5 Scale and Deposit Control Polymers for Industrial Water Treatment

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CONTENTS

5.1 INTRODUCTION

The accumulation of unwanted deposits on equipment surfaces is a phenomenon that occurs in virtually all processes in which untreated water is heated. The deposits commonly encountered may be categorized into the following five groups: (a) mineral scales (e.g. $CaCO_3$, $CaSO_4 \cdot 2H_2O$, $BaSO_4$, $Ca_3(PO_4)_2$, CaF_2, SiO_2), (b) suspended matter (e.g. mud or silt), (c) corrosion products (i.e., Fe_2O_3, Fe_3O_4, ZnO, CuO), (d) microbiological, and (e) metal-inhibitor salts. The deposition of these materials, especially on heat exchanger surfaces in cooling, boiler, geothermal, and distillation systems, can cause a number of operational problems such as plugging of pipes and pumps, inefficient water treatment chemical usage, increased operation costs, lost production due to system downtime, and ultimately heat exchanger failure. Greater water conservation has been a driver for operating industrial water systems at higher cycles of concentrations, thereby increasing the potential for deposit buildup on heat exchanger surfaces. Operating industrial water systems under stressed conditions demands a better understanding of system (feed and recirculating) water chemistry as well as the development of new and innovative agents for controlling scale/deposit, corrosion, and biofouling.

Researchers have proposed several chemical addition options for controlling scale formation including the use of acids, chelants, or inhibitors. The most promising scale control method involves adding substoichiometric dosages, typically a few parts per million, to the feed water either nonpolymeric (e.g., polyphosphates, phosphonates, phosphonocitric acid) or polymeric (e.g., the homopolymers of acrylic acid (AA), maleic acid, aspartic acid, and copolymers containing monomers of different functional groups) water-soluble additives.

For carboxylic acid containing polymers, it appears that the precipitation inhibition of scale-forming salts is dependent on (a) polymer architecture (e.g., ionic charge, monomer size, monomer ratio, molecular weight [MW]) and (b) the scaling salt being formed. In addition, various factors (e.g., water chemistry; types and concentrations of flocculants, biocides, phosphonates, and deposit control polymers used as components of treatment programs; as well as a deposit control polymer's hydrolytic and thermal stability) also play important roles in the efficient operation of industrial water systems [1–4].

The use of synthetic polymers [e.g., poly(acrylic acids), poly(methacrylic acid), hydrolyzed polyacrylamides, acrylic acid/acrylamide copolymers] dates back to the 1950s. Researchers have shown that polymer MW is an important consideration relative to performance [5,6]. Eventually, copolymers of acrylic acid, methacrylic acid, and/or maleic acid with a variety of other comonomers [e.g., sulfonated styrene (SS), 2-acrylamido-2-methylpropane sulfonic acid (SA), acrylamides, acrylate esters, and so on] were found to provide improved performance characteristics in various applications including, boiler, cooling, geothermal, oil field, and desalination (thermal and membrane based) processes [7,8].

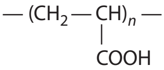
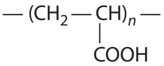
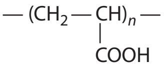
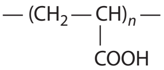
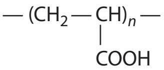
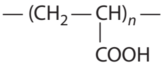
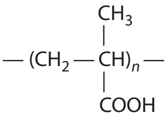
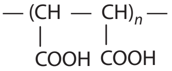
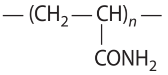
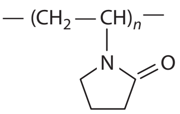
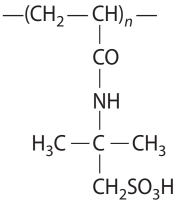
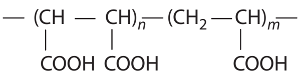
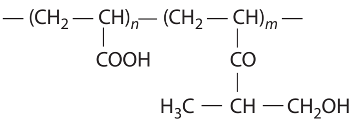
The impact of solution pH on corrosion rate and scaling tendency has been studied. It is well known that alkaline pH and high alkalinity generally reduce corrosion rates. However, a system water pH increase, especially in phosphate-based cooling water treatment (CWT) program can increase the scaling potential, thereby necessitating the use of a high-performance calcium-phosphate-inhibiting polymer. The influence of soluble impurities (i.e., Fe^{3+}, polymeric flocculant, cationic biocides, and so on) on the performance of calcium phosphate inhibitors has been investigated. The results of these studies reveal that polymeric impurities, when present at low concentration (<1 ppm), exhibit antagonistic effect on the performance of calcium-phosphate-inhibiting polymers [9,10]. Other factors that impact the selection of polymers as scale inhibitor and/or dispersant include compatibility with formulation ingredients, water hardness, polymer stability under harsh conditions, and environmental acceptability. Polymer performance retention under heat-stressed conditions is also an important property in high-temperature applications (e.g., geothermal and boiler). The data reviewed in this chapter provide water technologists a basis to select deposit control polymers that deliver performance under a variety of stressed operating conditions. The chapter is divided into two sections: (a) an overview of a deposit control polymer evaluation process and (b) an evaluation of deposit control polymer performance data using a variety of laboratory screening tests. Table 5.1 shows the structures of polymeric and nonpolymeric additives tested.

5.2 DEPOSIT CONTROL POLYMER EVALUATION PROCESS: AN OVERVIEW

A large variety of polymeric and nonpolymeric additives are available to water technologists for developing new and improved formulations for handling different challenges in treating industrial water systems. Water technologists typically use a combination of laboratory screening, small-scale or dynamic pilot testing, and field testing to evaluate and optimize the performance of deposit control polymers and/or water treatment formulations. Table 5.2 lists the commonly used methods to screen deposit control polymers for a variety of properties [e.g., scale inhibition, particulate dispersion, metal-ion stabilization, the prevention of scale deposition on equipment surfaced (heat exchangers and/or reverse osmosis membranes), the impact of soluble and suspended impurities on polymer performance, and the type of metallurgy]. The test methods listed in Table 5.2 provide a basis for comparing the performance of competitive polymers.

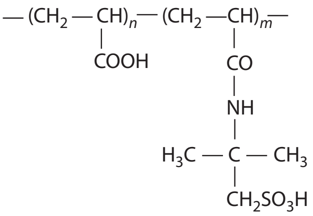
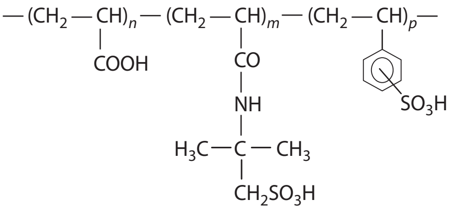
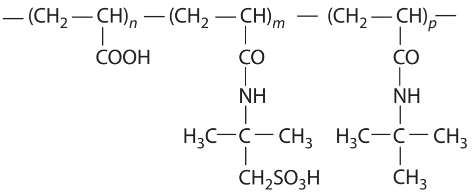
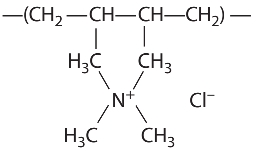
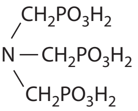
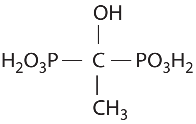
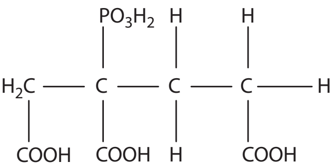
After selecting the deposit control polymer(s) that provide the best cost performance for a given application, the next step in the polymer evaluation process involves pilot testing of formulated

TABLE 5.1
Polymeric and Nonpolymeric Additives Tested

Polymer	Structure	Mol. Wt.	Acronym
Poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	800	P1
Poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	2,000	P2[a]
Poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	6,000	P3[a]
Poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	7,000	P4[b]
Poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	100,000	P5
Poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	<10,000	P6[c]
Poly(methacrylic acid)	 $-(\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{COOH}}{\mathrm{CH}}})_n-$	5,000	P7
Poly(maleic acid)	 $-(\underset{\mathrm{COOH}}{\mathrm{CH}}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	<1,000	P8
Poly(acrylamide)	 $-(\mathrm{CH_2}-\underset{\mathrm{CONH_2}}{\mathrm{CH}})_n-$	<10,000	P9
Poly(vinyl pyrrolidone)		PVP	P10
Poly(2-acrylamido-2-methylpropane sulfonic acid)	 $-(\mathrm{CH_2}-\underset{\underset{\underset{\underset{\mathrm{CH_2SO_3H}}{\mathrm{H_3C-C-CH_3}}}{\mathrm{NH}}}{\mathrm{CO}}}{\mathrm{CH}})_n-$	7,000	P11
Poly(maleic acid:acrylic acid)	 $-(\underset{\mathrm{COOH}}{\mathrm{CH}}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_m-$	<10,000	P12
Poly(acrylic acid:hydroxypropyl acrylate)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-(\mathrm{CH_2}-\underset{\underset{\mathrm{H_3C-CH-CH_2OH}}{\mathrm{CO}}}{\mathrm{CH}})_m-$	7,000	P13

(*continued*)

TABLE 5.1 (continued)
Polymeric and Nonpolymeric Additives Tested

Polymer	Structure	Mol. Wt.	Acronym
Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid)		<15,000	P14
Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:sulfonated styrene)		<15,000	P15
Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:*t*-butyl acrylamide)		<15,000	P16
Poly(diallyldimethyl ammonium chloride)		1,000,000	P17
Amino tris (methylene phosphonic acid)		206	AMP
Hydroxyethylidene-1,1-diphosphonic acid	 $H_2O_3P-C(OH)(CH_3)-PO_3H_2$	299	HEDP
2-Phosphonobutane-1,2,4-tricarboxylic acid		270	PBTC

[a] Organic solvent polymerized.

