Iron oxide dispersants for industrial water systems: types, performance, and selection criteria

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Abstract

Dispersion of solid particles separating out from fluids is very important for fouling due to deposition of unwanted materials. Dispersion and stabilization of suspended matter *i.e.*, clay, silt, corrosion products, precipitating salts, etc., is often overcome by incorporating a dispersant in the water treatment formulation. In this paper a variety of non-polymeric, natural polyelectrolytes, synthetic, and hybrid polymers were evaluated for their efficacy as iron oxide (Fe₂O₃, hematite) dispersants for industrial water systems. Results reveal that performance of dispersants strongly depends on dispersant dosage, dispersing time, dispersant architecture, and the impurities present in water. Among the non-polymeric additives evaluated phosphonates perform better than polyphosphates. Surfactants (anionic, non-ionic) tested are ineffective iron oxide dispersants. Performance data on natural polyelectrolytes show that lignosulfonate exhibits better performance compared to humic, fulvic, and tannic acids. Based on the performance of synthetic polymers the order of effectiveness is: terpolymer > copolymer > homopolymer. Results on the impact of impurities (i.e., trivalent metal ions, biocides, hardness ions, etc.) suggest that these impurities show negative influence on the polymers performance. Discussion on dispersion mechanism and dispersant selection criteria is also presented.

Key words: iron oxide, suspension, stabilization, mechanism, dispersant, types, performance, cooling system impurities.

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1. Introduction

The major cause of performance deterioration in industrial water system is the deposition of undesirable materials (foulants) on equipment surface. Affected application areas include boiler, cooling, geothermal, power generation, and other production processes. The problems associated with these foulants include: (a) flow restriction including blocked pipes, (b) reduced heat transfer due to the insulated characteristics of the foulants, (c) increased energy cost, (d) under deposit corrosion, and (e) premature equipment replacement [1]. Recently, the application of reverse osmosis (RO) membrane-based process has increased significantly. RO applications in the food processing industry are developing broadly and include fruit and vegetable juices, processing of milk, sugar, fats, and meat by-products. The RO process has become an integral and vital process in the desalination of brackish/sea waters, and ground water for potable water and industrial needs. In addition, RO processes are used widely in the production of high purity water for pharmaceutical, semiconductor, and power industries [2].

RO membranes are susceptible to fouling by a variety of materials *i.e.*, minerals, corrosion products, microbiological mass, suspended matter, *etc.* The fouling of RO membrane is a complex phenomenon involving the deposition of several different but related types of foulants on the membrane surface. RO system fouling problems are becoming more prevalent as the use of low quality feed water increases. In addition, surface water treated with cationic organic flocculants poses very different and challenging fouling problems. The following sections briefly discuss commonly encountered foulants in industrial water systems.

1.1 Inorganic fouling (scaling)

Scaling of heat exchanger, equipment, and RO membrane surfaces is caused by the precipitation of sparingly soluble salts dissolved in the feed water. During the industrial process such as cooling, desalination, oil and gas production, the solubility of scale forming minerals can be exceeded and precipitation may occur. Commonly encountered scale include carbonate, sulfate, and phosphate salts of alkaline earth metals. Occasionally, sulfides of copper and iron, and silica/silicate salts are also encountered. Scaling in industrial water system is generally controlled by the use of chemical additives. Figure 1A presents an example of scaling in industrial installation.



Figure 1. Photographs of metal tube fouled with mineral scale (A), cooling tower fill coated with gelatinous biofilm (B), and suspended matter fouling on RO membrane spacer (C).

1.2 Microbiological fouling

Fouling by microorganisms generally is a comparative slow process and thus, in many cases for a long period of time it is not detected. Biofouling can have several adverse effects on membrane systems including membrane biodegradation, increased poor quality and quantity of produced water, increased differential pressure, and increased energy consumption. Biofouling can occur when the feed and re-circulating waters contain sufficient nutrients to sustain rapid growth of organisms. Because microorganisms attach to heat exchanger and other metal-based surfaces, especially in the low lying areas, these are ideal conditions for optimum growth. In most re-circulating water systems, a thin biofilm is formed on the heat exchanger surface that does not interfere with short term performance. However, during long periods of operation, biofilm accumulates thereby affecting heat transfer efficiency. Additionally, biofouling is an expensive problem due to increased usage of biocides, cleaners, and antifouling agents. Biofouling is generally controlled by the use of various chemical agents that kill or slow down the growth of microorganisms. An example of biofouling on heat exchanger surface is presented in Figure 1B.

