility limit, the solution became turbid and was detected by a steep decrease in light transmittance. Data acquisition was continued with experimental solutions containing varying concentrations of phosphonates to precisely determine the inflection point.

Table 2 identifies the polymers evaluated in this study. As can be seen from Table 2, the deposit control polymers (DCPs) tested contain a variety of functional monomers (i.e., acrylic acid, maleic acid, sulfonic acid, sulfonated styrene).

Table 2. Polymers Evaluated

Polymer	Acronym	Molecular Weight
Poly(acrylic acid)	PAA	<5,000
Poly(maleic acid)	PMA	<2,000
Poly(acrylic:maleic)	AMC	<3,000
Poly(acrylic:sulfonic)	ASC*	<15,000
Poly(acrylic:sulfonic)	MFP	<15,000
Poly(acrylic:sulfonic:sulfonated styrene)	AST*	<15,000

** ASC and AST are Good-Rite® K-700 co- and terpolymers, respectively supplied by Noveon, Inc.*

Results and Discussion

Tolerance of Phosphonates with Calcium Ions

The tolerance of phosphonate with calcium ions is defined as the minimum concentration of phosphonate at given water chemistry (i.e., pH, temperature, hardness ion concentration) necessary to cause precipitation of phosphonate. It is recognized that precipitation of calcium phosphonate salts can cause fouling of heat exchanger surfaces and that these deposits can be construed as a calcium-phosphate foulant. In addition, the phosphonate concentration decreases in the system to the extent that severe $CaCO_3$ scaling can occur. It should be noted that calcium-phosphonate scales usually have the same inverse solubility features commonly observed with other mineral scales and they impede heat transfer.

Using the experimental procedure described above, a large number of experiments were conducted to determine the tolerance limits of various phosphonates. Figure 1 illustrates the typical "% transmittance" (% T) as a function of phosphonate concentration (i.e., PBTC) in the presence of 500 mg/L calcium ions, at pH 9.0, and 45 °C. The inflection point in the transmittance-PBTC concentration was used to calculate the point of onset of turbidity (i.e., minimum concentration of PBTC needed to cause precipitation). The good reproducibility (± 7 %) of phosphonate tolerance is also illustrated in Figure 1. The tolerance limit of PBTC as calculated from the data in Figure 1 is 56 ± 3 mg/L.

The tolerance of PBTC, AMP, and HEDP was also investigated in the presence of 250 mg/L calcium ions and at 45 °C. Results obtained for these phosphonates are shown in Figure 2. The phosphonates can be ranked according to their calcium tolerance in descending order (as mg/L soluble phosphonate per 250 mg/L calcium ions as follows:

PBTC (73 mg/L) > AMP (13.5 mg/L) > HEDP (7.5 mg/L)

Figure 1. PBTC Tolerance to Calcium (500 mg/L Ca, pH 9.0, 45 deg C)

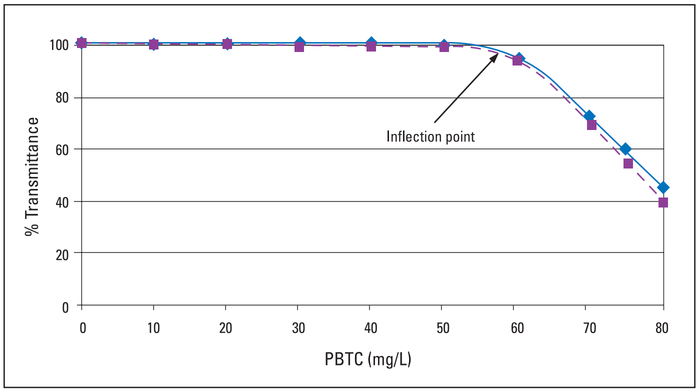
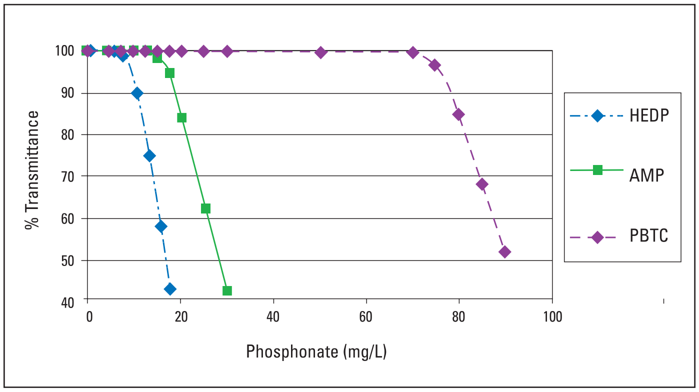


