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***The Influence of Water System Impurities
on the Performance of Deposit Control
Polymers as Particulate Dispersants***

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Carbosperse™ K-700
Water Treatment Polymers**

Introduction

During the last two decades, control of mineral scales in industrial waters has been extensively researched. Several reviews have compared the performance of various chemicals commonly used to control scale formation.¹⁻³ It is well documented that impurities present in feed and/or re-circulating waters markedly influence the performance of scale/deposit control agents.^{4,5} However, the role of chemical agents (or dispersants) to suspend/disperse particulate matter has been mostly overlooked. This paper reviews the physio-chemical processes involved in dispersing suspended matter and presents new data on the performance of various commercially available dispersants. The goal of this paper is to update water technologists, both from fundamental (science) and technology (application) perspectives, who seek technical input to design innovative formulations for systems where the potential deposition of suspended matter presents operational challenges.

Suspended Matter: Types, Sizes, and Other Characteristics

Suspended and colloidal matter cause turbidity in water. The type, size, and concentration of particles affect their behavior in industrial water systems. Examples of the types and sources of feed water particulates that impact industrial water systems include:

Types and/or Sources		Description
•	Inorganic	Silt, clay, asbestos, corrosion products
•	Coagulating/flocculating agent byproducts	Coagulant flocs [e.g., $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$] from upstream feed water treatment by aluminum and iron based coagulating/flocculating agents and cationic polymeric flocculants (e.g., diallyldimethyl ammonium chloride or DADMAC)
•	Organic	Humic substances (e.g., humic acid, tanic acid), debris from dead organisms

Collectively, these inorganic, organic, and coagulating/flocculating agent byproduct sources comprise the particulate mass and concentration in feed waters.

Among the wide variety of suspended and colloidal materials in surface water, there is a broad range of sizes from 10^{-3} to 10^2 micron (1 micron = 10^{-6} meter or 10^{-3} mm). This is a size differential of five (5) orders of magnitude. Figure 1 illustrates how particle size affects the tendency of particles to settle as a function of time in undisturbed water.⁶ Figure 1 shows that settling time strongly depends upon the size of the particles. For example, it takes 10 seconds for coarse sand particles (1,000 micron) to fall one (1) meter in undisturbed water. Under similar conditions, silt particles (10 micron) require 108 minutes compared to >2,500,000 minutes or >750 days for colloidal particles (0.1 micron). It should be noted that particles >100 microns are visible to naked eye and are considered to be settleable solids. Particles <10 micron are considered to be colloidal and particles <0.1 micron are visible by electron microscope.

Treatment Alternatives for Particulates

A wide variety of treatment chemicals are used for the purpose of preventing build-up of deposits on heat exchanger surfaces in industrial water system. The role of these treatment chemicals is to inhibit the precipitation of sparingly soluble mineral salts, modify the crystalline structure of mineral salts, prevent deterioration of heat exchanger and other metallic parts, and improve the fluidity of deposits (sludge).

Cooling water is generally contaminated with various forms of oxidized iron due to corrosion of steel equipment, and/or its introduction with the feed water. Maintaining this oxidized iron in soluble and in dispersed forms can prevent the fouling of heat exchanger surfaces. Although iron-based deposits are common in industrial water systems, there are no prognostic methods such as those for calcium carbonate, calcium sulfate, calcium phosphate or barium sulfate. Magnetite (Fe_3O_4) and hematite (Fe_2O_3) are the most common iron oxide deposits encountered in industrial water systems. Other suspended matters, which can contribute to deposit build-up, include clay, debris, biomass, sulfates and carbonates salts of alkaline metals, etc.

Among many dissolved impurities present in natural waters, iron-based compounds present one of the most serious problems in the efficient operation industrial water systems. Iron ion impurities come from various sources including boiler condensate, corrosion products (from pumps, pipes, etc.), biological activity (transformation of iron during bacterial processes), and unused flocculating agents. Regardless of the source, soluble iron can and does precipitate under certain conditions to form troublesome scalants and deposits (e.g., Fe_2O_3 , Fe_3O_4 , $\text{Fe}(\text{OH})_3$, FePO_4). In addition, soluble iron may have an antagonistic interaction with water treatment formulation ingredients.

The four major approaches to control iron oxide deposits are:

- Inhibiting corrosion at its source (this is achieved by the use of corrosion inhibitors).
- Stabilizing Fe(II) and Fe(III) ions in the feed water (involves the use of iron selective chelants).
- Removing iron oxides (corrosion products) from the systems (filtration).
- Treating iron oxides in the feed or recirculating water with iron oxide dispersant(s) to minimize iron oxide deposition within the system. The use of dispersant is generally considered to be the most economical method.

The suspended particles typically encountered in industrial water applications generally carry a slight negative charge. Therefore, anionic polymers are normally the most efficient dispersants because they increase negative surface charge and keep particles in suspension. 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.

Dispersion Mechanisms

It is important to recognize that the dispersion process consists of three steps (described below) and to separately consider each step in order to understand the various factors involved.⁷ The three steps discussed below are distinctively different but overlapping from a practical perspective:

- *Wetting of the suspended solid:* The wetting process depends upon surface characteristics of the particles, dispersion medium, and the stabilizer. Non-ionic polymers have been used as surfactants. Standard surfactants, although capable of wetting suspended solids, may cause severe foaming problems. It should be noted that not all dispersants exhibit good wetting/surfactant properties.
- *Breaking up (de-agglomeration) of the large particles:* Aggregates may require considerable mechanical energy to break them down completely such that each primary particle is available to the wetting liquid. Several factors are involved in achieving the primary particle state including type of cluster (agglomerate or large particle), bonds between particles in the cluster, wetting characteristics, etc.
- *Stabilization of the primary particles:* It is generally understood that most of the fouling materials in cooling waters are slightly negatively charged. The addition of anionic polymers to feed or recirculating water seems useful because they increase surface charges and therefore keep particles separated, dispersed, or stabilized.

Figure 2 illustrates the dispersion process.

Dispersant Types and Structures

Over the years, proper maintenance of industrial water systems has become increasingly challenging. This has been the result of several factors including poor quality feed water, environmental constraints, operating water systems under higher cycles of concentration and alkaline pH range, increased reuse of plant water before discharge, etc. During the last three decades a large variety of new chemicals (polymeric and non-polymeric) have been developed and are currently incorporated as components of water treatment formulations to control scale, corrosion, biological growth, and deposition of suspended solids. Polymers commonly used to disperse suspended solid fall into two main categories, namely: natural and synthetic. The following section presents a historical overview of these polymers.

Natural Polymers

The use of natural materials as dispersants began in the early nineteenth century.⁸ From 1860 to 1900, numerous patents were issued on the use of natural materials either alone or in combination with alkalis such as sodium/potassium hydroxide and/or sodium carbonate for controlling scale and deposit formation on boiler surfaces. During the period 1900 to 1930, a large number of natural extracts were also evaluated as dispersants for preventing deposit build-up in boilers. The extracts tested were from gall nuts, chest nuts, myrobalan, oak bark and others.⁸ Typical dosages tested were from 50 to 200 ppm.

Natural materials show mediocre dispersancy activity and suffer from several disadvantages including variable quality, stability, coloration, etc. In addition, dispersants such as starch and cellulose act as nutrients for microbiological growth and in some cases over dosing may cause the formation of gummy deposits.⁸ Natural dispersants also lose activity when exposed to elevated temperature, especially for boiler applications.