1.3 Suspended matter fouling

Fouling by suspended and colloidal matter is a constant threat to the efficient operation of industrial water system. Certain feed waters, especially surface waters, require far more extensive pretreatment than other sources such as deep well. Suspended matter typically encountered in industrial water system include clay, silt, organic debris, precipitated salts, corrosion products, *etc.* Changes in feed water composition can occur because of seasonal variations in the water supply. Heavy particles settle on a horizontal surface due to gravity and fine particles settle onto heat exchanger surfaces at different inclinations due to surface force or other mechanisms [3]. Feed waters containing suspended matter are typically treated with flocculating/coagulating agents. Currently, a variety of inorganic and organic clarifying agents are available, however, the performance of these agents depends on various factors including type of clarifying agent, dosage, mixing time, pH, and residence time. Figure 1C shows an example of suspended matter fouling on an RO membrane.

2. Suspended matter: types, sizes, and other characteristics

As noted above fouling of heat exchangers, pipes, RO membranes, *etc.*, is caused by various foulants. The focus of the present paper is on suspended matter fouling. In the following sections we will cover the mechanisms of suspended matter fouling, control strategies, types of additives available to mitigate fouling, *etc.*

Colloidal and suspended 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:

Inorganic – such as silt, clay, corrosion products, precipitated salts such as calcium carbonate, calcium phosphate, calcium sulfate, *etc*.

Organics – examples include humic substances (*e.g.*, humic acid, fulvic acid, tannic acid), debris from dead organisms.

Coagulating/flocculating by-products – such as aluminum hydroxide, iron hydroxide from upstream feed water treatment by aluminum and iron-based flocculating agents and cationic polymeric flocculants (*e.g.*, diallyldimethyl ammonium chloride).

Cationic-anionic polymer salts – Under certain system operating conditions any residual cationic polymer present in re-circulating water due to "carryover" can react with anionic polymeric scale control agents (*e.g.*, poly(acrylic acid), poly(maleic acid)) to form colloidal suspension. Collectively, these inorganic, organic, and coagulating/flocculating agent by-product sources comprise the particulate mass and concentration in feed waters.

Colloidal and suspended matter typically present in surface water fall into 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 2 presents how particle size affects the tendency of particles to settle as a function of time in undisturbed water [3]. It is evident from Figure 2 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. It is interesting to note that 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 is also worth noting that particles >100 microns are visible to the naked eye and are considered to be settable solids. Generally, particles <10 micron are considered to be colloidal and particles <0.1 micron are visible by electron microscope.



Figure 2. Particles settling time as a function of time in an undisturbed system.

2.1 Fouling control strategies

Solid particles attract each other. For this reason, energy (mechanical and/or chemical) is needed to separate the particles from each other. To mitigate particulate fouling by chemical means, dispersants are used to reduce the surface tension of deposits. Dispersants are very helpful in keeping the foulants away from the surface. In addition, corrosion inhibitors can be used to reduce corrosion. Crystal modifying agents can be used to mitigate fouling problem. Commonly used crystal modifying agents include homo- and copolymers of acrylic acid and maleic acid. These polymers distort the crystal habit and inhibit the formation of large crystals. The distorted crystal do not settle on the heat exchanger surface, but remain suspended in the bulk solution. Mitigation of fouling by other methods *i.e.*, increase in flow velocity, pulsating flow, mechanical vibration of heat exchanger surfaces, reversal of flow, *etc.*, has been reported [4].

