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Dispersion of iron oxide particles in industrial waters

The influence of polymer structure, ionic charge, and molecular weight

This paper deals with studies on the influence of polymeric and non-polymeric materials on the dispersion of iron oxide particles in aqueous system. The aim of the work was to evaluate the performance of a variety of additives as iron oxide dispersants. The polymers investigated include homopolymers of acrylamide, vinylpyrrolidone, acrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid, and acrylic acid based copolymers containing a variety of functional groups. It has been found that the addition of low levels of copolymers to the iron oxide suspension has a marked effect in dispersing iron oxide particles. The dispersancy data of several polymers indicate that the performance of the polymer depends upon the functional group, molecular weight, composition, and the ionic charge of the polymer. The results on non-polymeric materials such as polyphosphates, phosphonates, and surfactants show that these additives, compared to copolymers are ineffective as iron oxide dispersants.

In dieser Arbeit wird der Einfluß von polymeren und nicht-polymeren Stoffen auf die Dispergierung von Eisenoxidpartikeln in wäßrigen Systemen untersucht. Ziel dieser Arbeit war es, die Wirkung verschiedener Additive als Eisenoxid-dispergatoren zu bewerten. Die untersuchten Polymere waren homopolymeres Acrylamid, Vinylpyrrolidon, Acrylsäure, Maleinsäure, 2-Acrylamido-2-Methylpropansulfonsäure und Copolymere auf Acrylsäurebasis mit verschiedenen funktionellen Gruppen. Die Zugabe von geringen Mengen Copolymeren zur Eisenoxidsuspension hat einen deutlichen Einfluß auf die Dispergierung dieser Partikel. Die Daten zum Dispergierverhalten einiger Polymere zeigen, daß die Wirkung eines Polymers von der funktionellen Gruppe, dem Molekulargewicht, der Zusammensetzung und der Ionenladung des Polymers abhängt. Ergebnisse, die mit nichtpolymeren Substanzen wie Polyphosphaten, Phosphonaten und Tensiden erhalten wurden, zeigen, daß sich diese Additive nicht so gut als Dispergiemittel von Eisenoxid eignen wie Copolymere.

1 Introduction

A serious problem encountered in many industrial processes is the build-up of undesirable deposits on the walls of water handling equipment. The deposition of these materials, especially on heat exchanger surfaces in cooling, boiler, geothermal and distillation systems, leads to overheating, loss of system efficiency, unscheduled shutdown time, and ultimately heat exchanger failure. These deposits can be categorized into the following four groups:

- mineral scales i.e., CaCO_3 , $\text{CaSO}_4 \times 2\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$, CaF_2 , etc.
- suspended matter i.e., mud or silt
- corrosion products i.e., Fe_2O_3 , Fe_3O_4 , ZnO , CuO , etc.
- microbiological mass.

In a boiler, these deposits normally accumulate in low circulation areas, i.e., the bottom of the mud drum, and/or at the end of the steam drum in two drum boiler. These deposits may become immobilized during upset conditions resulting in deposits build-up in high input areas. In reverse osmosis systems, deposition of unwanted materials may result in a decrease in productivity, poor water quality, and premature membrane failure. In the oil industry, carbonates and sulfates salts of calcium, barium, and strontium are very common. The development of these salt layers on heat exchanger surfaces

results in production losses. Thus, effective operation of industrial water systems continues to depend on the control of deposits in these systems.

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

In cooling, boiler, and potable water applications iron-based deposits occur due to the presence of low levels of iron (soluble, colloidal) in feedwater, as a result of iron-based metal corrosion, and by the increased use of condensate for boiler feedwater. Although iron-based deposits are common in industrial water systems, there are no prognostic methods such as those for calcium sulfate, calcium carbonate or barium sulfate in use. Magnetite (Fe_3O_4) and hematite (Fe_2O_3) are the most common iron oxide deposits encountered in industrial water systems.

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 feedwater (involves the use of iron selective chelant)

- removing iron oxides (corrosion products) from the systems (utilizes chelation, filtration, etc.) and
- treating iron oxides in the feedwater/main system with good iron oxide dispersant to minimize iron oxide deposition within the system.