Synthetic Polymers

The first use of synthetic polymers (polyacrylates, methacrylates, hydrolyzed polyacrylamide, acrylic acid/acrylamide copolymers, and styrene maleic anhydride copolymers) occurred in the 1950s.⁸ The early synthetic polymers used were high molecular weight ($M_w > 100,000$) homopolymers of acrylic acid. With time, low molecular weight ($M_w < 10,000$) polyacrylates as well as polymethacrylates and polymaleic acids were found to be more effective.

Water conservation demands have led to the operation of cooling water systems at high cycles of concentrations resulting in greater driving forces for the precipitation of scale forming salts. Therefore, high performance polymers are required as components of cooling water treatment formulations to prevent the deposition of mineral scales on heat exchanger surfaces. During the last three decades, a variety of polymers containing different functional groups (e.g., -COOH, -COOR, -OH, -SO₃H, substituted Am, etc.) have been developed and are currently used to treat high scaling cooling waters. The importance of polymer architecture (e.g., monomer ratio, monomer type, molecular weight) on the performance of polymers as inhibitors, particulate dispersants, and metal ion stabilizers has been reviewed in numerous publications.^{9,10,11}

Dispersant Performance

A series of experiments were conducted to evaluate the performance of natural materials and synthetic polymers as iron oxide dispersants both without and with the presence of impurities including other water treatment chemicals that adversely impact performance. The materials evaluated include several natural materials and synthetic polymers (homopolymers and copolymers) as shown on Table 1. The experiments were designed to evaluate the performance of several the materials and determine the influence of dosage, polymer architecture, and the presence of impurities (e.g., cationic polymer, inorganic flocculant [iron and aluminum based], water hardness [Ca and Mg], and biocide).

Dispersant Testing Procedure

The experimental test procedure for performance of natural and synthetic materials as iron oxide dispersants was described previously.¹² A known amount (0.12 g) of iron oxide was added to synthetic water (600 mL) containing a known amount of dispersant solution in a 800 ml beaker. The synthetic water used in dispersancy test was made by mixing standard solutions of calcium chloride, magnesium chloride, sodium sulfate, sodium bicarbonate, and sodium chloride. The synthetic water composition included 100 ppm Ca, 30 ppm Mg, 314 ppm Na, 571 ppm chloride (Cl), 200 ppm sulfate (SO₄),

and 60 ppm bicarbonate (HCO_3). Other test conditions include pH 7.8, 70°F, and 1 ppm dispersant.

In a typical test, six experiments were run simultaneously using a gang-stirrer set to 100 rpm (revolutions per minute). At known time intervals, transmittance readings (% T) were taken with a Brinkmann PC/1000 colorimeter using 420 nm filter. Dispersancy (% D) was calculated from % T readings measured at 3 hr as a function of the amount of the iron oxide dispersed. Dispersant performance was determined by comparing the % D values of the slurries containing dispersant to the control (no dispersant). Thus, higher % D values indicate greater dispersancy. At the end of the experiments, samples were withdrawn and examined by optical microscopy for particle size reduction.

Natural Materials

As discussed above natural polymers such as starchy vegetables (i.e., potato) modified corn starches, lignosulfonate, alginate, tannins, etc., have been used for years to disperse particulate matter in industrial water systems. These natural materials show varying degrees of dispersancy power. However, their performance is very sensitive to the high temperatures normally encountered in treating boiler water.

Several natural materials including lignosulfonate (LS), starch (ST), sodium alginate (NaAL), polyaspartic acid (PAs), humic acid (HA), and tannic acid (TA) were evaluated as iron oxide dispersants using the test procedure and conditions described above. The dispersancy data presented in Figure 3 show the following rank order (from best to worst) performance of these materials:

LS >> HA >> NaAL > PAs ≈ TA > ST

These data reveal that materials containing sulfonate groups (LS), carboxyl groups (NaAL and PAs), or hydroxyl groups (HA and TA) perform better than starch (ST). To be effective as dispersants these materials are typically used at higher concentrations (50 to 200 ppm) to control deposit formation in boilers. Accordingly, the poor dispersancy activity observed in this study for the natural materials may be attributed to several factors including their relatively high molecular weight (effective dispersants normally have molecular weights <10,000 Daltons) and low testing dosage (1 ppm vs. typical >50 ppm in field conditions).

Synthetic Materials

Numerous studies on the influence of polymer architecture have shown that the monomer type (i.e., type of the functional group), monomer unit ratio, and the molecular weight) play key roles on the performance of the polymer as scale inhibitor, metal ion stabilizer, and dispersant. The effect of polymer architecture on iron oxide dispersancy was studied by conducting a series of experiments with polymers incorporating a variety of monomers containing different functional groups and ionic charge.

The dispersancy data presented in Figure 4 for a number of carboxyl containing homopolymers: polyacrylic acid (PAA), polymaleic acid (PMA), polymethacrylic acid (PMAA), polyacrylamide (PAm), polyvinylpyrrolidone (PVP), and poly-2-acrylamido-2-

methyl propane sulfonic acid (PSA) show a wide range of dispersancy power. For example, the dispersancy or “% D” values obtained for carboxyl containing polymers are 38% for PAA, 45% for PMA, and 22% for PMAA all of which are anionic charge polymers compared to <5% for PAm and PVP which are non-ionic or neutral charge polymers. By comparison, the much higher dispersancy value (i.e., 70%) obtained for PSA (see Figure 4) clearly shows that a polymer containing a sulfonic acid group exhibits better performance than those containing carboxyl groups.

The influence of substituting the carboxyl group with other groups of varying ionic charge (i.e., sulfonic acid, sulfonate styrene, and non-ionic) was investigated for their ability to disperse iron oxide. Results presented in Figure 5 reveal that amount and type of charge of the substitution group has an impact. It appears that the higher the ionic charge and larger the size of the substitution group of the polymer the better the performance in terms of dispersing iron oxide particles. For example, % D values obtained for the terpolymers (86% for AA/SA/SS and 88% for AA/SA/NI) are better than the values obtained for the copolymers (72% for AA/SA and 74% for AA/SMs). The observed marked better performance of the terpolymers (i.e., AA/SA/SS and AA/SA/NI) compared to the copolymers (i.e., AA/SA and AA/SMs) may be attributed to the stronger adsorption characteristics of additional comonomers in imparting more negative charges to the iron oxide particles thereby reducing particle size and thus improving dispersancy.

Natural vs. Synthetic Materials

Figure 6 provides a representative comparison of the iron oxide dispersion data for natural materials, synthetic homopolymers, and synthetic copolymers (previously shown in Figures 3, 4, and 5). The data suggest the following rank order for these materials groups as iron oxide dispersants:

Synthetic Copolymers > Synthetic Homopolymers > Natural Materials

Collectively, the data presented herein suggest that the presence of either sulfonate groups (e.g., LS, PSA, AA/SA, AA/SA/SS) or carboxyl groups (e.g., PAs, PAA, PMA, PSA, AA/SA, and AA/SA/SS) or both sulfonated and groups (e.g., AA/SA and AA/SA/SS) in a material is one predictor of a good iron oxide dispersant. In addition, molecular weight is also a factor in predicting performance of iron oxide dispersants (it is well documented that an effective dispersant normally has a molecular weight <10,000 Daltons).

Factors Affecting Dispersant Performance

It is well documented that various factors such as pH, temperature, total dissolved solids, and water contaminants affect the solubility of scale forming salts. It is also well known that solubility of scale forming salts such as calcium carbonate, calcium phosphate, and calcium sulfate are inversely dependent on the solution temperature. Results of recent studies on the influence various soluble and insoluble impurities present in the water and the chemicals commonly used in treating industrial water systems such as phosphonate, polyphosphate, biocides, and flocculating/coagulating agents have shown that these chemicals adversely affect the inhibitory power of various

commercial polymers.^{13,14} Thus, the presence of these chemicals or impurities in the water may necessitate higher polymer dosages to inhibit scale formation and growth on heat exchanger surfaces.