2.2 Dispersion mechanism

The dispersion is generally defined as a suspension of insoluble particles formed either through the de-flocculation, *i.e.*, breaking down of agglomerated particles, or from the stabilization of small suspended particles. The solid/liquid dispersion technology has many domestic and industrial applications. The suspension of particular matter by detergents for their removal in the rinse cycle of the washing machines is the principal example. Industrial applications of dispersant technology include paints, cosmetics, inks, and pulp and paper manufacturing.

Several types of additives can be used in the dispersion process in which solid particles, like iron oxide, clay, precipitated mineral, pigment, *etc.*, are dispersed and stabilized. Suspension and stabilization of particulate matter by the use of a chemical agent (dispersant) is a complex phenomenon. However, it is generally believed that the dispersion process consist of three steps namely; wetting of the suspended solid, breaking up of the large particles, and stabilization of primary particles [5]. The following section presents discussion on the three steps:

2.2.1 Wetting of the Suspended Solid: Wetting is the first step in the dispersion process. The wetting process depends on various factors including surface properties of the particles, characteristic of dispersion medium, and the type of dispersant. Wetting will occur when the surface tension of the liquid is low compared to the surface energy of the solid particles. In general, non-ionic polymers exhibit good wetting properties. However, some of these polymers may contribute to undesirable foaming. It should be recognized that not all dispersants (polymeric or non-polymeric) show good wetting/surfactant properties.

2.2.2 De-agglomeration (breaking up) of large particles: In this process large aggregates are de-agglomerated to small (primary) particles by mechanical energy for easy adsorption of the dispersant molecules. Various factors including agglomerate type and

size, wetting characteristics, bonds between particles in the agglomerate, etc., play roles in the de-agglomeration process.

2.2.3 Stabilization of the Primary Particles: The suspended matter typically encountered in industrial water applications generally carry a slight negative charge under the operating conditions. Therefore, anionic chemical compounds are normally the most efficient dispersants because they increase negative surface charge via adsorption process thereby stabilize primary particles in suspension. Although cationic polymers can potentially be used as dispersants, this requires relatively high polymer concentration in order to first neutralize the negative surface charges and then to transfer cationic charge to particles for efficient dispersion. Additionally, the use of cationic charged dispersants may not be practical for cooling system operating under alkaline conditions due to lack of cationic charge present on the dispersant molecules.



Figure 3. Various steps involved in the dispersion process.

3. Dispersant types, structures, and performance

During the last three decades, efficient operation of industrial water systems has become increasing important due to several factors including environmental constraints, lack of good quality feed water, increased use of plant waste water, increased cost of feed water, operating systems under higher cycles of concentrations, increased produced water from RO based process, *etc.* Recently, a large variety of dispersants (polymeric and non-polymeric) have been developed and are currently incorporated into water treatment formulations for effective control of deposition of unwanted materials on equipment and RO membrane surfaces.

Additives commonly used to disperse suspended matter in industrial water system fall into the following four categories:

- (a) Non-polymeric *i.e.*, polyphosphates, phosphonates, surfactants, *etc.*
- (b) Natural materials *i.e.*, lignosulfonates, tannic and humic acids, starch, alginate, *etc.*

- (c) Synthetic polymeric materials *i.e.*, homo-polymers of acrylic acid, methacrylic acid, maleic acid, aspartic acid, itaconic acid, and acrylic/maleic acid based co-and terpolymers containing monomers with different functional groups.
- (d) Hybrid polymers *i.e.*, carboxymethyl inulins with different degree of carboxylation.

The following sections provide details on the dispersant structures and their performance.

3.1 Non-polymeric additives performance

Numerous studies have been published and several patents have been issued since the earlier work regarding the control of scale forming minerals by threshold agents. In addition, polyphosphates have been reported to exhibit particulate matter dispersion, stabilization of metal ions such as copper, iron, and manganese, and control of aqueous corrosion of metals. Organophosphonates are a class of compounds which contain a phosphorus-carbon bond (P–C) bond unlike the P–O bond present in polyphosphates. As illustrated in Table 1 additives vary significantly both in terms of molecular weight and the functional groups (*i.e.*, -OH, $-PO_3H_2$, -COOH, $-SO_3H$, R_1-O-R_2 , *etc.*) *etc.*, present in the polyphosphates, phosphonates, and surfactants.