[b] Water polymerized.

[c] Contains phosphinate group.

product(s). The pilot testing enables water technologists to study the performance of formulated product under small-scale simulated field conditions and evaluate potential operating conditions. Upon completion of pilot testing, including performance optimization, water technologists select suitable customer sites to conduct field trials to confirm treatment program performance.

5.3 DEPOSIT CONTROL POLYMER PERFORMANCE EVALUATION

5.3.1 Inhibitor Interactions

5.3.1.1 Calcium–Polymer Interactions

Scale inhibitors (polymeric and nonpolymeric) used in water treatment formulations may form insoluble salts with hardness ions under conditions frequently encountered in cooling water systems. The trend toward the operation of cooling water systems under increasingly severe operating conditions (e.g., high hardness, high alkalinity, and higher pH and temperature) has increased the potential for the formation of insoluble calcium-inhibitor salts. For this reason, "Ca ion tolerance" or the ability of an inhibitor to remain soluble in the presence of high hardness ions is of increasing importance. *Ca ion tolerance* is defined as the maximum amount of the deposit control polymer that can be added to the water system without the significant precipitation of calcium polymer salt. When polymers form an insoluble salt with Ca ion, it causes both additional scaling problems and decreases the effective concentration of polymer thereby leading to additional scaling problem.

Figure 5.1 illustrates turbidity (100-%T), where "%T" is "% transmittance," as a function of P3 (polyacrylic acid, MW 6000 Dalton, hereafter "Da") concentration and shows good reproducibility (±7%). The inflection point in

TABLE 5.2
Laboratory Screening Tests for Evaluating Deposit Control Polymers

1. Threshold inhibition
   a. Calcium carbonate
      i. Static moderate conditions
      ii. Stirred severe conditions
   b. Calcium sulfate
   c. Barium sulfate
   d. Calcium phosphate
   e. Calcium phosphonate
   f. Silica polymerization
2. Dispersancy
   a. Iron oxide
   b. Hydroxyapatite
   c. Kaolin clay
3. Metal ion stabilization
   a. Iron
   b. Zinc
4. Deposit control
   a. Calcium carbonate
   b. Calcium sulfate
5. Product use considerations
   a. Calcium ion tolerance
   b. Chlorine compatibility
   c. Hydrolytic stability
   d. Thermal stability
   e. Total solids

Source: Lubrizol Advanced Materials, Inc. product bulletin, "Test procedures for evaluating deposit control polymers," CBS-TPEDCPP (Oct. 2007).

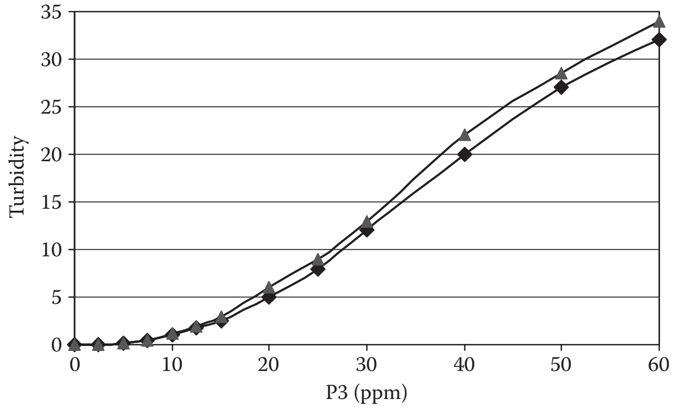


FIGURE 5.1 Calcium ion interactions with poly(acrylic acid), P3. Plots of turbidity versus P3 concentrations at pH 9.0, 25°C, and 1000 mg/L Ca.

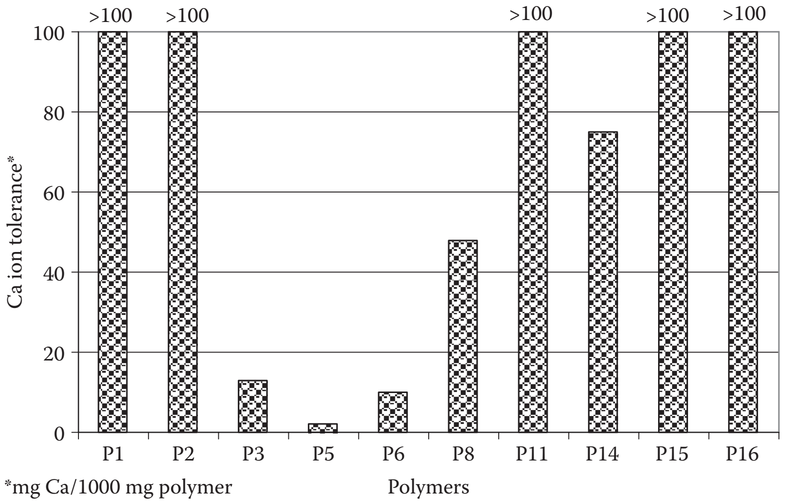


FIGURE 5.2 Calcium ion tolerance of homo-, co-, and terpolymers at pH 9.00, 25°C, 1000 mg/L Ca.

the turbidity versus P3 concentration profile was used to calculate the point of onset of turbidity. The tolerance value calculated for P3 is 13 ±1 ppm per 1000 mg/L Ca. Figure 5.2 presents Ca ion compatibility data for several homo-, co-, and terpolymers that indicate the following:

- The Ca ion compatibility of P-AA decreases with increasing polymer MW.
- Among homopolymers, P10 (polysulfonic acid, MW 7000 Da) is more tolerant to Ca ion than homopolymers of acrylic acid and maleic acid. This may be attributed to the weak interactions of Ca ions with SO_3H (SA) group versus COOH group.
- Replacing the portion of acrylic acid (AA) with sulfonic acid (SA) results in the improved tolerance of copolymer (e.g., P14).
- AA:SA copolymers incorporating either nonionic (P16) or sulfonated styrene (P15) monomer groups exhibit excellent Ca ion tolerance.

The calcium ion tolerance of several polymers exposed to thermal stress (200°C, 20 h) is presented in Figure 5.3. The data presented in Figure 5.3 indicate that the thermal treatment of acrylic

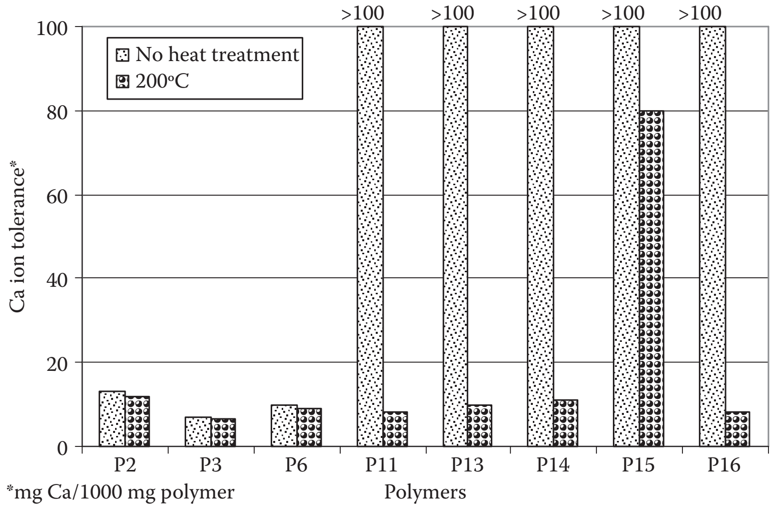


FIGURE 5.3 Effect of heat treatment on calcium ion tolerance of homo-, co-, and terpolymers.

acid homopolymers (i.e., P2, P3, and P4) does not significantly impact the compatibility of these polymers with calcium ion. These data also reveal that all SA containing homo-, co-, and terpolymers are affected by thermal treatment [11]. With the exception of terpolymer P15, all co- and terpolymers became significantly less tolerant to Ca. For example, the Ca ion tolerance values obtained for both P13 (AA:HPA) and P14 (AA:SA) were >100 ppm polymer/1000 mg/L Ca before thermal stress compared to <2 ppm after being subjected to thermal stress (200°C, 20 h). Because the resultant polymer is a P-AA, the poor compatibility obtained for both polymers is consistent with high MW P-AA [12]. The improved calcium ion compatibility of P15 versus P16 may contribute to the thermal stability of SS in the P16. Thus, from a practical viewpoint, polymers that exhibit high Ca tolerance should be favored for use in systems operating under higher cycles of concentrations.