Dispersant Dosage

Figure 7 presents the “% D” vs. dispersant dosage profiles for AA/SA/SS, AA/SA and lignosulfonate (LS). As illustrated, dispersant performance strongly depends upon the functional groups present in the dispersant. For example, at 1 ppm active dispersant dosages, the amount of iron oxide dispersed by AA/SA/SS and AA/SA are 86% and 72%, respectively compared to only 50% for LS. This observed performance difference between AA/SA/SS (containing three functional groups) and AA/SA (containing two functional groups) is consistent with an increase in anionic charge on the iron oxide particles with increasing availability of the dispersant. It is interesting to note that LS shows fair iron oxide dispersancy power but its ability to prevent the deposition of gypsum on heat exchanger when compared with AA/SA/SS is rather poor.¹⁵ Thus, from a practical point of view, the ability of a dispersant such as AA/SA/SS to provide superior performance at low dosage is a desirable characteristic.

Influence of Impurities

Organic Flocculants

Organic polymers are used in the water treatment industry to clarify water containing suspended matter. These polymers are of two major types, namely coagulants and flocculants. Coagulants are typically cationic and have molecular weights of <100,000 Daltons. Examples of cationic coagulants include polyamine, polyquarternies, and polydiallyldimethyl ammonium chloride (DADMAC). Flocculants are typically much larger cationic molecules (i.e., molecular weights >1,000,000 Daltons) that provide long bridges between small flocs to enhance particle growth. Commonly used flocculants include copolymers of acrylamide and dimethylammonium chloride.

To overcome the shortfall of linear polymers, branched and lightly crosslinked cationic polymers or “structured” polymers, have been commercialized. Some performance advantages for the structured flocculants compared to linear polymers have been reported. However, no detailed information on the molecular structures of these “structured” polymers or the relationships to flocculation effectiveness have been revealed.

The flocculant material is typically added to the raw water in an amount suitable to flocculate suspended matter. In most cases these large particles (flocs) are removed via settling in a clarifier and are recollected as sludge. Occasionally, clarifier upsets cause cationic polymer “carryover.” In such instances, cationic polymers may interfere with the performance of anionic polymers used as dispersants and/or scale control agents in the water treatment formulation.

A series of experiments was conducted in order to understand the influence of cationic polymers on the performance of synthetic copolymers as iron oxide dispersants. Figure 8 presents a comparison of the iron oxide dispersion by four synthetic polymers

in the absence and presence of 0.1 ppm of cationic polymer CP-1 (a homopolymer of diallyldimethyl ammonium chloride or [DADMAC]. A summary of the data shown in Figure 8 appears below:

<u>Condition or Observation</u>	<u>AA/SA/SS</u>	<u>AA/SA</u>	<u>AA/SMs</u>	<u>AA/SA/NI</u>
No CP-1 Present	86%	72%	74%	88%
With 0.1 ppm CP-1 [relative performance lost]	40% [53%]	28% [61%]	25% [66%]	33% [63%]

Figure 8 and the table above clearly show that CP-1 has a strongly antagonistic effect on the performance of all four polymers. However, it is interesting to note among the copolymers (AA/SA and AA/SMs) and the terpolymers (AA/SA/SS and AA/SA/NI), that the best (slightly better) performing polymers in their classes or AA/SMs and AA/SS/NI, respectively had relatively larger performance decreases and lower performances in the presence of 0.1 ppm CP-1 than AA/SA and AA/SA/SS, respectively.

Several dispersancy experiments were conducted to understand the interaction of cationic flocculants on the iron oxide dispersion of AA/SA/SS as function of varying cationic charge (CP-1 @ 100%, CP-2 @ 35%, and CP-3 @ 55%). The cationic flocculant used in these experiments were CP-1 (DADMAC) and two cationic copolymers (CP-2 and C-3) comprised of different ratios of acrylamide (Am) and 2-(acryloyloxy) ethyltrimethyl ammonium chloride (AETAC) or Am/AETAC.

Figure 9 presents a comparison of the iron oxide dispersion of AA/SA/SS (at 1 ppm dosages) in the absence and presence of 0.1 ppm of three cationic flocculants (CP-1, CP-2, and CP-3). As illustrated in Figure 9, all three cationic flocculants had an antagonistic effect on the performance of AA/SA/SS. In addition, the data presented in Figure 9 reveal that the degree to which a cationic flocculant affects the iron oxide dispersion by AA/SA/SS depends on both the polymer structure and the degree of cationic charge present on the cationic flocculant. The observed difference in cationic polymer influence on the dispersancy activity of AA/SA/SS may be due to differences in cation polymer chemistry and polymer composition (i.e., homopolymer [CP-1] vs. copolymer [CP-2 and CP-3]). From a practical point of view, a water technologist seeking to ensure optimum performance of cooling water treatment program needs to take into account several factors including type and amount of cationic polymer present in the feed water and its influence on dispersant performance.

Inorganic Flocculants

Aluminum and iron based compounds (e.g., alum, sodium aluminate, ferric sulfate) have been utilized for decades as coagulant aids to help facilitate municipal and industrial water clarification. These inorganic flocculating agents neutralize the charge of water borne turbidity particles and they hydrolyze to form insoluble hydroxide particles 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 these metal-ion containing flocs and/or unused flocculants to carryover or escape pretreatment system and become contaminants or impurities in cooling or boiler feed waters that can affect the performance of the treatment programs.

A series of experiments was conducted in order to evaluate the influence of low levels of soluble iron (III) on the iron oxide dispersion by polymers. Figure 10 and the table below, present iron oxide dispersion data for the four polymers in the absence and presence of 1.0 ppm iron (III).

<u>Condition or Observation</u>	<u>AA/SA/SS</u>	<u>AA/SA</u>	<u>AA/SMs</u>	<u>AA/SA/NI</u>
No iron (III)	86%	72%	74%	88%
With 1 ppm iron (III) [relative performance lost]	42% [51%]	36% [50%]	38% [49%]	46% [48%]

Figure 10 and the table above, clearly show that iron (III) has a significant and comparable antagonistic effect (approximately 50% performance decline) on the iron oxide dispersion by all four polymers.

Similarly, the effect of low levels of soluble Al (III) on oxide dispersion by polymers was evaluated by conducting a series experiments. Figure 11 and the table below, present the iron oxide dispersion data for the four polymers in the absence and presence of 0.25 and 1 ppm Al (III).

<u>Condition or Observation</u>	<u>AA/SA/SS</u>	<u>AA/SA</u>	<u>AA/SMs</u>	<u>AA/SA/NI</u>
No Al(III)	86%	72%	74%	88%
With 0.25 ppm Al(III) [relative performance lost]	64% [26%]	42% [42%]	38% [49%]	62% [30%]
With 1 ppm Al(III) [relative performance lost]	22% [74%]	15% [79%]	10% [86%]	12% [86%]

Figure 11 and the table above show that the presence of only 0.25 mg/L of Al (III) caused a pronounced decrease in the iron oxide dispersion by all four polymers ranging from a 49% decrease for copolymer AA/SMs to a 26% decrease for terpolymer AA/SA/SS. In addition, increasing the Al (III) by a factor of four (i.e., from 0.25 to 1 ppm) causes a dramatic decrease in performance for all the polymers. However, it is interesting to note that the relative performance lost by both copolymer AA/SMs and terpolymer AA/SA/NI was 86% compared to 79% for copolymer AA/SA and 74% for terpolymer AA/SA/SS. Thus, among the terpolymers, AA/SA/SS outperforms or retains more performance than AA/SA/NI and similarly among the copolymers AA/SA outperforms or retains more performance than AA/SMs.