Starchy vegetables, modified corn starches, tannins, and alginates have been used for several decades as dispersants and crystal modifying agents. These deposit control agents are not in use today because of marginal performance, temperature stability problems, and nutrients for biological growth, especially in the case of starch.

In the mid fifties a search for improved boiler water deposit control agents resulted in the development of an entirely new class of additives based on synthetic polymers. The earlier polymers which found widespread use as dispersants were poly(acrylic acid), P-AA; poly(methacrylic acid), P-MAA; and poly(maleic acid), P-MA. Recently, a new class of co- and terpolymers has been developed in large part due to the improved thermal stability and adsorption properties of these polymers. Previous studies [1–4] have shown that polymer performance as inhibitor for mineral scales strongly depends on the polymer characteristics i.e., molecular weight, type of comonomer, ionic charge of comonomer, etc.

In addition to the differences due to polymer characteristics, other factors including solution pH, temperature, ionic strength, and cation type and concentration can influence the performance of polymer as scale inhibitor or particulate dispersant. In previous papers, from our laboratories we have demonstrated that acrylic acid-based co- and terpolymers, compared to homopolymers such as P-AA and P-MA, are excellent calcium phosphate and calcium phosphonate inhibitors for cooling water systems [5, 6]. In other studies, it was reported that for other minerals such as calcium fluoride, calcium sulfate, barium sulfate, etc., low molecular weight homopolymers i.e., P-AA, P-MA, etc. perform better than co- and terpolymers thus suggesting that carboxyl group plays a key role in influencing the inhibitory power of the polymer.

Historically, the performance of polymers for mineral scale control has been heavily researched. However, the effect of polymer characteristics on particulate matter dispersion, especially for iron oxide, has been mostly overlooked. This paper explores the influence of several synthetic polymers as dispersants for iron oxide particles in aqueous system. The performance of a variety of polymers of varying composition, ionic charge, and molecular weight as iron oxide dispersants has been compared with natural dispersants and with other additives commonly used in water treatment formulations. Additionally, the polymers that have been exposed to thermal treatment were also evaluated for their dispersancy power. Optical microscopy was also used to study the effect of various polymers on iron oxide particle size and morphology. The results presented in this study help explain why a specific polymer does not perform as expected, and how polymer dosage can be adjusted to achieve optimum performance.

2 Experimental

Reagent grade chemicals and grade A glassware were used. Polymer solutions were made as 1000 mg/l (active polymer). The iron oxide (Fe_2O_3) used in this investigation was obtained from Fisher Scientific Co. The iron oxide dispersancy test was carried out as follows:

A known amount (0.12 g) of iron oxide was added to synthetic water (600 ml) containing a known amount of polymer (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 has the following elemental analysis: 100 ppm Ca, 30 ppm Mg, 314 ppm Na, 571 ppm chloride, 200 ppm sulfate, and 60 ppm bicarbonate.

In a typical test, six experiments were run simultaneously using a gang-stirrer. The gang-stirrer was set to 100 rpm (revolutions per minute) speed. At known time intervals transmittance readings (%T) were taken with a Brinkmann PC/1000 colorimeter using 440 nm filter. Dispersancy (%D) was calculated from %T readings measured at 3 hr as a function of the amount of iron oxide dispersed. The data presented in this study had good reproducibility ($\pm 5\%$ or better). The performance of the polymer was determined by comparing the %D values of the slurries containing polymer against control (no polymer). Greater dispersancy was therefore indicated by higher %D value. At the end of the experiments, samples were withdrawn and were examined by optical microscopy for particle size reduction. The analytical characteristics of the polymers evaluated in this study are summarized in Table 1.

A solution of polymer (530 g) was prepared containing 1% polymer (as the free acid) at pH 10.5. Sodium sulfite (0.3 g) was added as an oxygen scavenger. A 7 g sample of the polymer solution was retained. The balance was charged to a 2 liter 316 stainless steel stirred Parr Mini-Reactor. The polymer solution was heated with stirring at 150°C for 20 hours. The reactor was cooled and opened. A small amount of thermally treated polymer solution was removed for dispersancy tests. The balance of the polymer was dried for polymer characterization.

