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Investigations on the evaluation of polymeric calcium sulfate dihydrate (gypsum) scale inhibitors in the presence of phosphonates

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ABSTRACT

The effects of polymers with different architecture, phosphonates, and polymer/phosphonate blends on precipitation of calcium sulfate dihydrate (gypsum) precipitation are reported in this paper. It has been found that gypsum inhibition by polymers strongly depends on polymer architecture. Among the various phosphonates (i.e., aminotris(methylene phosphonic acid), AMP; 1-hydroxyethylidine 1,1-diphosphonic acid, HEDP; 2-hydroxyphosphono acetic acid, HPA; and 2-phosphonobutane 1,2,4-tricarboxylic acid, PBTC); tested AMP shows the best inhibition for gypsum precipitation. It has also been observed that presence of PBTC exhibits its synergistic effect on the performance of polymers containing carboxyl group. Under the experimental conditions used, no synergistic effects were observed with polymer/phosphonate (AMP, HEDP, HPA) blends.

Keywords: Polymers; Phosphonates; Calcium sulfate; Precipitation; Inhibition; Synergism

1. Introduction

The use of natural hard waters in boiler, cooling, desalination, and oil production can cause severe scaling and corrosion of equipment surfaces and pose serious technical and economic challenges. The scales commonly encountered are sulfates, carbonates, and phosphates of barium, calcium, magnesium, and strontium. The precipitation and deposition of these scales on equipment surfaces are influenced by various factors including feed and re-circulating water chemistry, pH, temperature, flow velocity, heat exchanger metallurgy, and types of additive used in the treatment program. Such scale deposits significantly reduce heat transfer efficiency, constricts flow (e.g., reduces internal pipe diameters), increase the operating pressure of pumps, and enhance the probability of corrosion damage. In many cases, the removal of deposits leads to discontinuous operation of the system, resulting in higher operating costs. In addition, treatment chemicals (i.e., flocculants and coagulants) used upstream to treat feed water also influence the performance of additives used to prevent the precipitation of scale forming salts [1]. One of the most effective approaches for controlling scale formation is the use of inhibitors. It is known that the addition of the scale inhibitor to the feed water would be an effective method to reduce or prevent scale formation in industrial water systems. The inhibitors commonly used include: a) non-polymeric i.e., polyphosphates, phosphonates, phosphonocitrate, etc., and b) polymeric i.e., poly(acrylic acid) poly(maleic acid), poly(aspartic acid), poly(itaconic acid) and acrylic/maleic acid-based copolymers containing other monomers with different functional groups.

Phosphonates and polyphosphates prevent scale formation at "sub-stoichiometric" dosages by adsorbing onto crystal growth sites of micro-crystallites thereby interfering with crystal growth and altering the crystal growth morphology. In addition, both phosphonates and polyphosphates have been shown to exhibit metal chelation and dispersancy activities. The influence of trace amounts of polyphosphates and phosphonates on the precipitation of gypsum has been investigated by academic and industrial researchers. Results of these studies have shown that tripolyphosphate is an effective inhibitor when added to $SrSO_4$, $CaC_2O_4{\cdot}H_2O$, and $BaSO_4$ systems while in the case of more soluble $CaSO_4{\cdot}2H_2O$ this inhibitor appeared to have only a slight effect on the growth kinetics [2–5]. Liu and Nancollas using seeded growth technique reported that trace amounts of phosphonates can stabilize supersaturated calcium sulfate solutions and lengthen the induction period before the onset of crystallization. The duration of induction periods were found to be greatly influenced by the concentration of phosphonates, amount of seed crystals added, and temperature [6]. Harmandes et al. in their study on the crystal growth inhibition of pyrite by AMP, aminotris(methylene phosphonic acid), and HEDP (1-hydroxyethylidine 1,1-diphosphonic acid) reported that AMP is an ineffective inhibitor for pyrite [7]. Recently, Amjad and Zuhl reported that performance of phosphonates such as AMP, HEDP, and PBTC (2-phosphonobutane 1,2,4-tricarboxylic acid) as calcium carbonate inhibitors could be improved by incorporating a high performance deposit control polymer in the formulation [8]. It was also shown that both polymer and phosphonate exhibit marked influence on the crystal morphology of calcium carbonate.