Hardness Ions

High hardness waters either due to harsh feed waters or high cycles of concentration are well known to create difficult operating conditions that demand high performance deposit control agents. A series of experiments was conducted in order to determine the influence of high hardness (400 mg/L Ca or 240 mg/L Mg) on iron oxide dispersion four polymers. Figure 12 illustrates the iron oxide dispersion by 1 ppm polymer dosages at three (3) conditions: the control (100 mg/L Ca and 30 mg/L Mg), 400 mg/L Ca (and 30 mg/L Mg), and 240 mg/L Mg (and 100 mg/L Ca). A summary of the data shown in Figure 12 appears below:

<u>Condition or Observation</u>	<u>AA/SA/SS</u>	<u>AA/SA</u>	<u>AA/SMs</u>	<u>AA/SA/NI</u>
Control (100 mg/L Ca and 30 mg/L Mg)	86%	72%	74%	88%
400 mg/L Ca (and 30 mg/L Mg) [relative performance lost]	56% [35%]	43% [40%]	38% [49%]	49% [44%]
240 mg/L Mg (and 100 mg/L Ca) [relative performance lost]	54% [37%]	40% [44%]	35% [53%]	47% [47%]

Figure 12 and the table above, indicate that increasing hardness levels decreases iron oxide dispersion of all four polymers. However, it is interesting to note among the copolymers, that AA/SA retains or outperforms AA/SMs and among the terpolymers that AA/SA/SS outperforms AA/SA/NI under high hardness conditions.

Biocides

It is well known that the growth and accumulation of microorganisms in a cooling water system leads to a several operating problems including corrosion, deposition of unwanted materials, odor, and environmental pollution. Thus, the proper design of treatment program is critical to achieving optimum system performance.

A variety of commercially available biocides are used to control biofouling in industrial water systems. The two commonly used types are oxidizing and non-oxidizing. Examples of oxidizing biocides include chlorine, chlorine dioxide, ozone, chloroisocyanurates and other halogen containing compounds. Although oxidizing biocides kill organisms in the system quickly, these biocides are not persistent and rapidly decay after the chemical feed stops. Additionally, oxidizing biocides also react with contaminants like H₂S, NH₃, pulp lignin, and other organics. Non-oxidizing biocides are often used in systems that are incompatible with chlorine, such as water systems high in organic matter and /or ammonia.

The interaction of both oxidizing (chlorine as hypochlorite [NaOCl] and bromochlorine [BrCl]) and non-oxidizing (gluteraldehyde [Glut] and tris (hydroxymethyl) nitromethane) [THM]) biocides at 10 ppm dosages with iron oxide dispersants was evaluated. As illustrated in Figure 13, neither the presence of NaOCl, BrCl, Glut, or THM showed any antagonistic effect on the iron oxide dispersion by AA/SA/SS. These results are consistent with the effect of oxidizing and non-oxidizing biocides on the calcium phosphate inhibition by AA/SA/SS.⁴

Figure 14 presents the results of the effect varying the concentration of a cationic poly-quat biocide on the iron oxide dispersion by four polymers. The data displayed graphically in Figure 14 are summarized in the table below:

<u>Condition or Observation</u>	<u>AA/SA/SS</u>	<u>AA/SA</u>	<u>AA/SMs</u>	<u>AA/SA/NI</u>
Control (no biocide)	86%	72%	74%	88%
With 0.1 ppm poly-quat [relative performance lost]	40% [53%]	25% [65%]	20% [73%]	35% [60%]
With 1 ppm poly-quat [relative performance lost]	26% [70%]	10% [86%]	10% [89%]	16% [82%]

These results clearly show that the poly-quat biocide has a strongly antagonistic effect on the iron oxide dispersion by all four polymers. These results are consistent with the poly-quats' effect on the calcium phosphate inhibition of these polymers.⁴ It is also interesting to note that terpolymer AA/SA/SS outperforms and retains more activity in the presence of the poly-quat biocide than any of the other polymers. This is consistent with the iron oxide dispersion of polymers in the presence of organic cationic flocculants shown in Figure 8 and discussed earlier.

At the end of the experiments above, iron oxide samples were withdrawn and examined by optical microscopy for particle size reduction. Figure 15 presents optical microscopy pictures of iron particles from (a) the control, (b) in the presence of terpolymer AA/SA/SS, and (c) in the presence of AA/SA/SS and poly-quat biocide. Comparing Figures 15 A to B shows the iron oxide particle size reduction by the terpolymer. Figure 15-C compared to Figures 15-A and 15-B illustrates the antagonistic effect of poly-quat biocide on the particle size reduction by the terpolymer.

Selecting a dispersant for a given cooling water application requires that water treatment technologists consider the role of biocide in the overall performance of the water treatment program. Although a variety of dispersants are commercially available, the dispersant that is most tolerant to process impurities typically provide the best performance.

Summary

Successful water treatment programs incorporate effective particulate dispersants that are typically synthetic polymers. The ability of dispersants to retain performance in the presence of naturally occurring impurities and/or resist loss of activity in the presence of other treatment chemicals should be a key selection criteria for deposit control agents. This study suggests the following conclusions:

- The iron oxide dispersancy increases with increasing dispersant concentration.
- The nature of the functional group(s) in the dispersant plays a key role in imparting the dispersancy power to the dispersant. In general, dispersants especially those containing sulfonic acid group(s) are better dispersants than polymers containing carboxyl and acrylamide group(s).
- Dispersant performance strongly depends upon the type and amount of impurities present in the water system.
- Organic cationic flocculants have a strongly antagonist effect on the iron oxide dispersion by polymers. This antagonist effect increases with cationic flocculant charge concentration.
- Among the metal ions evaluated, aluminum (III) ions exhibit a greater antagonistic effect than iron (III) ions on the performance of iron oxide dispersant.
- Oxidizing and non-oxidizing (with out charge groups) biocides had negligible impact on the performance of iron oxide dispersion of AA/SA/SS.
- Cationic biocides show significant adverse influence on iron oxide dispersant performance.
- The AA/SA/SS terpolymer was the material most resistant to the lost of iron oxide dispersion in the presence of organic cationic flocculants, inorganic flocculants, high hardness levels, and a cationic poly-quat biocide.

References

1. R.W. Zuhl and Z. Amjad, "The Role of Polymers in Water Treatment Application and Criteria for Comparing Alternatives," Association of Water Technologies' Annual Conference, Las Vegas, NV (1993).
2. Z. Amjad, J. Pugh, J.F. Zibrida, and R.W. Zuhl, "Performance of Polymers in Industrial Water Systems: The Influence of Process Variables," *Materials Performance*, 36 (1), pp. 32-38 (Jan-97).
3. E. Smyk, J. Hoots, K. Fivizzani, and K. Fulks, "The Design and Application of Polymers in Cooling Water," Paper No. 14, CORROSION/88, NACE International, Houston, TX (1988).
4. Z. Amjad, J.F. Zibrida, and R.W. Zuhl, "The Effect of Biocide on Deposit Control Polymer Performance," Association of Water Technologies' Annual Conference, Honolulu, HI (2000).
5. L. Perez and D. Zidovec, *Mineral Scale Formation and Inhibition*, Z. Amjad (Ed.), Chapter 5, Plenum Publishing Corporation, New York, NY (1995).
6. *The Nalco Water Handbook*, F. N. Kemmer (Ed.), McGraw-Hill Book Co. (1979).
7. *Dispersion of Powders in Liquids*, G. D. Parfitt (Ed.), Applied Science Publishers, Ltd., London (UK) (1973).