3 Results and discussion

3.1 Effect of synthetic polymers

3.1.1 Polymer concentration

The experimental conditions employed and the results of iron oxide dispersancy experiments are summarized in Table 2. In Fig. 1 profiles of %D-polymer concentration for two dispersants namely homo polyacrylic acid, P-AA, and terpolymer, P-AA:SA:SS are illustrated. The data clearly indicate that polymer concentration strongly affects the ability of a polymer to disperse iron oxide. For example, at a 0.25 ppm concentration P-AA shows poor dispersancy ($< 25\%$). However, as the polymer concentration is increased from 0.25 to 0.50 ppm concentration, polymer performance is significantly improved and maximum dispersancy is obtained at 1.0 ppm.

The %D vs. polymer concentration profile for P-AA:SA:SS as presented in Fig. 1. reveals that terpolymer is more effective than the P-AA in dispersing iron oxide particles in aqueous solution. This observed difference in polymer performance between terpolymer and homopolymer is consistent with earlier studies [5, 6] on these polymers as inhibitors for mineral salts thus suggesting that compared to the carboxyl group, the sulphonic acid(s) group exhibits stronger influence on the dispersancy power of the polymer.

Table 1. Inhibitors referenced in the present study

Inhibitor	Structure	Acronym	Designation
poly(acrylic acid)	$\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})\text{--}_n$	P-AA	GOOD-RITE K-732 ^a
poly(maleic acid)	$\text{--}(\underset{\text{COOH}}{\text{CH}}\text{--}\underset{\text{COOH}}{\text{CH}})\text{--}_n$	P-MA	Experimental
poly(methacrylic acid)	$\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\overset{\text{CH}_3}{\text{CH}}})\text{--}_n$	P-MAA	Experimental
poly(acrylamide)	$\text{--}(\text{CH}_2\text{--}\underset{\text{CONH}_2}{\text{CH}})\text{--}_n$	P-AM	Experimental
poly(2-acrylamido-2-methylpropane sulfonic acid)	$\begin{array}{c} \text{--}(\text{CH}_2\text{--}\underset{\text{CO}}{\text{CH}})\text{--}_n \\ \\ \text{NH} \\ \\ \text{H}_3\text{C--C--CH}_3 \\ \\ \text{CH}_2\text{SO}_3\text{H} \end{array}$	P-SA	Experimental
poly(acrylic acid:hydroxypropyl acrylate)	$\begin{array}{c} \text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{CO}}{\text{CH}})_m\text{--} \\ \\ \text{H}_3\text{C--CH--CH}_3\text{OH} \end{array}$	P-AA : HPA	Experimental
poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:sulfonated styrene)	$\begin{array}{c} \text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{CO}}{\text{CH}})_m\text{--}(\text{CH}_2\text{--}\underset{\text{NH}}{\overset{\text{SO}_3\text{H}}{\text{CH}}})_p \\ \\ \text{H}_3\text{C--C--CH}_3 \\ \\ \text{CH}_2\text{SO}_3\text{H} \end{array}$	P-AA : SA : SS	GOOD-RITE K-798 ^a
poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:substituted acrylamide)	$\begin{array}{c} \text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{CO}}{\text{CH}})_m\text{--}(\text{CH}_2\text{--}\underset{\text{CO}}{\text{CH}})_p \\ \quad \quad \quad \quad \quad \quad \\ \text{NH} \quad \quad \quad \text{NH} \quad \quad \quad \text{NH} \\ \quad \quad \quad \quad \quad \quad \\ \text{H}_3\text{C--C--CH}_3 \quad \quad \quad \text{R} \\ \quad \quad \quad \\ \text{CH}_2\text{SO}_3\text{H} \end{array}$	P-AA : SA : s-AM	Experimental
poly(acrylic acid:methylacrylic acid)	$\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\overset{\text{CH}_3}{\text{CH}}})_m\text{--}$	P-AA : MAA	Experimental
poly(acrylic acid:vinyl acetate)	$\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{OCOCH}_3}{\text{CH}})_m\text{--}$	P-AA : Vac	Experimental
poly(acrylic acid:ethyl methacrylate)	$\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{COOCH}_2\text{CH}_3}{\overset{\text{CH}_3}{\text{CH}}})_m\text{--}$	P-AA : EMA	Experimental