The effect of low concentrations (few parts per million, ppm) of polymeric inhibitors on both the rate and crystal modification of $CaSO_4{\cdot}2H_2O$ has been investigated by several researchers. Amjad showed that polymers containing carboxyl groups such as poly(acrylic acid), poly(aspartic acid), poly(itaconic acid), and poly(maleic acid) were particularly effective as $CaSO_4{\cdot}2H_2O$ growth inhibitors [9]. Dogan et al. arrived at similar conclusions after studying the effect of various acrylic acid-based copolymers as gypsum scale inhibitor [10]. Amjad and Hooley in their seeded growth study on the evaluation of polymers containing different functional groups concluded that polymer composition, type and amount of co-monomer, and molecular weight play important roles in imparting inhibitory activity to the polymers [11].

Campbell and coworkers in their study showed that poly(aspartic acid), and poly(glutamic acid) are effective calcium oxalate monohydrate crystal growth inhibitors [12]. The efficacy of poly(aspartic acid) as growth inhibitors for scale forming salts and as clay dispersant has been reported. The results of this study suggest that poly(aspartic acid) exhibits good inhibitory activity for calcium oxalate, calcium phosphate, and calcium carbonate and the performance poly(aspartic acid) is comparable with currently employed scale inhibitors [13]. Recently, Dogan et al. using the spontaneous precipitation method, investigated the influence of poly(ethylene oxide)-block-poly(meth(acrylic acid) and poly(butyl methacrylate)-block-poly(methacrylic acid) copolymers as gypsum growth inhibitors [14]. Results of their study reveal that the inhibition increases with acid content of the copolymer.

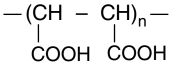
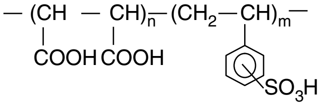
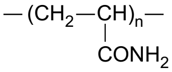
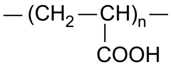
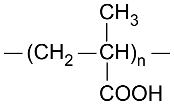
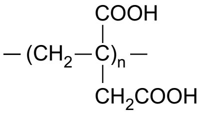
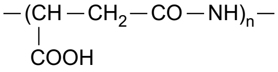
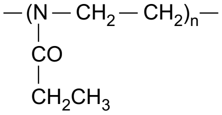
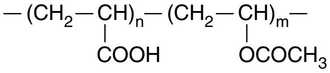
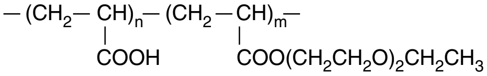
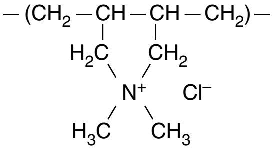
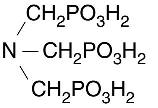
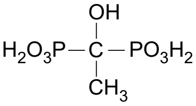
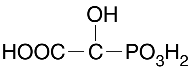
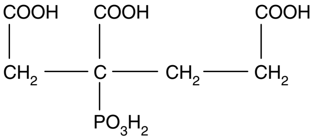
Over the years, the control of mineral scale, suspended matter, and corrosion in water treatment applications by various polymeric and non-polymeric additives has been well researched. However, the influence of additive blends in preventing mineral scale formation especially, gypsum has been mostly overlooked. In our previous papers we presented the results on the evaluation of inhibitor architecture and system impurities, on the performance of gypsum inhibitors [15,16]. The objective of the present paper is to investigate the performance of synthetic polymers and phosphonates as gypsum scale inhibitors. Additionally, this study also presents inhibitory data on the performance of polymer/phosphonate blends as gypsum precipitation inhibitors. Table 1 lists the inhibitors tested. It can be seen that inhibitors used differ significantly both in terms of composition and molecular weights. Although, there are many types of phosphonates available, the four of the most commonly used phosphonates in water treatment formulations include: a) aminotris(methylene phosphonic acid), AMP, b) 1-hydroxyethylidine 1,1-diphosphonic acid, HEDP, c) 2-phosphonobutane 1,2,4-tricarboxylic acid, PBTC, and d) hydroxyphosphono acetic acid, HPA.