8. J.F. Wilkes, "A Historical Perspective of Scale and Deposit Control," CORRISION/93, Paper No. 458, NACE International, Houston, TX (1993).
9. D. Wilson, "Influence of Molecular Weight on Selection and Application Polymeric Scale Inhibitors," CORROSION/98, NACE International, Houston, TX (1998).
10. Z. Amjad, "Factors to Consider in Selecting a Dispersant for Treating Industrial Water Systems," *ULTRAPURE WATER*, 16 (7), pp. 17-24 (Sep-99).
11. B.P. Boffardi and G. W. Schweitzer, "Advances in the Chemistry of Alkaline Cooling Water Treatment," CORROSION/85, Paper No. 132, NACE, Houston, TX (1985).
12. Z. Amjad, "Dispersion of Iron Oxide Particles in Industrial Waters," *Tenside Surfactants and Detergents*, 36, pp. 50-56 (1999).
13. Z. Amjad, "Development of Calcium Phosphate Inhibiting Polymers for Cooling Water Applications," Chapter 16, *Calcium Phosphates in Biological and Industrial Systems*, Z. Amjad (Ed.), Kluwer Academic Publishers, Boston, MA (1998).
14. Z. Amjad, J.F. Zibrida, and R.W. Zuhl, "Effect of Cooling Water Impurities on Deposit Control Polymer Performance," *Materials Performance*, NACE International, Houston, TX, Vol. 39 (5), pp. 54-58 (May-00).
15. Z. Amjad, "Calcium Sulfate Dihydrate (Gypsum) Scale Formation on Heat Exchanger Surfaces. The Influence of Scale Inhibitors," *J. Colloid Interface Science*, 123, pp. 523-536 (1988).

Table 1 - Materials Evaluated as Iron Oxide Dispersants

Description or Composition	Acronym
Lignosulfonate	LS
Starch	ST
Sodium alginate	NaAL
Humic acid	HA
Tanic acid	TA
Polyaspartic acid	PAs
Polyacrylic acid (PAA) - 5,000 M _w	PAA
Polymaleic acid (PMA) - 500 M _w	PMA
Polymethacrylic acid (PMAA) - 5,000 M _w	PMAA
Polyacrylamide (PAm) - 5,000 M _w	PAm
Polyvinylpyrrolidone (PVP) - 10,000 M _w	PVP
Poly-2-acrylamido-2-methyl propane sulfonic acid (PSA) - 6,000 M _w	PSA
Poly(acrylic acid : sulfonic acid : sulfonated styrene) or Poly (AA:SA:SS) – Good-Rite® K-798 acrylate terpolymer	AA/SA/SS
Poly(acrylic acid : sulfonic acid) or Poly (AA:SA) – Good-Rite® K-775 acrylate copolymer	AA/SA
Poly(acrylic acid : sulfonated monomers) – competitive copolymer	AA/SMs
Poly(acrylic acid : sulfonic acid : nonionic) or Poly (AA:SA:NI) – competitive terpolymer	AA/SA/NI

Note: AA/SA/SA and AA/SA are supplied by Noveon, Inc.