5.3.1.2 Calcium–Phosphonate Interactions

Organophosphonate compounds are a broad family of chemicals used in a variety of industrial process applications, including crude oil production, pigment dispersion, electroplating, paper and pulp slurries, scale removal, and industrial water treatment. Organophosphonates differ structurally from polyphosphates in that they have a P–C bond rather than a P–O bond and these structural differences account for the superior stability of organophosphonates versus polyphosphates under pH and temperature extremes. In water treatment processes, phosphonates are used for a variety of reasons but primarily for inhibiting the formation of scale-forming salts and inhibiting steel corrosion (as cathodic inhibitors). Phosphonates are key components of most CWT programs and play an important role in protecting heat exchangers from corrosion and calcium carbonate scale formation. It is well documented that phosphonates, under stressed operating conditions (e.g., high hardness, high pH, and/or high temperature), can react stoichiometrically with the calcium ion leading to calcium phosphonate precipitation. In addition, solution phosphonate concentration can be depleted due to calcium phosphonate precipitation, thereby causing severe corrosion and calcium carbonate scaling [13–15].

Although there are several types of phosphonates available, the three most commonly used phosphonates (see Table 5.1) in deposit control water treatment are (a) amino tris (methylenephosphonic acid), AMP, (b) hydroxyethylidene 1,1-diphosphonic acid, HEDP, and (c) 2-phosphonobutane-1,2,4 tricarboxylic acid, PBTC. Figure 5.4 presents turbidity data as a function of various concentrations of AMP, HEDP, and PBTC. As illustrated, all phosphonates form insoluble salts with Ca ions.

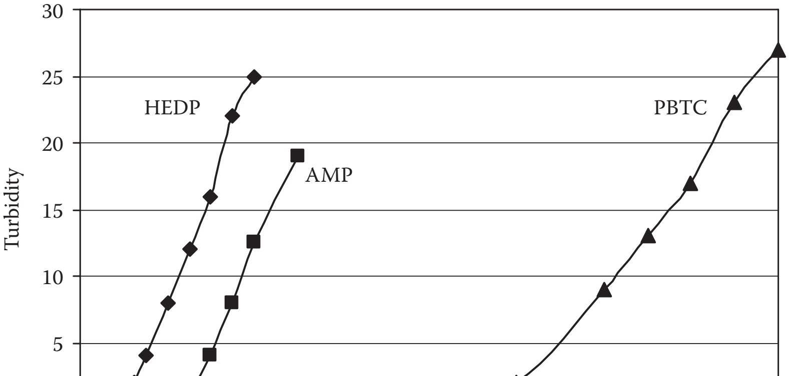


FIGURE 5.4 Calcium ion interactions with phosphonates. Plots of turbidity versus phosphonate concentration at pH 9.50, 250 mg/L Ca, 25°C.

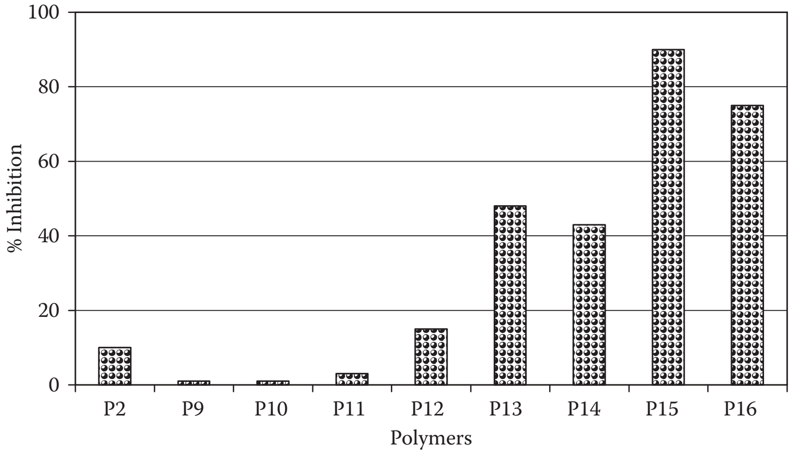


FIGURE 5.5 Ca-HEDP inhibition by polymers (150 mg/L Ca, 15 mg/L HEDP, 10 ppm polymer, pH 8.50, 50°C, 20 h).

Based on the compatibility data (250 mg/L Ca ions, pH 9.50, 25°C, 30 min), these phosphonates can be ranked (in the descending order) as follows:

PBTC (98 ppm) >> AMP (26 ppm) >> HEDP (12 ppm)

The influence of polymers on the precipitation of Ca-phosphonates has been the subject of numerous investigations. Boffardi and Schweitzer [16] reported that the relatively poor calcium tolerance of phosphonates could be overcome by adding an acrylic acid:2-acrylamido-2-methylpropane sulfonic acid copolymer. Smyk et al. [17], in their investigations, showed that acrylic-based terpolymers performed better than the homopolymers of acrylic acid and a copolymer of acrylic acid and hydroxylpropyl acrylate (AA:HPA). Figure 5.5 presents results on the performance of various polymers as Ca-HEDP inhibitors. Under the experimental conditions employed (150 mg/L Ca, 15 mg/L HEDP, 10 ppm polymer, pH 8.50, 50°C, 20 h), the data indicate that P2 [2000 MW poly(acrylic acid), homopolymer containing COOH group] performs better than other homopolymers containing either nonionic groups (i.e., P9 and P10) or a sulfonic group (P11). The data presented in Figure 5.5 also reveal that terpolymers (i.e., P15 and P16) perform better than copolymers with only two functional groups (i.e., P12, P13, and P14). Based on the inhibition data presented, the polymers can be ranked (in terms of descending order) as

Terpolymers > Copolymers > Homopolymers

5.3.1.3 Polymer–Polymer Interactions

Cationic polyelectrolytes have been used for decades as flocculants/coagulants to isolate and separate colloidal particles from water streams. Commonly used polyelectrolytes include aluminum- and iron-containing compounds (e.g., alum, ferric chloride, and ferric sulfate). These polyelectrolytes hydrolyze to form insoluble precipitates, neutralize the charge of the colloidal particles in the water, and entrap additional particles. In most cases, these large particles (flocs) are removed via settling in a clarifier and are collected as sludge. Occasionally, clarifier upsets cause metal containing flocs to “carry over,” which may lead to the formation of aluminum- and iron-based deposits on heat exchangers. Although aluminum- and iron-based compounds can exhibit positive effects in terms of clarifying the water, the optimum performance of these compounds is very sensitive to water pH and alkalinity. A variety (e.g., linear, branched, and lightly cross-linked) of more versatile synthetic polyelectrolytes (linear, branched, and lightly cross-linked) have been developed. Among the commercial cationic polyelectrolytes, a diallyldimethyl ammonium chloride homopolymer (P17) is frequently the choice due to its high performance and reasonable cost.

It has been reported that pairs of opposite-charged polymers typically form complexes (soluble and insoluble) in aqueous solution [18,19]. Depending primarily on MW and linear-charge densities, these complexes may be amorphous solid or soluble (colloidal) aggregates. The forces driving the formation of these complexes are primarily electrostatic, and therefore parameters such as polymer charge density, solution pH, and ionic strength are particularly important.

The interactions between anionic polymers (APs) commonly used in water treatment applications and a cationic polymer (CP, diallyldimethyl ammonium chloride, P17, MW >1 MM Da) were investigated using a turbidimetric method. The test conditions employed (100 mg/L Ca, 100 mg/L Mg, 110 mg/L Na, 470 mg/L Cl, 150 mg/L SO_4, 100 mg/L HCO_3, pH 8.0) involved mixing 5 ppm CP with 5 ppm APs. The solutions were stirred at 25°C and the progress of reaction was monitored by measuring turbidity at 30 min. Higher turbidity indicates the poor compatibility of APs with CP. Figure 5.6 presents the compatibility data of CP with APs, leading to the following observations regarding anionic polymer: (a) MW: the compatibility of CP with P-AAs depends on polymer MW (e.g., low MW P1 is more compatible than high MW P2); (b) ionic charge: among the homopolymers tested, P2, P3, and P8 are less compatible than nonionic polymers (i.e., P9 and P10); and (c) composition: the incorporation of hydrophobic and bulkier groups increases the compatibility of co- and terpolymers. It has been shown that polymeric and nonpolymeric scale inhibitors, when present at low concentrations in recirculating water, form insoluble complexes/salts with cationic-charged polymeric flocculants/coagulants and/or biocides.

The data presented in Figure 5.6 show that cationic-charged polymeric flocculants/coagulants form insoluble complexes/salts with anionic polymers present at low concentrations in recirculating water. The driving forces in the formation of such insoluble complexes between cationic and anionic additives are electrostatic in nature. Therefore, water technologists must understand the system water chemistry and take appropriate actions to avoid the formation of AP-CP salts in recirculating waters. This could be achieved by ensuring that proper pretreatment is applied and the concentration of CP is maintained extremely low (<0.1 ppm).

As discussed above, water chemistry, formulation components, and polymer architecture all impact the deposit control performance in cooling water applications. For example, it was shown that the tendency of CWT formulation components (i.e., deposit control polymer and phosphonates) to form insoluble salts with Ca ion increases with increasing Ca concentration, increasing pH, and increasing temperature [20,21]. In addition, it was also shown that cationic polymeric biocides and flocculating agents form insoluble salts with anionic polymers commonly used in water treatment applications.