(continued)

Table 1. (continued)

Inhibitor	Structure	Acronym	Designation
poly(acrylic acid: carbitol acrylate)	$\text{--}(\text{CH}_2\text{--}\underset{\text{COOH}}{\text{CH}})_n\text{--}(\text{CH}_2\text{--}\underset{\text{COO}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_3}{\text{CH}})_m\text{--}$	P-AA : CA	Experimental
poly(diallyldimethyl ammonium chloride)	$\text{--}(\text{CH}_2\text{--}\underset{\text{H}_3\text{C}}{\text{CH}}\text{--}\underset{\text{H}_3\text{C}}{\text{CH}}\text{--}\text{CH}_2\text{--})\text{--}$ N^+Cl^-	P-DMAC	Experimental
amino tri(methylene phosphonic acid)	$\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3$	AMP	Commercial ^b
hydroxyethylidene phosphonic acid	$\begin{array}{c} \text{OH} \\ \\ \text{H}_2\text{O}_3\text{P--C--PO}_3\text{H}_2 \\ \\ \text{CH}_3 \end{array}$	HEDP	Commercial ^b
sodium pyrophosphate	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{NaO--P--O--P--ONa} \\ \quad \\ \text{ONa} \quad \text{ONa} \end{array}$	PYP	Commercial ^c
sodium hexametaphosphate	$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\ \quad \quad \quad \quad \quad \\ \text{NaO--P--O--P--O--P--O--P--O--P--ONa} \\ \quad \quad \quad \quad \quad \\ \text{ONa} \quad \text{ONa} \quad \text{ONa} \quad \text{ONa} \quad \text{ONa} \quad \text{ONa} \end{array}$	HMP	Commercial ^c
sodium lauryl sulfate	$\text{H}_3\text{C}(\text{CH}_2)_{10}\text{CH}_2\text{SO}_4^- \text{Na}^+$	SLS	Commercial ^c

^aThe BF Goodrich Company^bMonsanto Chemical Company^cFischer Scientific

3.1.2 Polymer structure

In industrial water treatment formulations various types of additives are used to achieve a variety of benefits (e.g., scale inhibition, chelation, corrosion prevention, dispersancy, etc.) Some commonly used additives include: Polyphosphates (i.e., pyrophosphate, PYP; triphosphates, TPP; hexametaphosphate, HMP), phosphonates (i.e., aminotris methylenephosphonic acid), AMP; 1-hydroxyethylidene-1,1-diphosphonic acid, HEDP; 2-phosphonobutane-1,2,4-tricarboxylic acid, PBTC; etc.), homopolymers (i.e., poly(acrylic acid), P-AA; poly(acrylamide), P-AM; etc.), and acrylic-, maleic-, and sulphonic acid-based copolymers. Numerous studies on the influence of polymer composition have shown that both the monomer unit ratio and the type of the functional group in the polymer play key roles on the inhibitory activity of the polymer in terms of preventing the precipitation of scale forming salts. In addition, it has also been demonstrated that nature of the comonomer exhibits

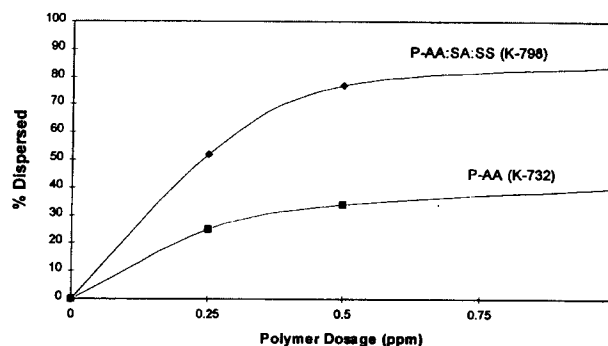


Fig. 1. Dispersancy of acrylate homopolymer compared to terpolymer

marked inhibitory effect on the kinetics of crystal growth and also on the crystal morphology. Gill and Varsanik [7] reported that the matching between the acidic groups of the inhibitors and the cations at the crystal surface play an

important role in determining the performance of the inhibitor.