Figure 2. Phosphonates Tolerance to Calcium (250 mg/L Ca, pH 9.0, 45 deg C)



Effect of Hardness Ion Concentration

Cooling water systems are increasingly operated at higher cycles of concentrations causing greater driving forces for the precipitation of scale forming salts especially $CaCO_3$. Figure 3 illustrates the effect of hardness ion in the range 250 to 750 mg/L calcium ions on the tolerance of AMP, HEDP, and PBTC at 45 °C. It is evident that tolerance of these phosphonates decreases as the calcium ion concentration is increased. For example, in the presence of 250 mg/L calcium ions, the tolerance values obtained for AMP, HEDP, and PBTC are 13.5, 7.5, and 73 mg/L, respectively compared with 7.0, 4.8, and 50 mg/L obtained in the presence of 750 mg/L calcium ions. Thus, calcium ion tolerance decreases by a factor of 1.5 to 2.0 times for AMP, HEDP, and PBTC. It is evident from Figure 3 that PBTC is much more resistant to precipitation as calcium salt than either HEDP or AMP.

Effect of Solution Temperature

Figures 4 to 6 present data for our investigations to determine the

Figure 3. Phosphonates Tolerance to Calcium (pH 9.0, 45 deg C)

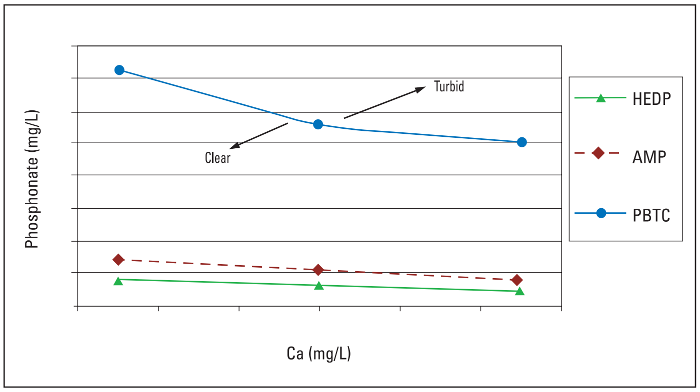
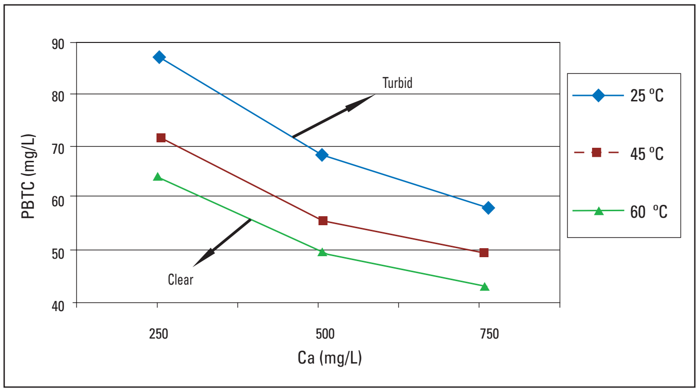


Figure 6. PBTC Tolerance to Calcium (pH 9.0)



influence of solution temperature (25 to 60 ˚C) in the presence of 250 to 750 mg/L calcium ions at pH 9.0 for AMP, HEDP, and PBTC. These data clearly indicate that solution temperature has a pronounced effect on the tolerance of phosphonates with calcium ions. Figures 4 to 6 show that increasing the solution temperature from 25 to 60 ˚C results in corresponding 1.5x to 2x decreases in phosphonate tolerances.

Extending Phosphonate Tolerance of Calcium Ions

For industrial water treatment, phosphonates have been shown to be broadly effective in controlling scale and low carbon steel corrosion. A loss of scale and corrosion control can occur if calcium phosphonate salts precipitate. Although phosphonates are generally considered tolerant to hardness ions, harsh conditions (i.e., high hardness, high pH, high temperature) such as discussed above can cause phosphonates to precipitate as calcium salts or co-precipitate with other salts and deposit on heat exchanger surfaces. Thus, for better scale and corrosion control it is important to prevent the precipitation of calcium phosphonates or extend the hardness tolerance limit of phosphonate by using an appropriate DCP.