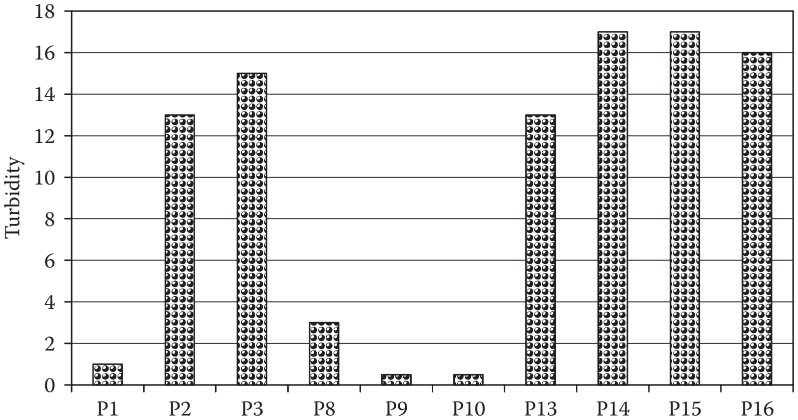


FIGURE 5.6 Plots of turbidity for the interaction of anionic polymers (5 ppm) with 5 ppm cationic polymer (100 mg/L Ca, 100 mg/L Mg, 110 mg/L Na, 470 mg/L Cl, 150 mg/L SO_4, pH 8.0, 25°C).

5.3.2 SCALE INHIBITION

5.3.2.1 Calcium Phosphate

Over the years, many different treatment programs have been developed for open recirculating cooling water systems. These treatment programs include (a) "soft" phosphate or dispersant, (b) "stabilized" phosphate, (c) "all organic," (d) molybdate, (e) alkaline zinc, and (f) chromate/zinc. The incorporation of multifunctional deposit control polymers is critical to the success of these CWT programs. Since the 1960s, molybdates, silicates, polyphosphates/phosphates, phosphonates, and zinc salts are among the more environmentally acceptable mild steel corrosion inhibitors that have displaced chromates. Phosphates, from the perspective of versatility, cost, and performance, have become a new performance standard. However, phosphate-based CWT programs require more careful system parameter control than do chromate programs, mainly because they rely on relatively high phosphate levels for corrosion protection. These high phosphate levels, and especially cooling systems operating at alkaline pH and high calcium hardness water, can lead to calcium phosphate precipitation and heat exchanger fouling. The key to the successful use of phosphate-based CWT program lies in the proper selection of polymeric calcium phosphate inhibitor that has a dual role: (a) controls the thickness of the calcium phosphate film on the metal surface and (b) prevents precipitation of the calcium phosphate in the recirculating water.

Currently, a variety of deposit control polymers are commercially available for developing water treatment formulations. However, it is recommended that water technologists consider the following criteria in selecting polymer(s) for optimizing the performance of systems operating under stressed conditions: (a) calcium phosphate inhibition, (b) tolerance to hardness ions, (c) compatibility with organic cationic flocculant, (d) tolerance to thermal stress, (e) retention of performance in the presence of inorganic and organic flocculant, (f) retention of activity in the presence of cationic biocides, (g) environmental acceptability, (h) formulation flexibility in a wide pH range, and (i) compatibility with oxidizing biocides.

5.3.2.1.1 Polymer Composition

Figure 5.7 shows performance data for several deposit control polymers before and after heat treatment at 200°C. It is evident from Figure 5.7 that heat treatment exposure has varying effects on deposit control polymer performance. For example, the heat treatment of carboxylic acid

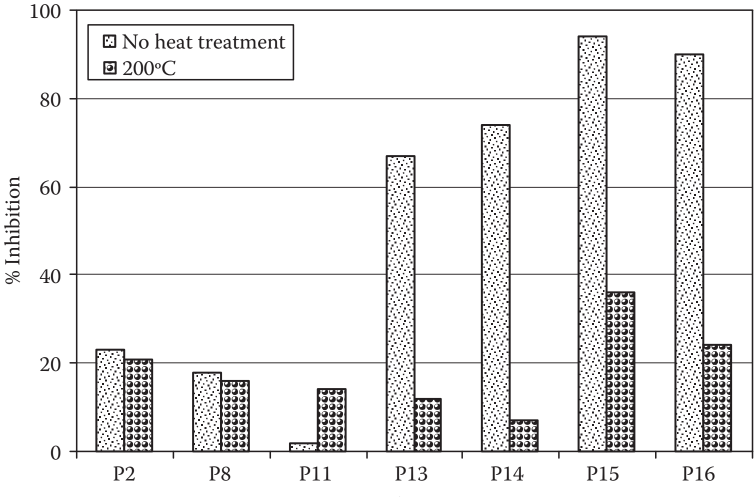


FIGURE 5.7 Calcium phosphate inhibition by heat-treated and non-heat-treated polymers (140 mg/L Ca, 9.0 mg/L PO_4, 10 ppm polymer, pH 8.50, 50°C, 22 h).

containing homopolymers (i.e., P2 and P8) shows no negative impact on the performance of these polymers, indicating that there is no significant loss of carboxylic acid group. However, for the copolymers containing carboxylic acid and either acrylate ester or sulfonic acid groups (i.e., P13 and P14), the situation is dramatically different; these copolymers lost ~90% inhibitory power upon heat treatment. This suggests that the SA and ester components of the AA:SA (P14) and AA:HPA (P13) copolymers underwent essentially complete degradation, leading to the formation of P-AA. The poor performance (<10% calcium phosphate inhibition) exhibited by thermally treated copolymers is consistent with the performance of high (>10,000) MW P-AA [22]. Figure 5.7 also presents calcium phosphate inhibition data for the two terpolymers (i.e., P15 and P16). As shown in Table 5.1, the primary difference between these two terpolymers is the third monomer [i.e., sulfonated styrene (SS) for P15 and nonionic for P16]. It is interesting to note that P16 lost more inhibitory power (~73%) compared to ~60% loss for P15, indicating that SS is more thermally stable than the nonionic monomer present in P16.

5.3.2.1.2 *Polymer Dosage*

The impacts of thermal stress shown in Figure 5.7 are amplified in Figure 5.8 wherein P15 dramatically outperforms both the P14 copolymer and the P16 terpolymer at the baseline 10 ppm dosage and to a greater extent as polymer dosage increases to 20 ppm. The excellent performance shown by the heat-treated P15 may be attributed to the superior thermal stability of the SS component.

5.3.2.1.3 *Polymer Solution Temperature*

Figure 5.9 presents the calcium phosphate inhibition performance data for the two terpolymers (i.e., P15 and P16) before and after various levels of thermal stress. As shown in Figure 5.9, P14, compared to P15, is a more effective calcium phosphate inhibitor after heat treatment (at 150°C, 200°C, and 240°C).

5.3.2.1.4 *Effect of Iron (III)*

The presence of iron in the recirculating water, whether originating from the feed water as a result of the carryover from the clarifier operating on iron-based flocculating agents or as a result of the corrosion in the system, may influence the performance of calcium-phosphate-inhibiting polymer and the CWT program. Figure 5.10 shows results for iron sensitivity testing for several

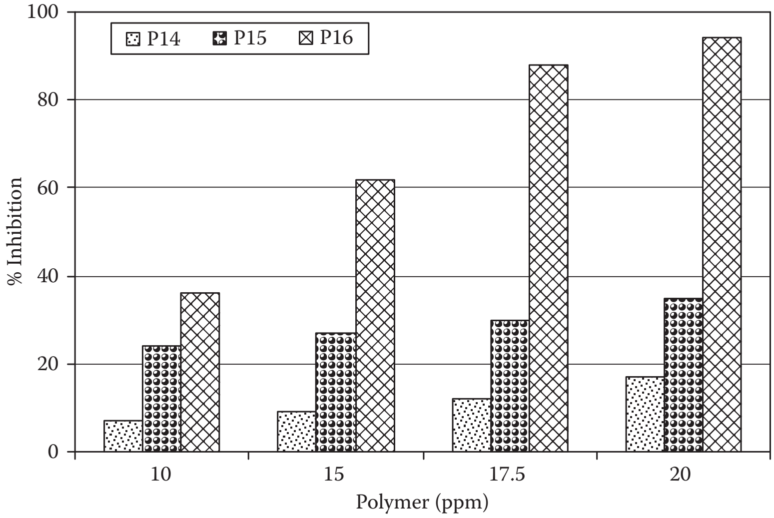


FIGURE 5.8 Calcium phosphate inhibition by thermally stressed (200°C, 20 h) polymers versus dosage (140 mg/L Ca, 9.0 mg/L PO_4, 10 ppm polymer, pH 8.50, 50°C, 22 h).