The effect of polymer structure on iron oxide dispersancy was studied by conducting a series of experiments with polymers containing a variety of comonomers. Results are summarized in Table 2. The dispersancy data presented in Fig. 2 for a number of carboxyl groups containing homopolymers (i.e., P-AA, P-MAA, P-MA, etc.) indicate that these polymers exhibit dispersancy power but to a varying degree. For example, under similar experimental conditions, % dispersancy values obtained for carboxyl containing polymers are 38, 45, and 22, respectively for P-AA, P-MA, and P-MAA, compared to < 5% obtained for P-AM. It is worth noting that the performance trend observed for homopolymers in dispersing iron oxide is consistent with earlier reports on these polymers regarding their effects in preventing the precipitation of calcium phosphates and calcium sulfate from aqueous solutions [8, 9].

The influence of substituting the carboxyl group with other groups of varying chain length and ionic charge (i.e., methacrylic acid, MAA; vinyl acetate, Vac; ethylmethacrylate, EMA; hydroxypropyl acrylate, HPA; carbitol acrylate,

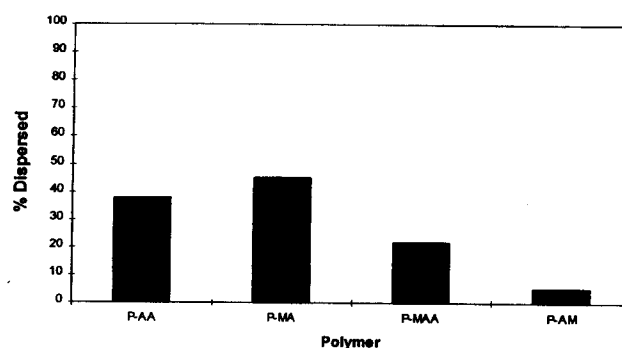


Fig. 2. Comparison of dispersancy of various homopolymers

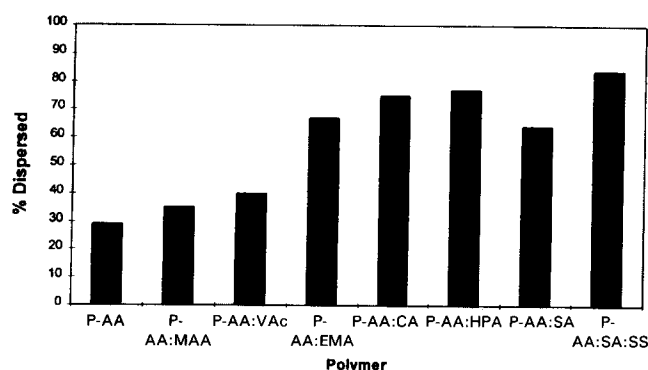


Fig. 3. Dispersancy at 3 hours for polymers of varying ionic charges

CA; 2-acrylamido-2-methyl propane sulfonic SA; sulphonated styrene, SS; etc.) was investigated for their ability to disperse iron oxide. Results summarized in Table 2 and presented in Fig. 3 clearly show that, compared to homopolymers, the copolymers exhibit superior performance as iron oxide dispersants. For example, %D values obtained for P-AA, P-AA:MAA, P-AA:VAc, P-AA:EMA, P-AA:HPA, and P-AA:CA are 29, 35, 40, 67, 75, and 77, respectively. The observed ranking in copolymer performance may be attributed to the increased size of the comonomer. Thus, for these copolymers both factors i.e., anionic character and the monomer size play important roles in imparting dispersancy power to the polymer.