Additive	Functional Group	Ionic Charge	MW	Acronym
Sodium pyrophosphate	Р-О-Р	Neutral	266	РҮР
Sodium hexametaphosphate	P-O-P	Neutral	612	HMP
Sodium tripolyphosphate	P-O-P	Neutral	368	TPP
Hydroxyphosphono acetic acid	-COOH -PO ₃ H ₂ -OH	Anionic Anionic Non–ionic	156	HPA
Aminotris(methylene phosphonic acid)	$-PO_3H_2$	Anionic	299	AMP
Hydroxyethylidine 1,1-diphosphonic acid	-PO ₃ H ₂ -OH	Anionic Non–ionic	206	HEDP
2-phosphonobutane 1,2,4-tricarboxylic acid	-COOH -PO ₃ H ₂	Anionic Anionic	270	PBTC
Polyether polyamino phosphonic acid	$-PO_{3}H_{2}$ -O-(ether)	Anionic Non–ionic	600–630	PAPEMP
Sodium xylene sulfonate	-SO ₃ Na	Anionic	208	SXS
Cocamidopropyl betaine	$R_1R_2N^+R_3$ -COO	Anionic Cationic	342	CAPB
Octylphenolethoxylate	$R_1 - O - R_2$	Neutral	625	OPE

Table 1. Polyphosphates, phosphonates, and surfactants evaluated.

3.1.1 PAPEMP performance vs. dosage

To study the dispersing activity of phosphonates, several experiments were carried out in the presence of varying concentrations of PAPEMP using iron oxide dispersancy protocol described in our earlier publication [6]. Percent dispersion (%D) data, calculated using the equation reported earlier [6], presented in Figure 4 clearly show that percent dispersancy (%D) values increase with increasing dispersion time and increasing PAPEMP concentration. For example, %D value obtained at 0.5 and 1.0 h in the presence of 1.0 mg/L of PAPEMP are 11 and 18% respectively, compared to 24% obtained at 3 h. Dispersion data presented in Figure 4 also show that %D value increases with increasing PAPEMP concentration. For example, at 3 h %D values obtained in the presence of 1.0 and 3.0 mg/L are 24 and 28%, respectively. As illustrated, increasing the PAPEMP concentration by twofold (*e.g.*, 5 to 10 mg/L) does not significantly increase the %D value.



Figure 4. Iron oxide dispersion as a function of time and in the presence of varying concentration of PAPEMP.

To compare the performance of various phosphonates and polyphosphates, a series of experiments were carried out in the presence of 5.0 mg/L of additives. It is evident from Figure 5 that all additives exhibit poor performance (<25%D) as iron oxide dispersants. It is worth noting that whereas addition of hydroxyl and/or carboxyl groups (*e.g.*, HEDP, PBTC) does not seem to improve the dispersing ability of phosphonates, the incorporation of neutral moiety *i.e.*, polyether, appears to enhance the PAPEMP performance. The poor performance shown by phosphonates may be attributed to either poor adsorption of phosphonate molecules on iron oxide particles and/or weak interactions between the functional groups present in phosphonates and iron. It is worth noting that whereas phosphonates *i.e.*, CaCO₃, CaHPO₄·2H₂O, CaSO₄·2H₂O, *etc.* [7–9]. Based on the data presented in Figure 5, phosphonates as iron oxide dispersants may be ranked as follow: PAPEMP > HEDP ~ AMP ~ PBTC > HPA.



Figure 5. Comparative iron oxide dispersion data at 3 h in the presence of 5.0 mg/L of phosphonates, polyphosphates, and surfactants.

The performance of phosphonates as inhibitors for calcium carbonate (CaCO₃) and calcium sulfate dihydrate (CSD) has been reported [10,11]. Results of these studies reveal that efficacy of phosphonates depends upon the concentrations of phosphonates present in the scaling system. For example, the performance trend observed for CaCO₃ in the presence of 5.0 mg/L phosphonates (at 180x saturation) is HEDP \geq AMP >> PBTC. However, at higher concentrations of phosphonates (*i.e.*, 40 mg/L) the performance trend observed is PBTC >> HEDP \geq . The improved performance of PBTC at higher CaCO₃ saturation has been attributed to better tolerance of PBTC to calcium ions under alkaline pH conditions. It is interesting to note that for CSD scaling system the performance trend observed for phosphonates is: AMP >> PBTC > HEDP \sim AMP. Thus, it is clear that phosphonate performance depends on both the type of phosphonate and scaling system being investigated.