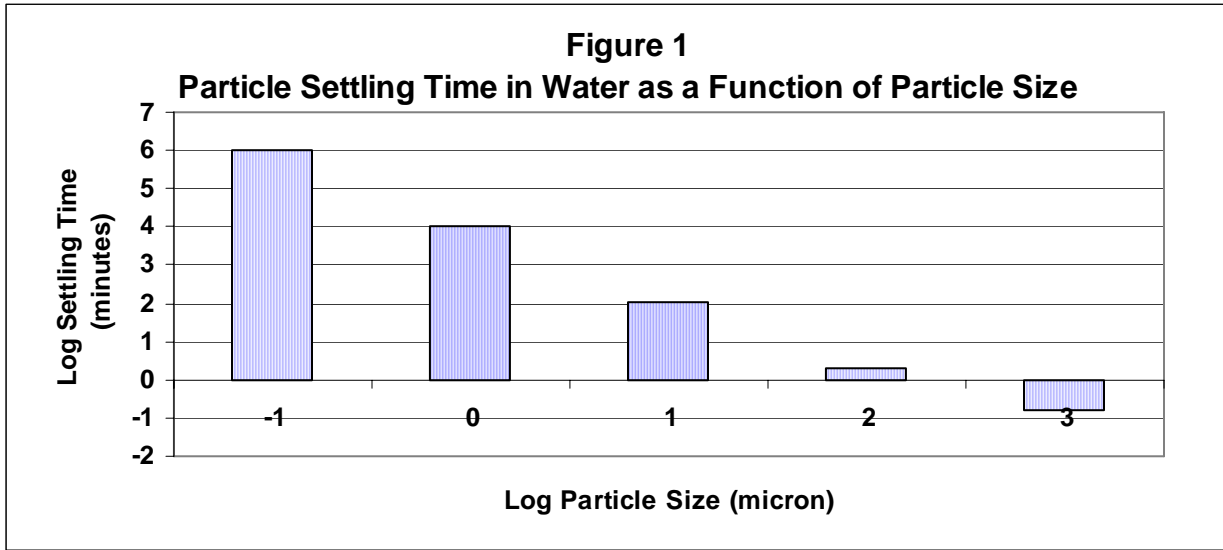


Figure 2
Dispersion of a Large Particulate Cluster

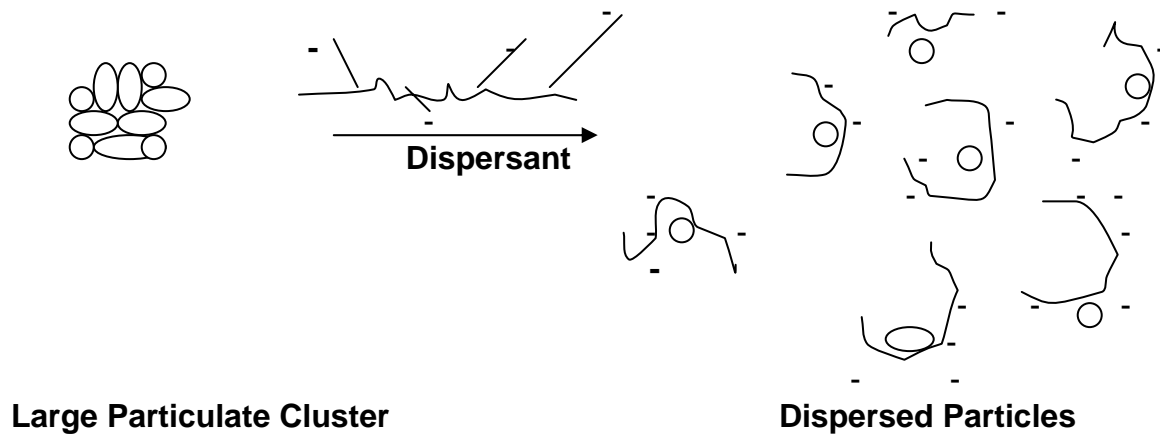


Figure 3
Iron Oxide Dispersion by Natural Materials

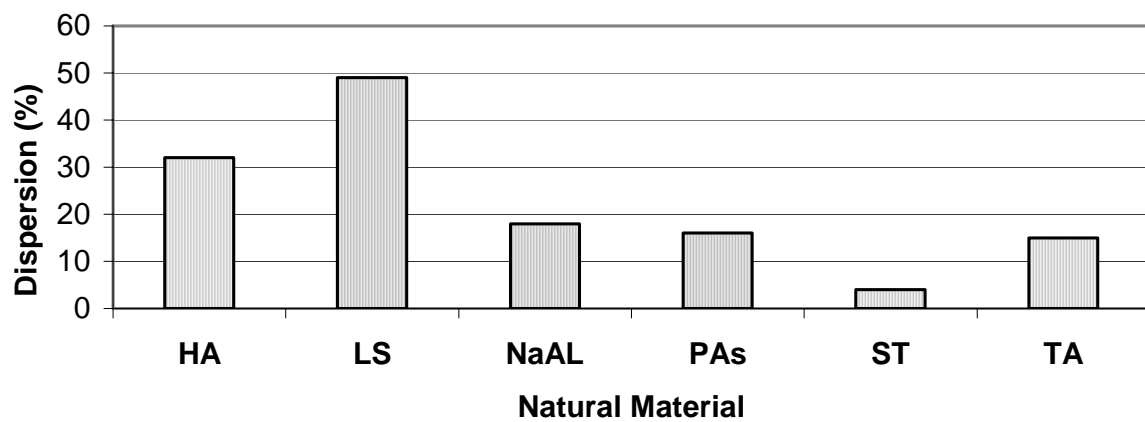


Figure 4
Iron Oxide Dispersion by Homopolymers

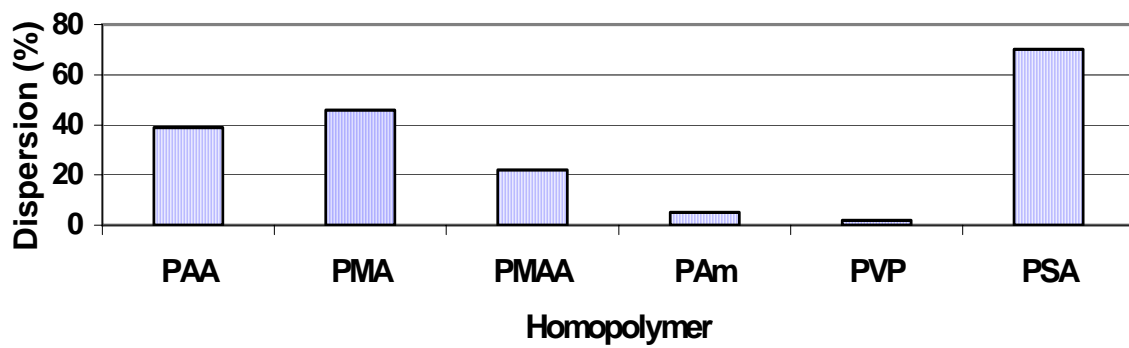


Figure 5
Iron Oxide Dispersion by Copolymers

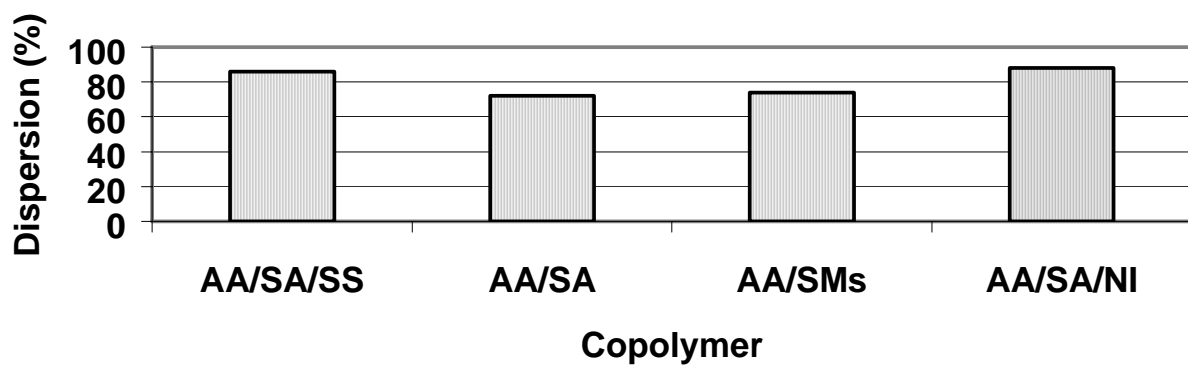


Figure 6
Iron Oxide Dispersion
by Natural and Synthetic Materials

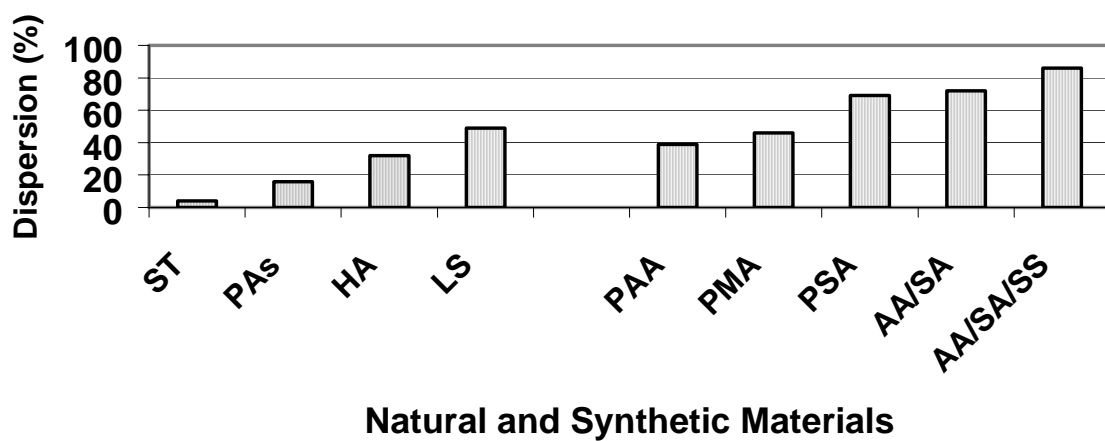


Figure 7
Iron Oxide Dispersion as a Function
of Dispersant Dosage

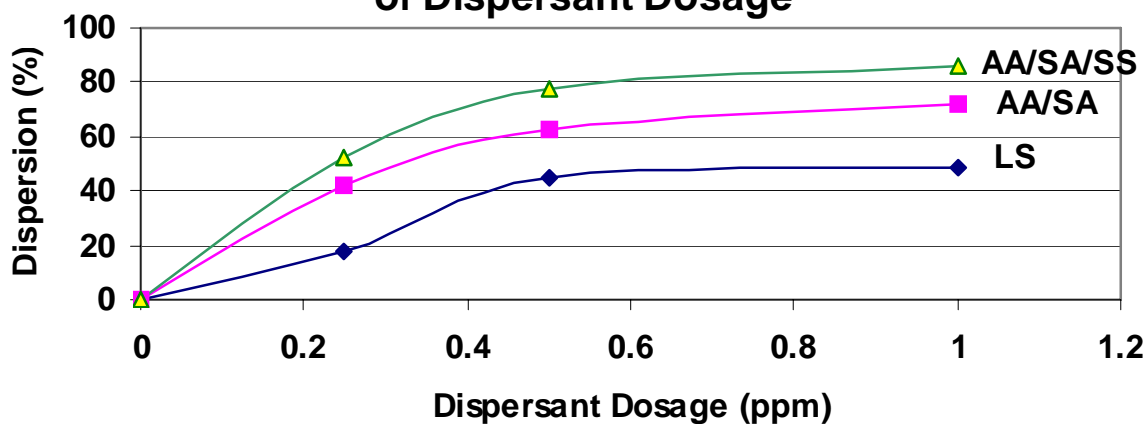


Figure 8
Effect of Organic Cationic Flocculant (DADMAC)
on Iron Oxide Dispersion by Copolymers