DCPs have been used extensively to prevent the precipitation of various scale forming salts such as calcium phosphate, calcium phosphonate, calcium carbonate, calcium sulfate, calcium oxalate, and calcium fluoride. However, polymer efficacy is affected by the cooling system operating conditions (i.e., pH, temperature, and relative supersaturation of scale forming salts). The ability of polymers to extend the tolerance of phosphonates to calcium ions was investigated using the turbidity method.

Figure 7 illustrates the effect of acrylic co- and terpolymers (ASC and AST) to extend the limit of HEDP tolerance to calcium. As shown, a 10 mg/L addition of either AST or ASC provides a marked improvement in HEDP tolerance to calcium ions. For example, at 750 mg/L calcium concentration, the HEDP tolerance values obtained in the presence of 10 mg/L of AST and ASC were 6.0 and 8.2 mg/L, respectively, compared to 4.2mg/L obtained in the absence of polymer. Thus, an improvement of approximately

Figure 4. AMP Tolerance to Calcium (pH 9.0)

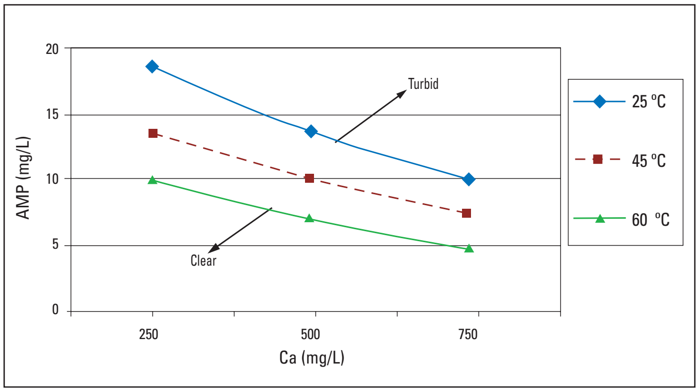


Figure 5. HEDP Tolerance to Calcium (pH 9.0)

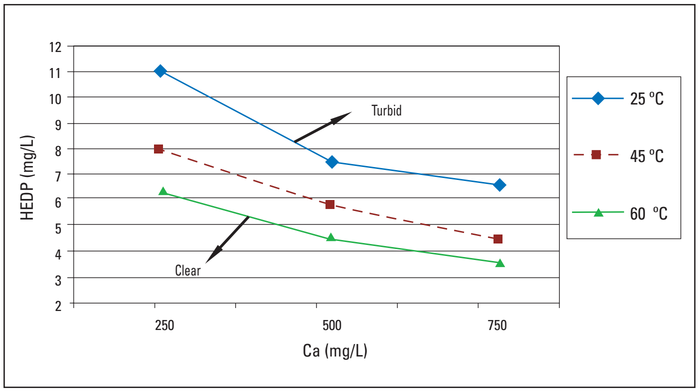
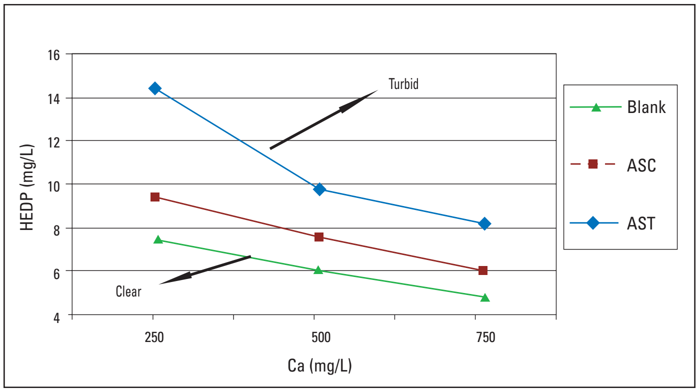


Figure 7. Effect of Polymers on HEDP Tolerance to Calcium (10 mg/L polymer, pH 9.0, 45 deg C)



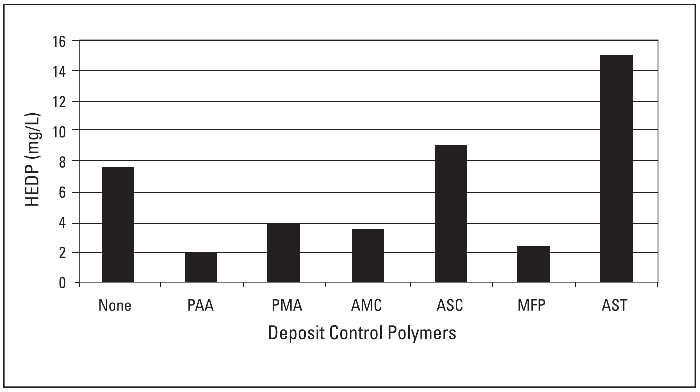
2x in HEDP tolerance is observed with AST. From a practical point of view, incorporating an appropriate DCP in a treatment program for a high stressed cooling water system would increase HEDP tolerance to calcium (i.e., would decrease the potential of Ca-HEDP precipitation in re-circulating water containing high calcium ions) and thereby extend the operating range.