The dispersancy data for sulphonic acid containing groups is summarized in Table 2. Plots of amount of iron oxide dispersed for P-AA:SA and P-AA:SA:SS as presented in Fig. 3 reveal that the higher the ionic charge on the polymer the better the performance in terms of dispersing iron oxide particles. The observed marked improvement in the performance of these copolymers may be attributed to the stronger adsorption characteristic of comonomer in imparting more negative charge to the iron oxide particles thus resulting in reduced particle size (deagglomeration). Based on the dispersancy data, the overall ranking of the polymers is:

P-AA : SA : SS > P-AA : HPA > P-AA : CA > P-AA : EMA >
P-AA : SA > P-AA : Vac > P-AA : MA > P-AA

3.1.3 Polymer ionic charge

The role of ionic charge in influencing the dispersancy power of the polymer was studied by carrying out the series of experiments with polymers containing varying ionic

Table 2. Iron oxide dispersancy data and non-polymeric additives

Additive	Concentration, ppm	% D (dispersancy)
P-AA ^b	0.25	25
P-AA ^b	0.50	34
P-AA ^b	0.75	36
P-AA ^b	1.00	40
P-AA ^b	1.00	39
P-AA ^c	1.00	44
P-AA ^d	1.00	35
P-AA ^e	1.00	27
P-AA ^f	1.00	22
P-AM	1.00	5
P-MA	1.00	45
P-MAA	1.00	22
P-VP	1.00	2
P-SA	1.00	73
P-DMAC	1.00	2
P-AA : SA	1.00	64
P-AA : SA : SS	0.25	52
P-AA : SA : SS	0.50	77
P-AA : SA : SS	0.75	80
P-AA : SA : SS	1.00	84
P-AA : SA : SS	1.00	86
P-AA : VAc	1.00	40
P-AA : EMA	1.00	67
P-AA : CA ^g	1.00	75
P-AA : CA ^h	1.00	68
P-AA : CA ⁱ	1.00	52
P-AA : MAA	1.00	35
Lignosulfonate	1.00	49
Sodium alginate	1.00	12
SLS	1.00	3
PYP	1.00	2
HMP	1.00	3
AMP	1.00	11
HEDP	1.00	12
P-AA : SA : SS	1.00	86
P-AA : SA : SS ^j	1.00	81
P-AA : SA : sAM	1.00	87
P-AA : SA : sAM ^j	1.00	61

^a100 ppm Ca, 30 ppm Mg, 314 ppm Na, 571 ppm Cl, 200 ppm SO₄, 60 ppm HCO₃, ^bMW 2000, ^c1600, ^d5 000, ^e10 000, ^f20 000, ^g5 000, ^h10 000, ⁱ20 000, ^jthermal treatment@150°C

charges (i.e., neutral, anionic, and cationic). The dispersancy data presented in Fig. 4 clearly show that polymer charge strongly affects the dispersancy power of the polymer. For example, neutral polymers (i.e., poly (acrylamide), P-AM; poly(vinylpyrrolidone), P-VP) are ineffective dispersants (%D < 5). Similarly, cationic charged polymer, poly(diallyldimethylammonium chloride), P-DMAC, is also a poor iron oxide dispersant. On the other hand, anionic charged polymers show dispersancy activity but to a varying degree. For example, %D values obtained for P-AA are 41 compared to 77 obtained for P-SA. The data suggest that the polymer which imparts more negative charge (i.e., P-SA) on the iron oxide particles, is a better dispersant. It is interesting to note that whereas P-SA has been shown to be ineffective crystal growth inhibitor for CaF_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{CaPO}_4 \cdot 2\text{H}_2\text{O}$ [10–12], it exhibits superior performance as iron oxide dispersant. This observed difference in performance between P-AA, P-MA and P-SA may be attributed to the strong affinity (or adsorbing characteristic) of the sulphonic group as compared to $-\text{COOH}$ group towards iron oxide particles.

3.1.4 Polymer molecular weight

The influence of polymer molecular weight on the precipitation of scale forming salts has been the subject of numerous investigations. Results of these studies reveal that effectiveness of polymers as scale inhibitors in industrial waters is markedly influenced by the polymer molecular weight [5, 13–15].

Amjad, in studies on the effect of P-AA in controlling the precipitation of CaF_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, BaSO_4 , CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$ from aqueous solutions reported that molecular weight of P-AA and copolymers plays an important role in the inhibition of scale forming salts. Results of these studies indicate that especially for P-AA, the optimum performance is obtained with ≈ 2000 MW (molecular weight).