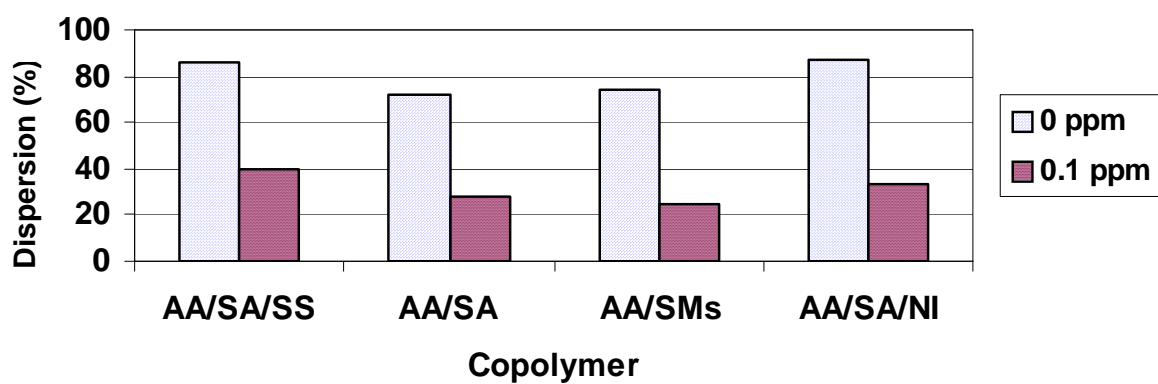


Figure 9
Effect of Organic Cationic Flocculants
on Iron Oxide Dispersion by AA/SA/SS

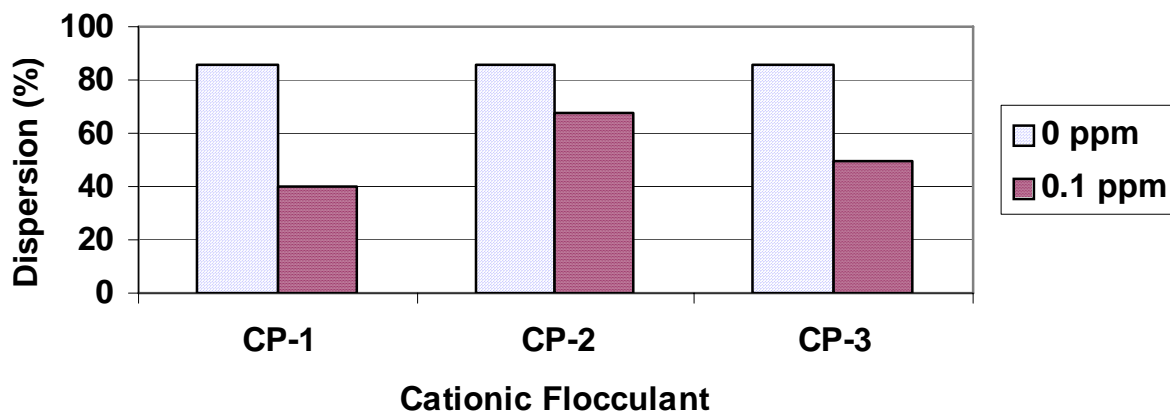


Figure 10
Effect of Fe(III)
on Iron Oxide Dispersion by Copolymers

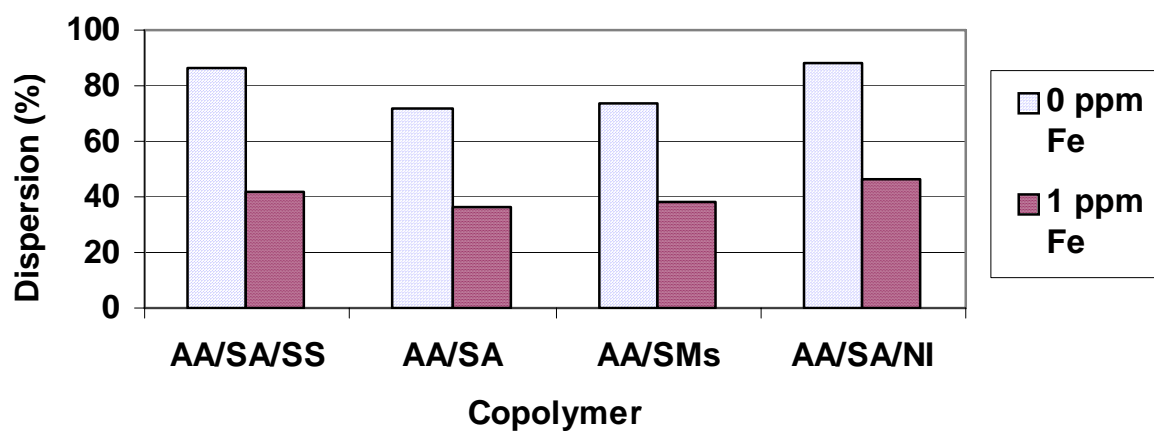


Figure 11
Effect of Al(III)
on Iron Oxide Dispersion by Copolymers

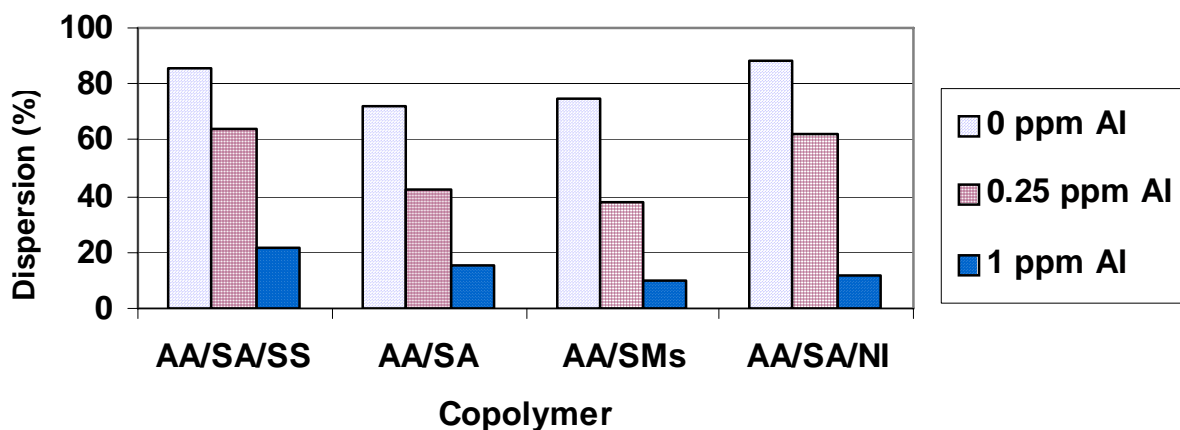


Figure 12
Effect of High Hardness (Ca or Mg) Levels
on Iron Oxide Dispersion by Copolymers

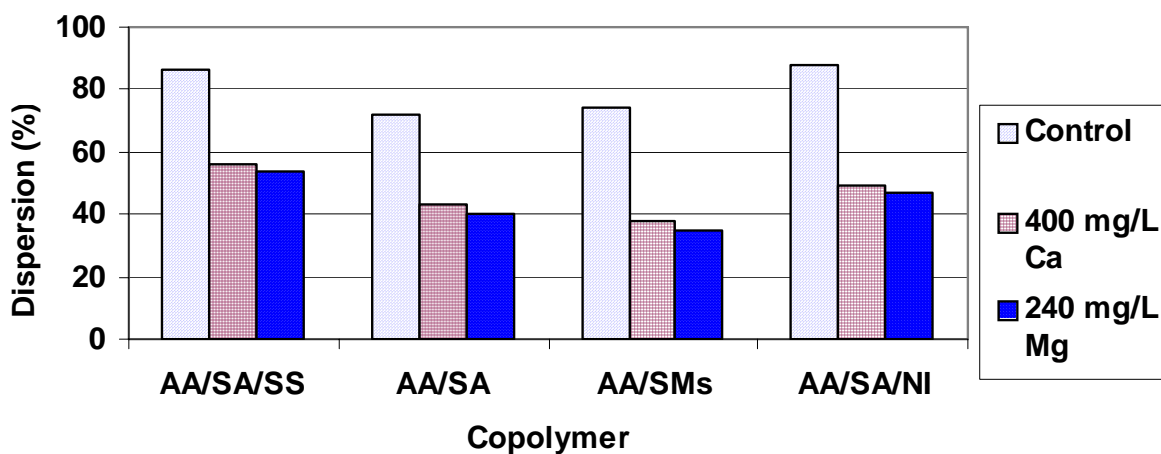


Figure 13
Effect of Oxidizing and Non-Oxidizing Biocides
on Iron Oxide Dispersion by AA/SA/SS