The efficacy of various polymphosphates was also evaluated. Data presented in Figure 5 reveal that all polyphosphates evaluated exhibit poor performance as iron oxide dispersants. Additionally, efficacy data on various anionic (*i.e.*, sodium xylene sulfonate, SXS), zwitter ion surfactant (*i.e.*, cocamidoprpyl betaine), and non-ionic surfactant (*i.e.*, octyphenol ethoxylate, OPE) also show that surfactants under the conditions tested are ineffective (< 5%D) as iron oxide dispersants.

Based on the data presented the non-polymeric additives may be ranked as follows: Phosphonates >> polyphosphates \geq surfactants.

3.2 Natural additives performance

Natural polymers *i.e.*, starches, lignosulfonates, alginates, and natural organic polyelectrolytes including humic, fulvic, and tannic acids were also evaluated for their efficacy as iron oxide dispersants. Natural organic polyelectrolytes such as tannic substances are commonly encountered in surface water and ground water used for water supply. Humic substance are generally considered to be composed of three operationally distinct fractions: (1) fulvic acid (FA), which is soluble in both acidic and basic solution,

(2) humic acid, which is soluble in basic solutions, but insoluble in acidic solutions. The bulk of river water humic substances generally resemble more readily solubilized FA, with the relative amount of less soluble humic acid probably being dependent on the pH of the natural water. Natural polymers such as starches, aliginates, and lignosulfonates have been used for years to disperse particulate matter in industrial water systems. These polymers function as dispersants but their performance is very sensitive to high temperature normally encountered in treating boiler water.

Lignosulfonates (LSs) are chemically modified biopolymers that are produced during the production of cellulose with the use of sulfites. The biopolymer basis of LS is lignin, found in wood and other plants. The structure of LS contains two functional groups (phenolic (-OH) and $-SO_3H$) responsible for surface-active properties. Table 2 lists structures, functional groups, and MW of natural additives tested.

Additive	Functional Group	Ionic Charge	MW	Acronym
Tannic acid	-COOH	Negative	N/A	TA
Humic acid	-COOH	Negative	N/A	HA
Fulvic acid	-COOH	Negative	N/A	FA
Alginatic acid (Na)	-COOH	Negative	216	ALG
Starch	С–О–С, –ОН	Neutral	N/A	ST
Lignosulfonate	$-OH, -SO_3H$	Negative	2.300	LS

 Table 2. List of natural additives tested.

Figure 6 presents performance data on natural polymers and organic polyelectrolytes. It can be seen that the LS containing a strong acidic group (*i.e.*, $-SO_3H$) exhibits good performance compared to other additives evaluated containing either a carboxyl group (-COOH) or non-ionic groups (-OH, C-O- in starch *etc.*). The better performance shown by LS compared natural organic polyelectrolytes, *i.e.*, FA, TA, HA, *etc.*, may be attributed strong affinity of $-SO_3H$ group over -COOH with iron oxide particles. Based on the data presented the ranking of natural additives in terms of decreasing effectiveness follows: $LS > HA > FA >> ALG \sim ST$.



Figure 6. Iron oxide dispersion at 3 h in the presence of 1.0 mg/L of various natural additives.

3.4 Synthetic polymers performance

During the last three decades, a variety of acrylic acid- and maleic acid-based homo-and copolymers have been developed to treat various scaling and deposit problems in industrial water installations including boiler, cooling, desalination, geothermal, and oil and gas production. These polymers serve three objectives: (1) to inhibit precipitation of scale forming salts, (2) to complex and/or stabilize metal hydroxides *i.e.*, Cu, Mn, Fe, Zn., *etc.*, and (c) to disperse suspended matter, that is, corrosion products, clay, and silt. In the case of supersaturated solutions of sparingly soluble salts, polymer interferes with the nucleation and crystal growth processes via the interactions of metal ions (*i.e.*, Ca, Ba, Sr, Mg) with the functional groups (*i.e.*, -COOH, -SO₃H) present in the polymer. The metal ions–polymer interactions not only delay the precipitation of sparingly soluble salts but in some cases polymer also influences the crystal morphology of the sparingly soluble salts.