The dispersancy data summarized in Table 2 for a series of dispersancy experiments in the presence of 1.0 ppm P-AA and poly(acrylic acid: carbitol acrylate), P-AA:CA of varying molecular weight (MW) and presented in Fig. 5 show that iron oxide dispersancy is strongly dependent upon polymer MW. For example, %D values obtained in the presence of P-AA (MW 1600 to 10 000 Dalton) are 45, 38, 34, and 26, respectively. Similar polymer MW dependence is observed for P-AA:CA in the MW range (5 to 20 000 Dalton). Although the optimum MW for these two polymers are different, the trend however is the same, i.e., performance decreases as the MW is increased. It is interesting to

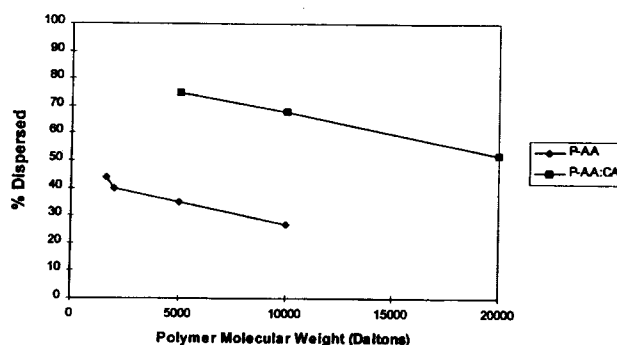


Fig. 5. Effect of polymer molecular weight of dispersancy

note that Amjad [10], Williams [15], and Libutti [16] in their studies on the performance of P-AA and P-MAA in the MW range 2000 to 120 000 as CaCO_3 , and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystal growth inhibitors, reported that high MW polymers were least effective and the effectiveness increased as the molecular weight of the polymer decreased.

3.2 Effect of natural polymers

Natural polymers such as starches, lignosulfonates, and alginates 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 the high temperatures normally encountered in treating boiler water. The development of new synthetic polymers has overcome the problems inherent in the use of natural polymers. To compare the performance of natural polymers with synthetic polymers, several dispersancy experiments were performed using natural polymers as dispersants. Results illustrated in Fig. 6 show the following order in terms of decreasing effectiveness: P-SA, lignosulfonate, P-AA, and alginate.

3.3 Effect of polyphosphonates, phosphonates, and surfactants

Numerous papers have been published and several patents have been issued since the earlier work regarding the control of scale forming salts by threshold agents. In addition, polyphosphates, in the 2 to 10 mg/L range have been reported to exhibit particulate dispersion, stabilization of metal ions such as iron and manganese, and control of aqueous corrosion of metals. Organophosphonates are a