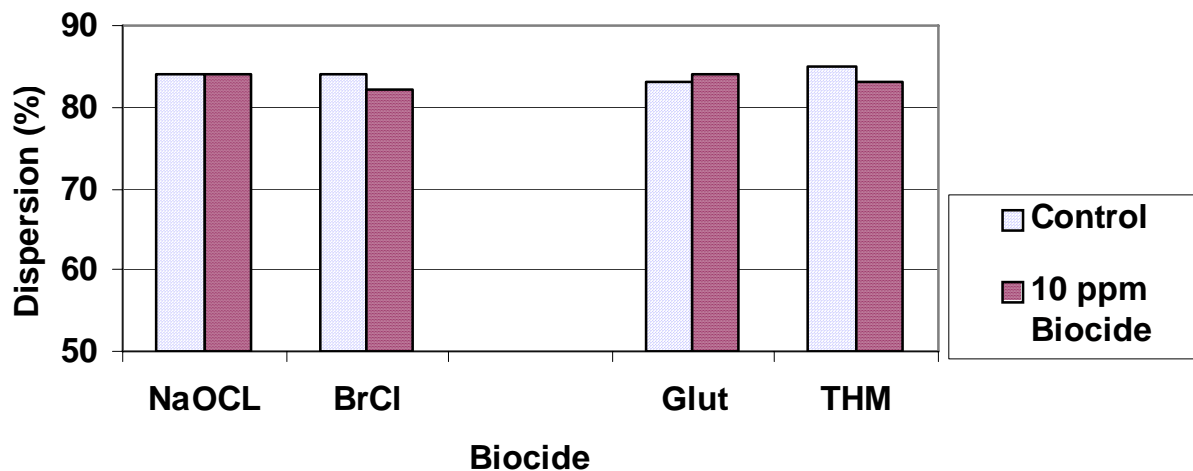


Figure 14
Effect of Poly-Quat Biocide
on Iron Oxide Dispersion by Copolymers

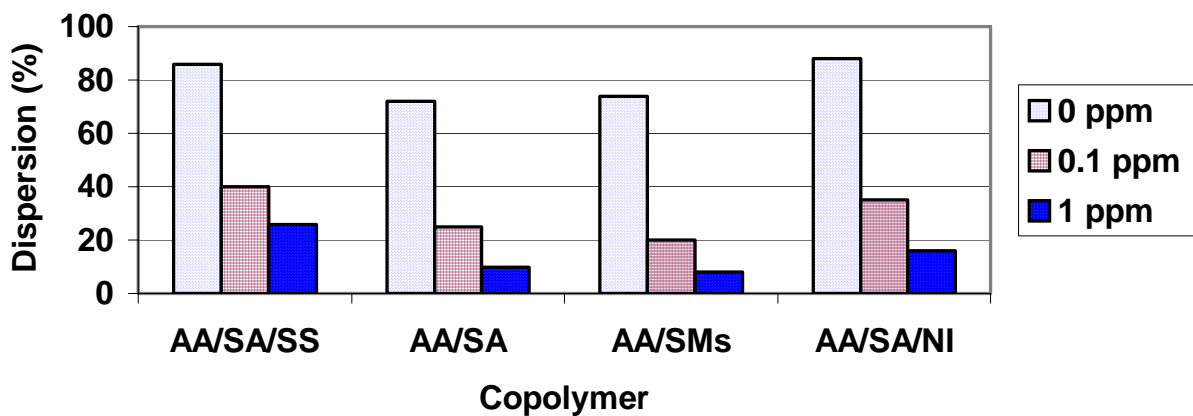
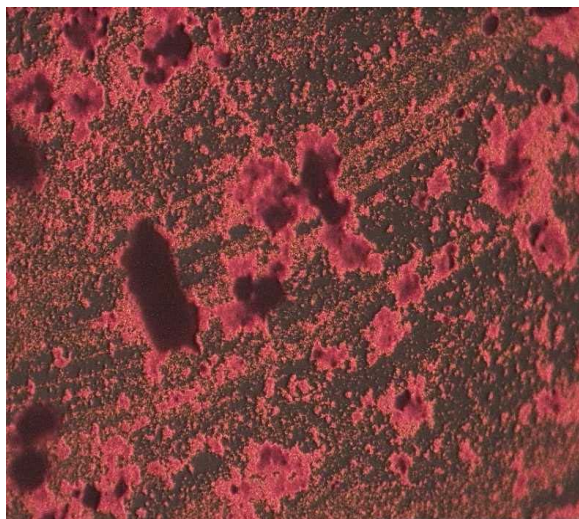
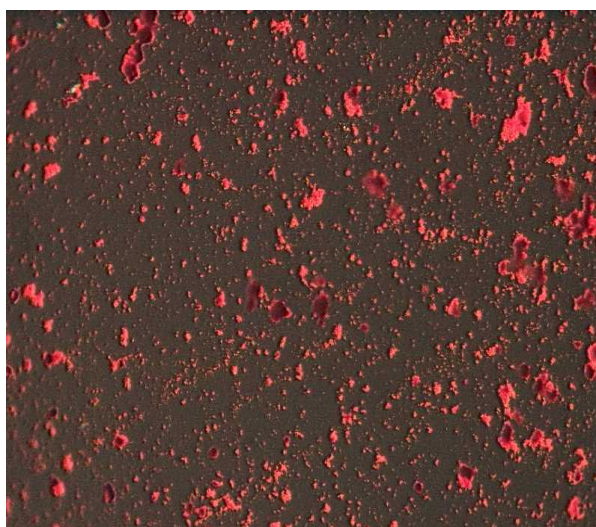


Figure 15
Optical Microscopy Pictures of Iron Oxide Samples

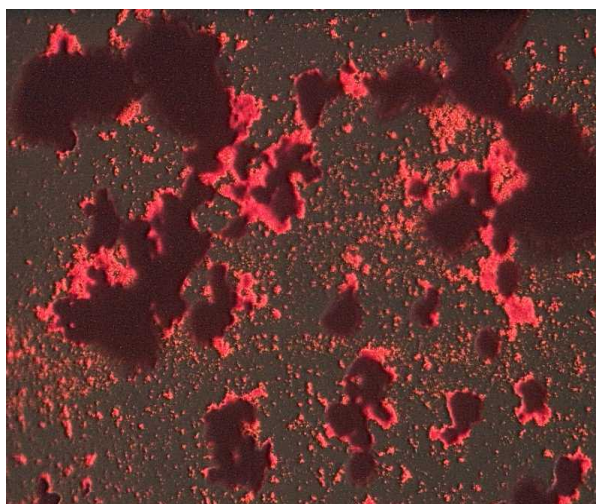
A. Control



B. In Presence of AA/SA/SS



**C. In Presence of AA/SA/SS
and Poly-Quat Biocide**



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