Homo-polymers: The performance of homopolymers (Table 3) containing different functional groups was investigated by carrying out a series of dispersion experiments under similar experimental conditions. Figure 7 shows %D data as a function of time for experiments conducted in the presence of 1.0 mg/L of polymers. It can be seen that performance of –COOH group containing polymers *i.e.*, PAA, PMA, PMAA depends on dispersion time. For example, %D values obtained in the presence of 1.0 mg/L of PAA at 1 and 2 h are 20 and 29% respectively, compared to 33% obtained at 3 h. It is worth noting further increase in dispersion time *i.e.*, from 3 to 4 h does not exhibit any significant improvement in PAA performance as iron oxide dispersant. Data presented in Figure 6 also reveals that ionic charge of the functional group present in the polymer also plays an important role in dispersing iron oxide particles in aqueous solution. For example, %D values obtained in the presence of 1.0 mg/L PAA and PMAA are 33 and 20% respectively, compared to <5% obtained for polymers containing non-ionic groups *i.e.*, PEOX, PVP, PAM.

Functional Group	Ionic Charge	MW	Acronym
-COOH	Negative	6,000	PAA
-COOH	Negative	900	PMA
-COOH	Negative	6,000	PMAA
-CONH ₂	Negative	6,000	PAM
-N- CO	Neutral	5,000	PEOX
-CH- N	Neutral	15,000	PVP
–COOH –SO ₃ H	Negative	<15,000	PASA
-COOH	Negative Neutral	<10,000	PMVP
–COOH –COOR	Negative Neutral	7,000	PAHP
-COOH -SO ₃ H	Negative	<15,000	PASS
-COOH -C-O-C	Negative Neutral	3,500	CMI-15
	Functional Group $-COOH$ $-COOH$ $-COOH$ $-CONH_2$ $-CONH_2$ $-COH$ $-COH$ N $-COH$ $-COH$ $-COH$ $-COH$ $-COH$ $-SO_3H$ $-COOH$ $-COOH$ $-SO_3H$ $-COOH$ $-SO_3H$	Functional GroupIonic Charge $-COOH$ Negative $-COOH$ Negative $-COOH$ Negative $-CONH_2$ Negative $-CONH_2$ Neutral $-COH -$ CO Neutral $-COH -$ N Neutral $-COOH$ $-SO_3H$ Negative $-COOH$ $-COOH$ Negative Neutral $-COOH$ $-COOH$ Negative Neutral $-COOH$ $-COOH$ Negative Neutral $-COOH$ $-SO_3H$ Negative Neutral $-COOH$ $-SO_3H$ Negative Neutral $-COOH$ $-SO_3H$ Negative Neutral	Functional GroupIonic ChargeMW $-COOH$ Negative $6,000$ $-COOH$ Negative 900 $-COOH$ Negative $6,000$ $-CONH_2$ Negative $6,000$ $-CONH_2$ Negative $6,000$ $-CONH_2$ Neutral $5,000$ $-COH{1}$ Neutral $5,000$ N Neutral $15,000$ $-COOH_{Negative}$ $<15,000$ $-COOH_{-SO_3H}$ Negative $7,000$ $-COOH_{-COOR}$ Negative $7,000$ $-COOH_{-SO_3H}$ Negative $<15,000$ $-COOH_{-SO_3H}$ Negative $3,500$

Table 3. List of homo-, co- and hybrid polymers investigated.

Carboxylmethylinulin

It is interesting to note that although PVP and PEOX exhibit poor performance as iron oxide dispersant, these additives however, has been shown to exhibit good to excellent performance for silica polymerization process [12, 13]. Thus, it is clear that performance of additive as a dispersant and/or inhibitor depends on both the inhibitor architecture and nature of the particles to be dispersed and/or scaling system being inhibited.