The influence of DCP composition in extending phosphonate tolerance was also investigated. Figure 8 presents performance data for several commercial DCPs that are used to prevent deposition in cooling water systems. The data in Figure 8 clearly show that DCP performance as a Ca-HEDP inhibitor strongly depends on polymer architecture. The data also demonstrate that polyacrylic acid (PAA), polymaleic acid (PMA), acrylic acid/maleic acid copolymer (AMC), and the multifunctional polymer (MFP) exhibit poor performance in preventing Ca-HEDP precipitation. For example, HEDP tolerance values obtained in the presence of 10 mg/L PAA, PMA, AMC, and MFP are 2, 4.0, 3.5, and 2.5mg/L, respectively, compared to 7.5 mg/L tolerance obtained in the absence of the polymer. The observed decrease in HEDP tolerance may be attributed to poor polymer tolerance of calcium ions under similar experimental conditions. The poor polymer tolerance of PAA and PMA with calcium ions observed in the present investigation is consistent with our previously published report on polymer-calcium interactions.[8] The excellent performance exhibited by AST in extending HEDP tolerance is also shown in Figure 8.

Summary

The purpose of this study was to identify water chemistries where the potential exists for calcium-phosphonate salts precipitation due to poor tolerance of phosphonates with calcium ions and determine the feasibility of using deposit control polymers to prevent the deposition of calcium phosphonates on heat exchangers. In this study, a sulfonic acid containing terpolymer (AST) was identified as an effective inhibitor for calcium phosphonates.

Figure 8. Ca-HEDP Inhibition by Polymers
(250 mg/L Ca, 100 mg/L polymer, pH 9.0, 45 deg C)



The conclusions drawn from this study are as follows:

1. Phosphonates (e.g., AMP, HEDP, and PBTC) are effective components in cooling water treatment programs. However, these phosphonates form insoluble salts with calcium ions under typical cooling water conditions. Ca-PBTC salt is more soluble than Ca-HEDP and Ca-AMP salts.
2. The potential for precipitation of calcium-phosphonate salt increases with increasing pH, temperature, and calcium ion concentrations.
3. The tolerance of phosphonate with calcium ions can be extended by incorporating an effective deposit control polymer (i.e., AST or sulfonated terpolymer) as a component of high performance water treatment programs.

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References

1. R. H. Ashcraft, "Scale Inhibition under Harsh Conditions by 2-Phosphonobutane 1, 2, 4-tricarboxylic acid," CORROSION/85, Paper No. 132 (Houston TX: NACE International, 1985).
2. E. E. Smyk, H. E. Hoots, K. F. Fivizzani, and K. E. Fulks, "The Design and Application of Polymers in Cooling Water Programs," CORROSION/88, paper No. 14, (Houston TX: NACE International, 1988).
3. J. A. Wohlever, Z. Amjad, and R. W. Zuhl, "Performance of Anionic Polymers as Precipitation Inhibitors for Calcium Phosphonates," in Advances in Crystal Growth Inhibition Technologies, Kluwer Academic Publishers, New York, NY (2001).
4. Z. Amjad, "Performance of Polymers as Precipitation Inhibitors for Calcium Phosphonate," Tenside Surfactants Detergents 34, 102 (1997).
5. L. A. Perez and D. T. Freese, "Scale Prevention at High LSI, High Cycles, and High pH without the Need for Acid Feed," CORROSION/97, paper No. 174, (Houston TX: NACE International, 1997).
6. Z. Amjad, "Calcium Sulfate Dihydrate (Gypsum) Scale Formation on Heat Exchanger Surfaces. The Influence of Scale Inhibitors," J. Colloid and Surface Science, 123, 523 (1988).
7. Z. Amjad, "Controlling Metal Ion Fouling in Industrial Water Systems," ULTRAPURE WATER, 17, 4 (2000).
8. Z. Amjad, R. W. Zuhl and J. F. Zibrida, "Factors Influencing the Precipitation of Calcium-Inhibitor Salts in Industrial Water Systems," Association of Water Technologies® 2003 Annual Conference, (McLean, VA: AWT 2003).