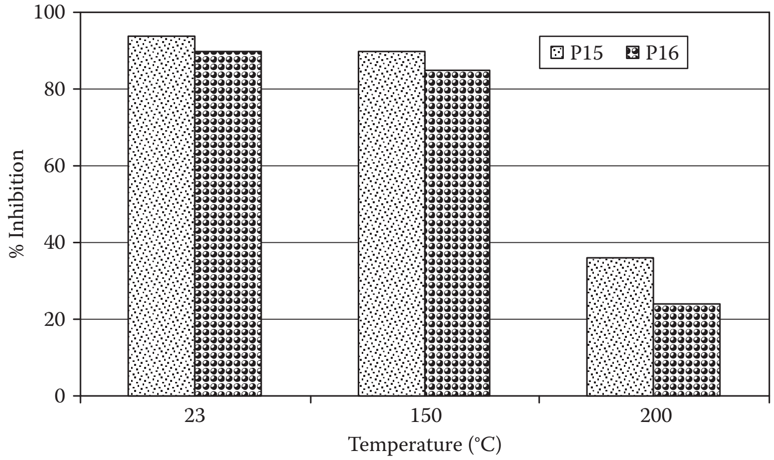


FIGURE 5.9 Calcium phosphate inhibition by thermally stressed terpolymers (140 mg/L Ca, 9.0 mg/L PO_4, 10 ppm polymer, pH 8.50, 50°C, 22 h).

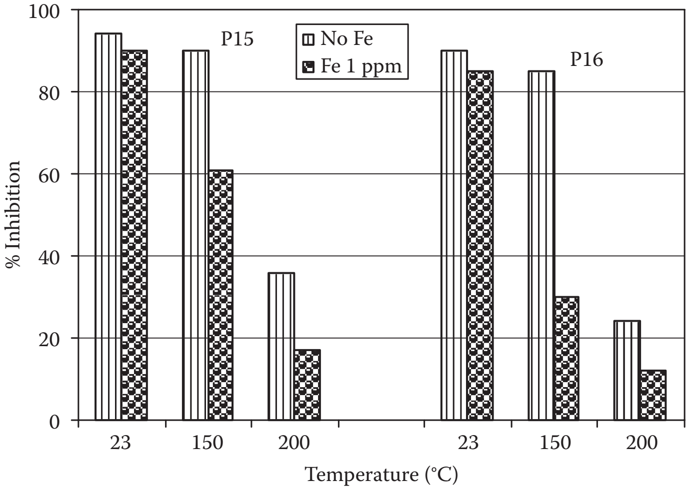


FIGURE 5.10 Calcium phosphate inhibition in the presence of 0 and 1 ppm Fe (III) by thermally stressed terpolymers (140 mg/L Ca, 9.0 mg/L PO_4, 10 ppm polymer, pH 8.50, 50°C, 22 h).

calcium-phosphate-inhibiting polymers in the presence of 0 and 1.0 ppm Fe (III). As shown, terpolymer P15 exhibits better tolerance to iron than the terpolymer P16. In addition to inhibiting calcium phosphate precipitation and dispersing iron oxide, the ability to resist the negative effects of iron should be a part of the deposit control polymer selection criteria for effective CWT programs. Polymer thermal stability is a key consideration to ensure the optimum performance of boiler water treatment programs.

5.3.2.2 Calcium Carbonate

Calcium carbonate ($CaCO_3$) is one of the most commonly encountered scale deposits. $CaCO_3$ is found in different crystalline forms in the following order of increasing solubility: calcite, aragonite, vaterite, $CaCO_3$ monohydrate, and $CaCO_3$ hexahydrate. Calcite, the thermodynamically most stable polymorph of $CaCO_3$, forms tenaciously adhering, hard mineral deposits. The precipitation and stabilization of $CaCO_3$ polymorphs depend on the precipitation conditions (i.e., supersaturation level, pH, temperature, pressure, and the concentration and architecture of the additives).

The influence of polymeric and nonpolymeric additives such as $CaCO_3$ inhibitors has been of great interest to both academic researchers and industrial technologists. Common nonpolymeric inhibitors evaluated include organophosphonates, polyphosphates, polycarboxylic acids, and fulvic acids. It has been reported that these inhibitors, when present at low concentrations, markedly inhibit the $CaCO_3$ precipitation from supersaturated solutions. A surface adsorption method involving a simple Langmuir adsorption model has been proposed to account for the inhibition of $CaCO_3$ crystal growth. Among the polymeric inhibitors evaluated were P-AA; P-MA; and copolymers comprising AA, MA, and other monomers containing different functional groups. This section discusses the performance of various polymers exposed to different heat treatment. In addition, results are presented on the efficacy of polymers, phosphonates, and polymer/phosphonate blends as calcium carbonate scale inhibitor under varying calcite super-saturations.

5.3.2.2.1 Polymer Dosage

Figure 5.11 presents $CaCO_3$ % inhibition data as a function of P-AA (P3) dosage [560 mg/L Ca, 630 mg/L HCO_3, 30 mg/L CO_3 (all expressed as $CaCO_3$), pH 8.25, 67°C, 24 h]. Figure 5.11 shows that adding relatively small amounts of P3 significantly inhibits $CaCO_3$ precipitation: 1.0 ppm inhibits precipitation by 35%, increasing P3 to 3 ppm increases inhibition ~2× (to 67%), and increasing the P3 dosage to 5.0 ppm results in a 75% inhibition value.

5.3.2.2.2 Heat Treatment of Homopolymers

Figure 5.12 presents the performance comparison of homopolymers with and without heat treatment at 200°C. It is evident from Figure 5.12 that the exposure of aqueous solutions of carboxylic acid containing homopolymers (i.e., P-AAs, P-MAA, and P-MA) to heat treatment has varying effects on polymer performance. For example, the heat treatment of polymers (i.e., P3, P6, and P7) has no negative impact on their performance, indicating that under the experimental conditions employed there is no significant loss of carboxylic acid group. Furthermore, neither of the P-AAs (i.e., P3 and P6) made in different solvents (i.e., organic and water, respectively) and with different end group (i.e., phosphonate for P6) appears to be impacted by heat treatment. Similarly, no significant loss in performance was observed for P7 or the P-MAA whose composition differs from the P3 and P6 primary because the hydrogen in acrylic acid was replaced with a methyl group. However, for the P-MA (P8), containing two carboxylic acid groups on the adjacent carbons, the situation is significantly different; P8 lost ~12% inhibitory power. This suggests that the maleic acid component of P8 underwent more severe degradation than the acrylic acid or methacrylic acid in P3 and P7.

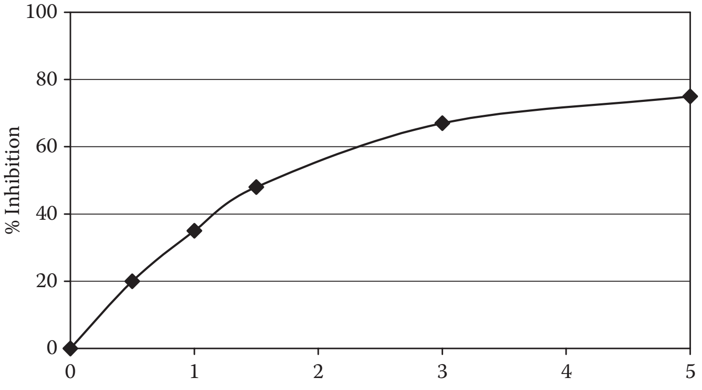


FIGURE 5.11 Calcium carbonate inhibition by poly(acrylic acid), P3 (560 mg/L Ca, 630 mg/L HCO_3, 30 mg/L CO_3, pH 8.25, 67°C, 24 h).

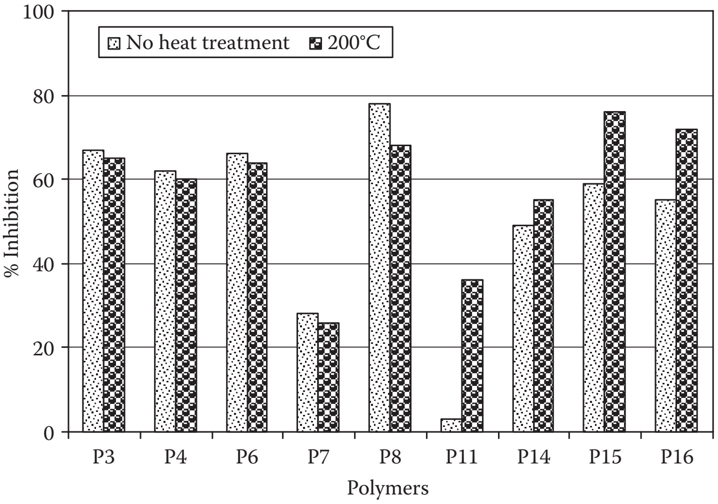


FIGURE 5.12 Calcium carbonate inhibition by thermally stressed homo-, co-, and terpolymers (560 mg/L Ca, 630 mg/L HCO_3, 30 mg/L CO_3, 3 ppm polymer, pH 8.25, 67°C, 24 h).

Masler [23], in his investigation on the effect of the thermal treatment (250°C, 18 h, pH 10.5) of several homopolymers, reported that P-MAA lost slightly less MW than P-AA which lost considerably less MW than P-MA. In terms of decarboxylation, P-AA decarboxylated less than P-MAA, which decarboxylated less than P-MA. In addition, it was reported that P-MA lost ~40% activity as a $CaCO_3$ inhibitor after heat treatment. It is interesting to note that under similar experimental conditions, P-AA and P-MAA lost only ~5% to 8% inhibitory activity, thus suggesting that carboxyl content in the polymer plays an important role in inhibiting the precipitation of calcium carbonate. The inhibition data presented in Figure 5.12 suggest that there was insignificant loss of inhibitory activity or carboxyl content for P3 and P6 under the experimental conditions employed in the present conditions.