-COOH

-C-O-C

Negative

Neutral

4,500

CMI-25

Co-and terpolymers: To under the impact of second or third monomer containing different functional groups, a number of experiments was conducted under similar experimental conditions. Results illustrated in Figure 7 clearly show that substituting partly acrylic acid or maleic acid with monomers containing bulkier and hydrophobic groups significantly improves the performance of copolymers. For example, %D values obtained at 3 h for PAA and PMA are 33 and 42%, respectively, compared to 66 and 74% obtained for PASA and PMSS. Interesting, incorporating a third monomer (*i.e.*, sulfonated styrene) in PASA results in marked improvement in the terpolymer (PASS) performance.



Figure 7. Plots of %D vs. time in the presence of various hompolymers (1 mg/L).

3.3 Hybrid polymers performance

Recently, there has been increasing interest in the development and application of biodegradable, environmentally friendly biopolymers. Carboxymethyl inulin (CMI) is a chemical derivative produced by carboxymethylation of inulin, a polysaccharide based polymer present in roots of chicory plants. Figure 8 presents dispersion data collected in the presence of 1.0 mg/L of CMI-15 and CMI-25. It can be seen that additive performance as iron oxide dispersant depends on the nature of the functional group. As shown, CMIs performance is strongly affected by the degree of carboxylation *i.e.*, CMI-25 with 25% degree of carboxylation performs better than CMI-15 with 15% degree of carboxylation. For comparison, performance data on LS and PASS are also illustrated in Figure 8. It is interesting to note among the additives tested from three categories namely; natural, synthetic, and hybrid polymers, PASS exhibits the best overall performance in dispersing iron oxide in aqueous solution.



Figure 8. %D dispersion data for hybrid and synthetic polymers (1 mg/L, 3 h).

According to the data presented in Figure 8, polymers efficacy as iron oxide dispersant is: terpolymer > copolymer > homopolymer \ge hybrid polymers.

4. Hardness ions concentration effect

Waters containing high levels of hardness ions (*i.e.*, Ca, Mg) create challenging operating conditions that demand high performance scale control and dispersing agents. To understand the impact of hardness ions on the performance of dispersants, a series of experiments were carried out in the presence of 1.0 mg/L dispersant and varying concentrations of calcium ions. Figure 9 presents dispersion data on hybrid polymer (*i.e.*, CMI-25), natural polymer (*i.e.*, LS), copolymer (*i.e.*, PAHP), and terpolymers (*i.e.*, PASS). The data clearly show that Ca ions concentrations exhibit a marked antagonistic influence on the performance of polymers. It is interesting to note that PASS compared to CMI-25 and LS, retains better dispersancy activity in the presence of harness ions. The decline in polymer performance may be attributed to the shielding of iron oxide particles by Ca ions, precipitation of Ca-polymer salts, or the increase in random coil nature of the polymer chain in high hardness water.



Figure 9. Effect of hardness ions on polymers performance (1 mg/L, 3 h).

5. Trivalent metal ions effect

Aluminum and iron-based compounds (*e.g.*, alum, ferric chloride) have been utilized for decades as coagulating aid 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 and boiler waters that can affect the performance of treatment programs.

The impact of trace levels of trivalent ions on the dispersancy activity was carried out under similar experimental conditions. Dispersancy data collected in the presence of 1.0 mg/L polymers and 1.0 mg/L of Al^{3+} and Fe^{3+} at 3 h are shown in Figure 10. It is evident from the data that both trivalent ions exhibits antagonistic effect on the performance of homo-, co-, and terpolymers. It is interesting to note that reduction in polymers performance is more pronounced in the presence of Al^{3+} than in Fe^{3+} .



Figure 10. Effect of 1.0 mg/L of Al^{3+} and Fe^{3+} on polymers performance (1.0 mg/L, 3 h).