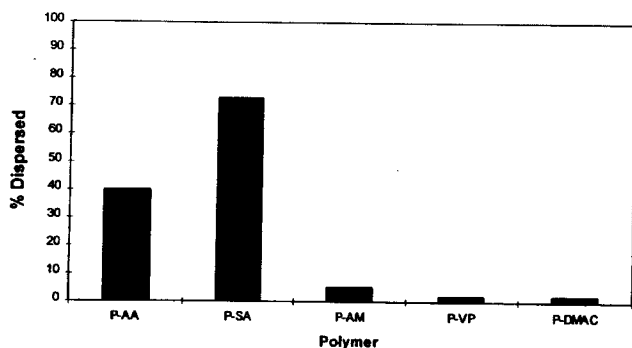


Fig. 4. Dispersancy of differently charged homopolymers

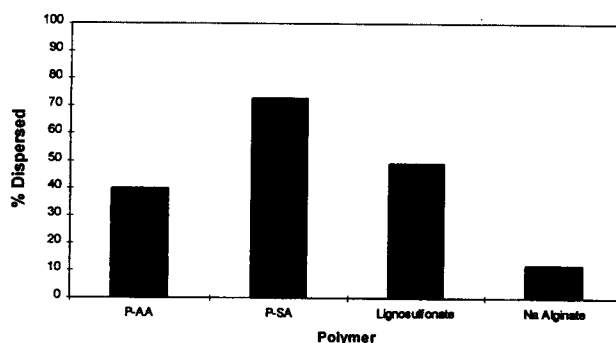


Fig. 6. Dispersancy of natural and synthetic polymers

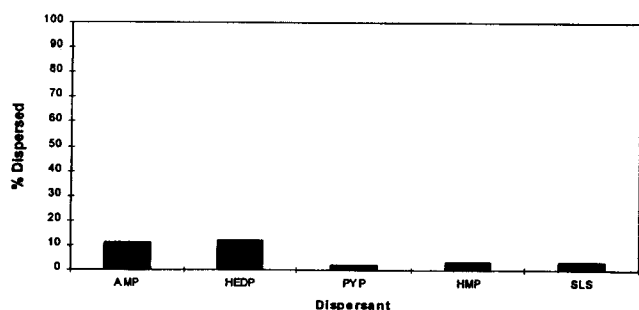


Fig. 7. Dispersancy of non-polymeric phosphonates, phosphates and surfactant

class of compounds which contain a phosphorus-carbon bond (P—C). Unlike the P—O bond present in polyphosphates, the P—C bond is not as susceptible to hydrolysis.

The dispersancy data in Table 2 and illustrated in Figure 7 show that compared to P-AA, inorganic polyphosphates such as pyrophosphate, PYP and hexametaphosphate, HMP are ineffective dispersants. Figure 7 also shows the data for a number of phosphonates and a surfactant (sodium lauryl sulfate, SLS) indicating that phosphonates and SLS are not useful as particulate iron oxide dispersants. It is interesting to note that while both polyphosphates and phosphonates are excellent crystal growth inhibitors for a variety of sparingly soluble salts i.e., CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, BaSO_4 , CaF_2 , etc., these compounds exhibit poor dispersancy activity. It is also worth pointing out that although the PO_3H_2 group present in hydroxyethylidene phosphonic acid, HEDP and amino tri(methylene phosphonic acid), AMP is a strong acidic group, its performance as compared to the SO_3H group present in P-SA may be attributed to both the ionic charge and the presence of a bulkier group in the polymer, thus providing better overall dispersancy performance.

3.4 Effect of thermal treatment

Polymers used in boiler water treatment should be able to sustain high temperature and high pressure environments normally associated with boiler operations. Synthetic polymers are generally more thermally stable than naturally occurring products and the superior thermal stability of P-AA, P-MAA compared to P-MNA has been reported in terms of their efficacy in inhibiting calcium carbonate precipitation in aqueous solutions. The effect of thermal treatment on dispersant performance is given in Figure 8 for P-AA, P-AA:SA:SS and P-AA:SA:sAM thermally treated at 150°C thus suggesting that comonomers especially SS are less susceptible to thermal degradation. Under similar experimental conditions performance of P-AA:SA:sAM terpolymer is significantly decreased due to possible degradation of acrylamide. Thus, the ability of the polymer to exhibit excellent thermal stability under high temperature conditions and to provide superior performance is important.

4 Summary

This study has shown that

- The iron oxide dispersancy by polymer increases with increasing polymer concentration.
- Homopolyacrylic acid and acrylic acid based copolymers exhibit iron oxide dispersancy power of varying degree.

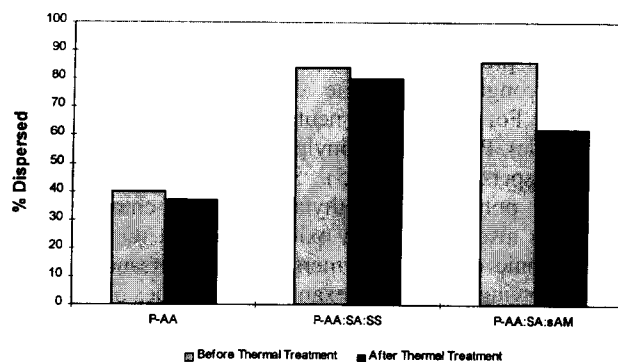


Fig. 8. Effect of thermal treatment on iron oxide dispersion

- Polymer composition and molecular weight exhibit significant influence in imparting dispersancy activity to the polymer.
- Among the various polymers evaluated, terpolymers containing sulphonic acid groups show the best performance as iron oxide dispersants.
- Non-polymeric materials such as polyphosphonates, phosphonates, and surfactants, compared to acrylic acid containing homo and copolymers, show poor performance in dispersing iron oxide.

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