Figure 5.12 also presents inhibition data collected in the presence of 3 ppm P11 (P-SA) and shows that P11, without heat treatment, exhibits poor inhibitory activity (<5% inhibition). This suggests that SO_3H group present in P11, compared to COOH in P3, shows weak interaction with calcium ions. However, after heat treatment, the P11 inhibition value increases (from 3% to 36%) may be attributed to the formation of P-AA during heat treatment process. The influence of polymer MW on the precipitation of scale-forming salts has been the subject of numerous investigations [24–26]. The results of these studies reveal that especially for P-AA, the optimum performance is obtained with ~2000 MW. The poor performance of heat-treated P11 (36%) compared to P2 (67%), as observed in the present investigation, is consistent with previous studies on the influence of polymer MW in inhibiting calcium carbonate precipitation.

5.3.2.2.3 Heat Treatment of Co- and Terpolymers

Comparative inhibition data on several co- and terpolymers are depicted in Figure 5.12. As shown, both the co- and terpolymers in the absence of thermal stress exhibit mediocre (<60%) $CaCO_3$ inhibition. However, heat treatment (200°C, 20 h) results in varying performance changes. For example, % $CaCO_3$ inhibition values obtained for the AA:SA copolymer (P14) before and after heat treatment were 49% and 55%, respectively. The slight improvement in the inhibitory power of heat-treated P14 may be attributed to changes in MW and the loss of SA to form COOH.

$CaCO_3$ inhibition data for terpolymers (i.e., P15 and P16) are shown in Figure 5.12 and indicate that both terpolymers in the absence of heat treatment show mediocre (<60%) inhibitory power. It is evident from Figure 5.12 that both terpolymers had significant $CaCO_3$ inhibition improvement following heat treatment (200°C, 20 h); % inhibition values obtained for P15 and P16 before heat treatment were 59% and 52% compared to 72% and 76%, respectively, for heat-treated terpolymers. As shown in Table 5.1, the key structural difference between P15 and P16 is the dissimilar third monomer [i.e., sulfonated styrene (SS) in P15 versus nonionic monomer in P16]. From the data presented in Figure 5.12, it's clear that upon subjecting the terpolymers to heat treatment, P15 and P16 gained more inhibitory power compared to P14. The observed increase in performance between these two terpolymers and P14 may be attributed to the difference in MW (<10,000 for terpolymers vs. <40,000 for copolymer). It is worth noting that both terpolymers showed performance improvement in this testing, whereas these terpolymers have been shown to lose performance as calcium phosphate inhibitors when they were exposed to heat treatment (200°C, 20 h).

5.3.2.2.4 Effect of Temperature

The performance data presented in Figure 5.13 illustrate excellent thermal stability for the P-MAA (P7) and two P-AAs (i.e., P2 and P3) evaluated at 150°C, 200°C, and 240°C. However, for P8, the situation is markedly different. As shown in Figure 5.13, increasing the temperature (from 150°C to 200°C to 240°C) results in gradual and significant decrease in P8 performance. The drop in inhibitory activity may be attributed to loss in MW and increased decarboxylation with increasing solution temperature. Figure 5.13 also shows a comparison of the terpolymers that have the same baseline performance before heat treatment. However, as the terpolymers are exposed to thermal stress, a marked increase in polymer performance is observed. For example, % inhibition values for P15 and P16 without heat treatment are 59% and 55% compared to 76% and 70%, respectively, for heat-treated (200°C, 20 h) terpolymers. As noted in Figure 5.13, increasing the solution temperature from 200°C to 240°C results in further (~5%) inhibition improvement. The performance data presented in Figure 5.13 suggest that essentially all of SA and nonionic monomers present in P15 and P16 are degraded to form P-AA or create a copolymer of acrylic acid and SS.

5.3.2.2.5 Phosphonates, Polymers, and Phosphonate/Polymer Blends

The performance of phosphonates as $CaCO_3$ inhibitors has been the subject of numerous investigations [27–29]. It is generally agreed that conventional phosphorus-based and polymeric $CaCO_3$ scale inhibitors are effective up to a maximum of 100× to 125× calcite saturation (equivalent to a LSI of +1.9 to 2.2). As previously discussed, phosphonate tolerance to Ca ions plays an important role in cooling water systems operating under stressed conditions. Good performance demands that phosphonates remain in solution and be available to prevent $CaCO_3$ precipitation and deposition on heat exchangers.

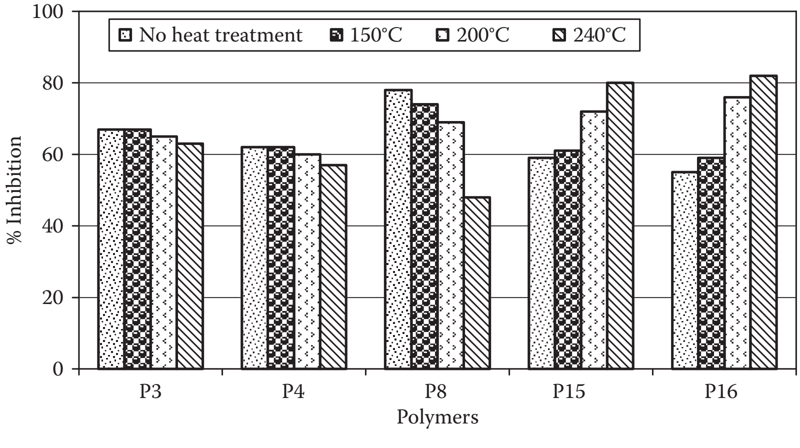


FIGURE 5.13 Calcium carbonate inhibition by thermally stressed (150°C, 200°C, and 240°C) homo-, co-, and terpolymers (560 mg/L Ca, 630 mg/L HCO_3, 30 mg/L CO_3, 3 ppm polymer, pH 8.25, 67°C, 24 h).

Figures 5.14 and 5.15 present $CaCO_3$ inhibition data in the presence of varying concentrations of phosphonates at two different water chemistries (i.e., 180× and 223× calcite saturation). Results obtained for both water chemistries (see Table 5.3) suggest that $CaCO_3$ inhibition increases as the phosphonate concentration is increased from 5 to 40 ppm. As illustrated, the $CaCO_3$ inhibition is rapid up to 5 ppm for both AMP and HEDP, then begins to level off, and finally reaches a plateau at ≥20 ppm for both phosphonates. However, the PBTC performance increases gradually as the concentration of PBTC is increased from 5 to 40 ppm. It should be noted that 100% $CaCO_3$ inhibition was not obtained for either water chemistry A or B (see Table 5.3) up to 40 ppm phosphonate concentrations. The data clearly indicate that the three phosphonates (i.e., AMP, HEDP, and PBTC) evaluated cannot completely prevent the precipitation of $CaCO_3$. Based on the results collected under both water chemistries A and B, $CaCO_3$ scale inhibition using 5 ppm phosphonate has the following order of effectiveness: HEDP ≥ AMP ≥ PBTC. However, at a 40 ppm phosphonate dosage, the performance-based ranking changes to PBTC ≥ HEDP ≥ AMP. This trend observed for phosphonate as $CaCO_3$ inhibitor is consistent with the trend noted above for phosphonate tolerance to Ca ions. Thus, it is clear from the data presented in Figures 5.14 and 5.15 that PBTC performs better than both AMP and HEDP in waters containing high calcite saturations.

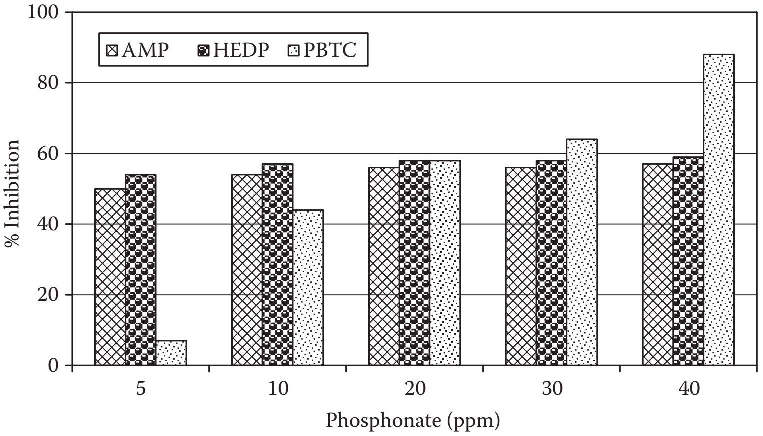


FIGURE 5.14 Calcium carbonate inhibition at 180× calcite saturation by varying dosages of phosphonates.