6. Biocide concentration effect

Currently, a variety of biocides, biodispersants, biostats is commercially available and used to prevent microbiological growth as well as disperse dead biomass in industrial water. The two commonly used biocides are oxidizing and non-oxidizing. 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 feed pump stops. Oxidizing biocides also react with contaminants like hydrogen sulfide, ammonia, pulp, lignin, and other organics. Non-oxidizing biocides are often used in system that are incompatible with chlorine, such as water high in organic matter or ammonia.

The impact of oxidizing biocide (chlorine as hypochlorite, OCl) and non-oxidizing biocide (glutaraldehyde, GLT), at 10 mg/L and cationic biocide (polyquat) at 1.0 mg/L was investigated with 1.0 mg/L of homopolymer *i.e.*, PMA, and copolymers *i.e.*, PMAS, PAHP, PASS. It can be seen that OCl and GLT even at higher concentration (*i.e.*, 10 mg/L) exhibit no significant effect on the dispersing ability of the homo- and copolymers. As illustrated in Figure 11, the strong antagonistic effect shown by cationic charge biocide (polyquat) on polymers may be attributed to the formation of complex formed with anionic polymers, which results in the reduction of anionic polymer concentration.



Figure 11. Effect of oxidizing (1 mg/L) and non-oxidizing (10 mg/L) biocides on polymers performance (1.0 mg/L, 3 h).

7. Dispersant Selection Criteria

The use of synthetic deposit control polymers in water treatment applications has increased dramatically since the 1950s. The demands on deposit control polymer performance have increased significantly due to trends toward operating cooling water systems using more environmentally friendly corrosion inhibitors and under more severe operating conditions to increase process efficacy, safety, and water conservation. Modern deposit control polymers have multifunctional properties that are typically the key to the successful water treatment program application/performance.

The selection of polymer for a particular application can be very challenging and time consuming process. Water treatment technologists must consider a myriad of factors and have a great variety of polymers available from several manufacturers. Polymers used in water treatments are characterized in many ways including composition, molecular weight, charge density, ionic charge, and product form (solid or liquid) [14].

Criteria for selecting a dispersant should include:

- Suspended matter characteristics (*i.e.*, clay, corrosion products, calcium carbonate, *etc.*)
- Effective at low dosages
- Compatible with chemicals commonly used in water treatment formulation
- Hydrolytically stable: amide (-CONR₁R₂ and ester (-COOR) groups are susceptible to hydrolysis especially when formulated in alkaline conditions, and may result in some performance loss.
- Retains activity in the presence of high calcium and magnesium
- Tolerant to high temperature conditions (compared to carboxyl group, amide and ester groups are prone to thermal degradation, and may affect some performance loss).
- Compatible with cationic biocides
- Tolerant to cationic flocculants/coagulants

- Environmental acceptability
- Retains activity in the presence of iron and aluminum

Summary

Successful water treatment formulations incorporate a variety of additives to effectively control mineral scales, suspended solids, corrosion, and microbiological growth in industrial water systems. Typical additives used include polyphosphates, phosphonates, homo- and copolymers containing a variety of monomers with different functional groups, and molecular weight. Biocides are fed separately to control microbiological growth in industrial water system. The ability of dispersants to retain activity in the presence of other treatment chemicals should be a key selection criteria for deposit control polymers.

The study shows that:

- The iron oxide dispersancy increases with increasing dispersion time and dispersant dosages,
- Dispersancy activity strongly depends on the nature of the functional group(s). In general, dispersants containing strong acidic group (*i.e.*, -SO₃H) and hydrophobic and bulkier monomer(s) are better dispersants than polymers containing neutral and/or weak acidic groups.
- Among the non-polymeric additives tested phosphonates perform better than polyphosphates as iron oxide dispersants.
- The order of effectiveness for natural additives is: LS > HA > TA > FA >> ALG, ST.
- Among synthetic polymers the order of effectiveness is: terpolymer > copolymer > homopolymer
- Dispersant performance strongly depends on the concentration of hardness ions.
- Among the trivalent metal ions evaluated, Al³⁺ ions shows a greater negative impact than Fe³⁺ on the performance of dispersants.
- Cationic biocide show marked antagonistic effect on dispersant performance.

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