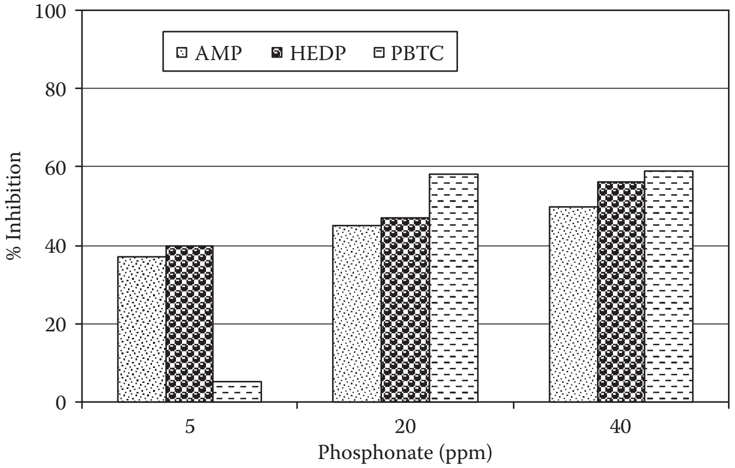


FIGURE 5.15 Calcium carbonate inhibition at 223× calcite saturation by varying dosages of phosphonates.

TABLE 5.3
Water Chemistries Used in Calcium Carbonate Inhibition

Parameter	Condition A	Condition B
LSI	2.89	2.76
Calcite saturation	223	180
Calcium (mg/L as Ca)	250	210
Magnesium (mg/L as Mg)	75	63
Sodium (mg/L as Na)	240	228
Bicarbonate (mg/L as bicarbonate)	450	380
Carbonate (mg/L as carbonate)	100	100
Chloride (mg/L as chloride)	626	558
pH	9.00	9.00
Temperature (°C)	50	50

Figure 5.16 shows the $CaCO_3$ inhibition data for several deposit control polymers of varying compositions (Table 5.1) commonly used as the components of CWT formulations. It can be seen that P3 (P-AA) performs better than P8 (P-MA). Although, P8 contains two carboxylic acid groups compared to one carboxylic acid group present in P-AA, the poor performance shown by P-MA may be attributed to the lower MW of P-MA and/or the poor Ca ion compatibility of P-MA. Among the copolymers tested, P14 (AA:SA) exhibits better $CaCO_3$ inhibition than P12 (AA:MA), which may be attributed to the poor calcium ion compatibility of P12. In addition, P15 is a slightly better $CaCO_3$ inhibitor than P16 which may be attributed to polymer MW and polymer composition differences.

Figure 5.17 shows the performance of polymer/PBTC (3:1) blends as a function of dosage (10 to 40 ppm) at 180× calcite saturation as $CaCO_3$ inhibitors. It is clear from Figure 5.17 that the performance of PBTC and polymer/PBTC blends increases with increasing inhibitor dosages. Among the various polymer/PBTC blends evaluated, the P15/PBTC blend is the most effective.

Figure 5.18 shows the $CaCO_3$ inhibition for several polymer/HEDP (3:1) blends at 30 ppm dosage and at 180× calcite saturation and indicates the following order of effectiveness: P15/HEDP > P16/HEDP > P-AA/HEDP. As illustrated, all of the polymer/HEDP blends provide better $CaCO_3$ inhibition than HEDP alone. Consistent with the observations for the P15/PBTC blend, the P15/HEDP blend provides the best performance.

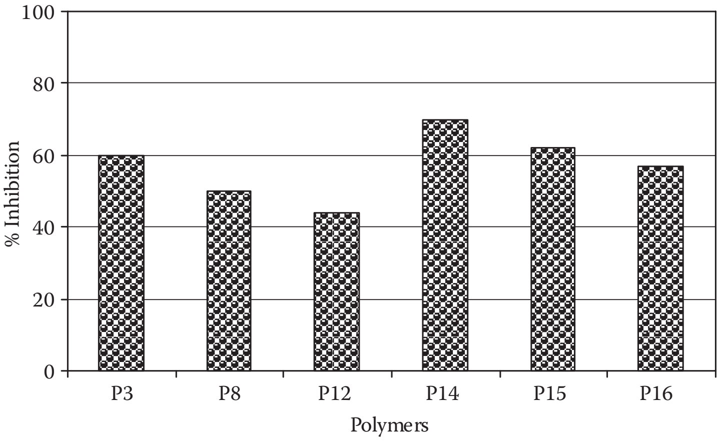


FIGURE 5.16 Calcium carbonate inhibition at 180× calcite saturation by homo-, co-, and terpolymers.

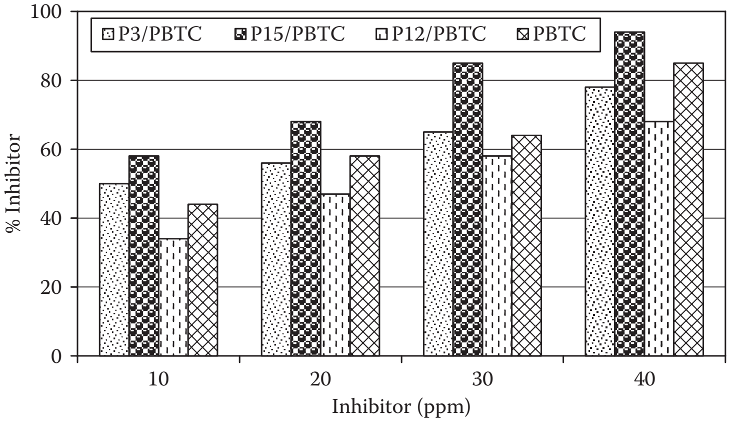


FIGURE 5.17 Calcium carbonate inhibition at 180× calcite saturation by varying dosages of polymer/PBTC (3:1) blends.

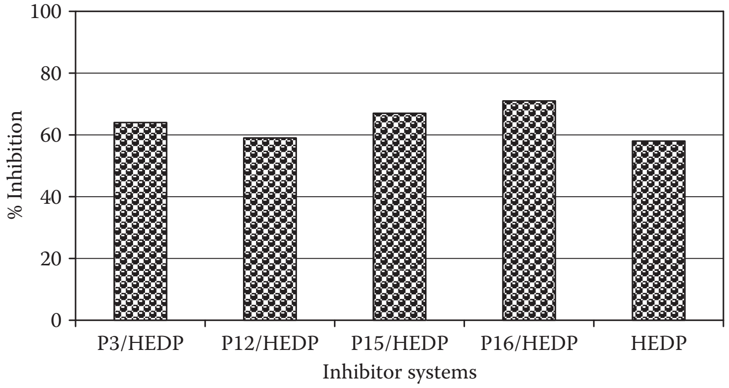


FIGURE 5.18 Calcium carbonate inhibition at 180× calcite saturation in the presence of 30 ppm of polymer/HEDP (3:1) blends.

5.3.2.2.6 Calcium Carbonate Crystal Morphology

Crystals formed during the $CaCO_3$ precipitation experiments in the absence (control) and presence of the inhibitor P15/PBTC (3:1) blend are shown in Figures 5.19 and 5.20, respectively. Figure 5.20 illustrates that $CaCO_3$ crystals are <10 microns and have regular shapes (major: calcite, minor: aragonite). Whereas the $CaCO_3$ crystal structures in Figure 5.20 (inhibited system) are fewer in number, most are >10 microns, spherically shaped, significantly distorted, and are all calcite.

5.4 POLYMER ARCHITECTURE INFLUENCE ON DISPERSING PARTICULATE MATTER

Suspended and colloidal matter causes turbidity in water. The type, size, and concentration of particles affect their behavior in the industrial water system. Examples of the types and sources of feed water particulates that impact industrial water systems include: (a) inorganic (i.e., silt, clay, asbestos, corrosion products, and calcium phosphates), (b) coagulant/flocculating agents by-products, and (c) organic (i.e., humic acid, tannic acid, and debris from dead organisms). The suspended particles typically encountered in industrial water applications generally carry a slight negative charge. Therefore, anionic polymers that increase negative surface charge and

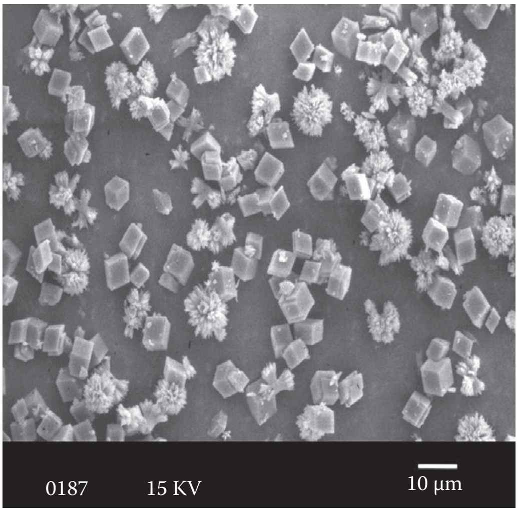


FIGURE 5.19 $CaCO_3$ (control).

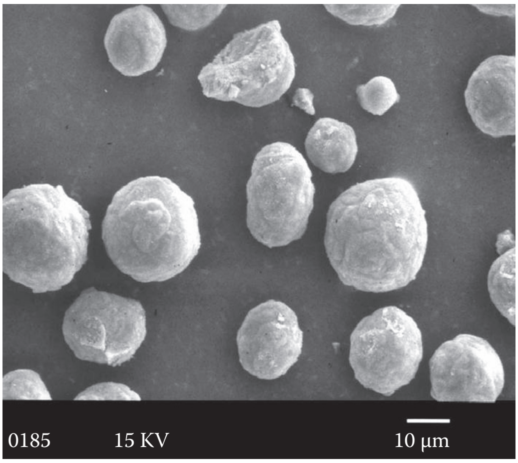


FIGURE 5.20 $CaCO_3$ in presence of P15/PBTC (3:1) blend.

keep particle in suspension are normally the most efficient dispersants. Cationic polymers can be used as dispersants, but this requires relatively high polymer concentrations in order to first neutralize the negative surface charges and then to transfer cationic charge to particles for efficient dispersion.

5.4.1 IRON OXIDE DISPERSION

Among many dissolved impurities present in natural waters, the iron-based compounds present one of the most serious problems in the efficient operation of industrial water systems. The sources of iron-ion impurities include boiler condensate, corrosion products (from heat-transfer equipment, pipelines, pumps, and so on), biological activity (the transformation of iron during bacterial processes), and water treatment residuals or by-products (e.g., excess iron-based flocculating agents). Regardless of the source, soluble iron can and does precipitate under certain conditions to form troublesome scales and deposits (e.g., Fe_2O_3, Fe_3O_4, $Fe(OH)_3$, $FePO_4$). For this reason, deposit control polymers are used to keep iron oxide particles dispersed and transported

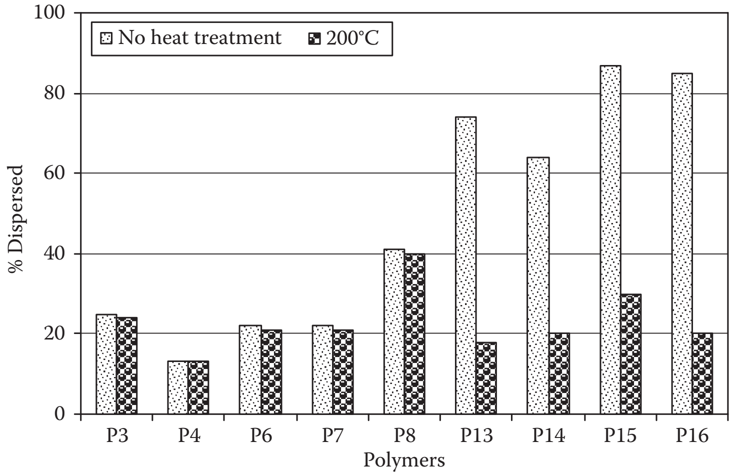


FIGURE 5.21 Iron oxide dispersion by thermally stressed polymers (100 mg/L Ca, 30 mg/L Mg, 314 mg/L Na, 200 mg/L SO_4, 561 mg/L, 60 mg/L HCO_3, 200 ppm iron oxide, 1 ppm polymer, 23°C, 3 h).

in boiler water systems. This dispersion activity results from the adsorption of polymer onto the surface of iron oxide particles, thereby changing particle charge characteristics and minimizing agglomeration.

Figure 5.21 presents performance data for several polymers under standard test conditions (200 ppm iron oxide, 1 ppm active polymer, 3 h, 7.8 pH, 100 mg/L Ca, 30 mg/L Mg, 314 mg/L Na, 200 mg/L sulfate, 571 mg/L Cl, 60 mg/L bicarbonate, 23°C). As shown, the homopolymers (P3, P4, P6, and P7) before thermal treatment provide relatively poor (<45%) iron oxide dispersion. Furthermore, the iron oxide dispersion values are very similar for both heat-treated and nonheat-treated homopolymers. This indicates that thermal stress has a negligible detrimental effect on the dispersing ability of these homopolymers. Although the absolute performance levels of these homopolymers are poor, it is interesting to note that the solvent polymerized P-AA (P3) performs better than the water polymerized P-AA (P4) and is comparable to P6 that is promoted in boiler water applications for iron stabilization.

Figure 5.21 also presents comparative dispersion data for several copolymers (P13 and P14) and terpolymers (P15 and P16). As illustrated, both the co- and ter-polymers in the absence of thermal stress exhibit excellent (>75%) iron oxide dispersion. However, when these co- and ter-polymers are exposed to thermal stress (200°C, 20 h), the iron oxide dispersion decreases drastically (by a factor 4). For example, % iron oxide dispersion values obtained for P15 and P16 before heat treatment were both >85% compared to 26% and 18%, respectively, after thermal stress. The data indicate that the performance of heat-treated terpolymers is similar to that obtained for homopolymers. As illustrated in Figure 5.21, the performance of copolymers is drastically affected by heat treatment.

5.4.2 IRON (III) STABILIZATION

Iron exists in two oxidation states: Fe^{2+} (ferrous) and Fe^{3+} (ferric). The chemistry of iron compounds is considerably more complex than carbonate- and sulfate-containing scales. When these two iron oxidation states (Fe^{2+} and Fe^{3+}) combine with the same anion, the result is usually the formation of compounds with significant differences in solubility. Iron deposits typically are in the form of FeO, FeS, Fe_2O_3, iron silicate, and so on, and frequently include traces of manganese. Iron-based scale deposition on heat exchanger surfaces occurs as a result of corrosion processes throughout the systems. Thus, it is very important to implement a good corrosion control program. Iron fouling sometimes occurs in cooling waters as a result of high incoming iron levels from the feed water (e.g., some

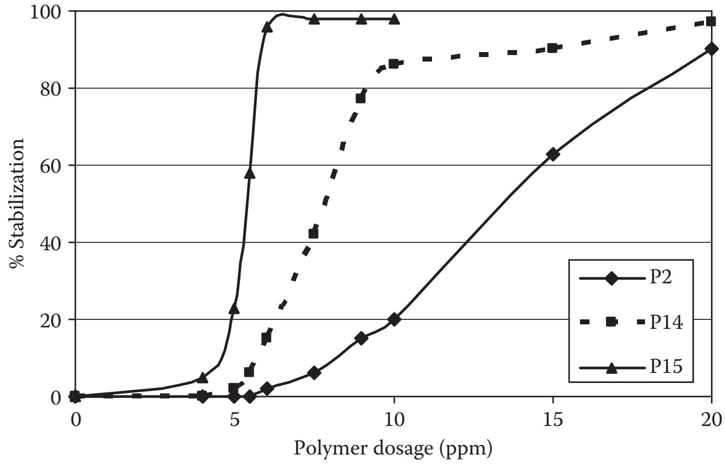


FIGURE 5.22 Stabilization of Fe^{3+} by homo-, co-, and terpolymers (104 mg/L Ca, 31 mg/L Mg, 361 mg/L Na, 202 mg/L SO_4, 600 mg/L Cl, 146 mg/L HCO_3, 3 ppm Fe^{3+}, pH 7.0, 23°C).

well waters or carryover from clarifiers where iron salts may be used as coagulants). Iron levels ≥2 ppm in the recirculating water typically can be controlled through the use of iron dispersants or deposit control agents. The use of an iron dispersant is strongly recommended to avoid major equipment failure problems. In cooling waters, Fe_2O_3 (hematite) and FeO are the most common deposits. Magnetite (Fe_3O_4) is rarely found in cooling systems; it needs high temperatures and/or anaerobic conditions. The formation of iron sulfide scale on equipment surfaces has been reported during oil and gas production from the formations containing large amounts of hydrogen sulfide. 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.

Figure 5.22 compares the performance of homo-, co-, and terpolymers as Fe^{3+} ions stabilizing agents. The stabilization data indicate that performance increases with increasing deposit control polymer concentration. It is also evident that sulfonic acid groups (SA or both SA and SS), in combination with acrylic acid, exhibit a positive influence on the performance of co- and terpolymers. For example, % stabilization values obtained in the presence of 7.5 ppm P2, P14, and P15 are 6%, 42%, and 98%, respectively. Thus, the partly substitution of acrylic acid in P-AA with two sulfonated monomers (i.e., SA and SS) markedly improves the performance of terpolymer.

5.5 SUMMARY

Currently, a wide variety of chemicals (e.g., flocculants, coagulants, scale inhibitors, biocides, corrosion inhibitors, and so on) with different ionic charges and molecular architecture are available to water technologists to develop formulations capable of achieving desired performance objectives of the water treatment programs. The results reviewed in this chapter show that the performance of polymeric and nonpolymeric additives depends on both the water chemistry and inhibitor architecture. It has been shown that deposit control polymer performance as scale inhibitor, dispersant, and metal ions stabilization increases with increasing polymer concentration. The calcium ion compatibility exhibited by the polymers tested ranged from poor for the homopolymers to excellent for the sulfonic acid containing co- and ter-polymers. However, thermal stress profoundly impacts the calcium ion compatibility of all the copolymers. Test data suggest that the blends of PBTC with a high-performance terpolymer (i.e., AA:SA:SS, P15) exhibit synergistic influence on calcium carbonate precipitation inhibition. In addition, when selecting deposit control polymers as a component of boiler and cooling water treatment programs, it is important to understand the operating conditions of the system, water chemistry, the type and level of impurities, and the thermal stability of the polymers.

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