2. Experimental

Grade A glassware and analytical grade chemicals were used. Stock solutions of calcium chloride and sodium sulfate were prepared using distilled water, filtered through 0.22 micron filter paper and analyzed by EDTA and atomic absorption spectroscopy methods. Inhibitor solutions were prepared on as active solids basis.

Supersaturated solutions of calcium sulfate for precipitation experiments were prepared by adding a known volume of stock solutions of sodium sulfate and inhibitor solutions to glass bottles containing known volume of distilled water maintained at 66°C. Following temperature equilibration, a known volume of calcium chloride stock solution was added in such amount that the final $CaSO_4$ solution concentration would be 4.50 mM. The total volume of calcium sulfate containing varying concentrations of inhibitor was 100 ml.

Table 1
Analytical characteristics of synthetic polymers and surfactants tested

Inhibitor	Structure	Mol. Wt.	Acronym
Poly(maleic acid)	 $-(CH(COOH)-CH(COOH))_n-$	>1k	P-MA
Poly(maleic acid:sulfonated styrene) (P-MA:SS)		<3k	P-MA:SS
Poly(acrylamide)	 $-(CH_2-CH(CONH_2))_n-$	~6k	P-AM
Poly(acrylic acid)	 $-(CH_2-CH(COOH))_n-$	~6k	P-AA
Poly(methacrylic acid)	 $-(CH_2-CH(CH_3)(COOH))_n-$	~6k	P-MAA
Poly(itaconic acid)	 $-(CH_2-C(COOH)(CH_2COOH))_n-$	~8k	P-IA
Poly(aspartic acid)	 $-(CH(COOH)-CH_2-CO-NH)_n-$	<20k	P-Asp
Poly(2-ethyloxazoline)	 $-(N(COCH_2CH_3)-CH_2-CH_2)_n-$	~6k	P-Eox
Poly(acrylic acid:vinyl acetate)	 $-(CH_2-CH(COOH))_n-(CH_2-CH(OCOCH_3))_m-$	~7k	P-AA:Vac
Poly(acrylic acid:carbitol acrylate)	 $-(CH_2-CH(COOH))_n-(CH_2-CH(COO(CH_2CH_2O)_2CH_2CH_3))_m-$	~8k	P-AA:Cac
Poly(diallydimethyl ammonium chloride)		~10k	P-DA
Aminotris(methylene phosphonic acid)	 $N(CH_2PO_3H_2)_3$	299	AMP
1-hydroxyethylidine 1, 1-diphosphonic acid)	 $H_2O_3P-C(OH)(CH_3)-PO_3H_2$	206	HEDP
2-hydroxyphosphono acetic acid	 $HOOC-C(OH)-PO_3H_2$	156	HPA
2-phosphonobutane 1,2,4 tricarboxylic acid	 $(COOH)CH_2-C(COOH)(PO_3H_2)-CH_2-CH_2(COOH)$	270	PBTC

Precipitation in these solutions was monitored by analyzing aliquots of the filtered (0.22 micron filter paper) solution for calcium by EDTA titration. Experiments involving inhibitors were performed by adding the inhibitor solution to the sodium sulfate solution, before the addition of calcium chloride solution. Solution pHs of calcium sulfate supersaturated solution were adjusted to 7.00 ± 0.05 with dilute HCl and/or NaOH solutions.

The performance of additive as $CaSO_4{\cdot}2H_2O$ inhibitor was calculated using the following equation:

$$\text{Percent Inhibition (\%1)} = 100 \times [(Ca)_{exp} - (Ca)_{final}]/[(Ca)_{ini} - (Ca)_{final}] \qquad (1)$$

where $(Ca)_{exp}$ is the Concentration of calcium in the filtrate in the presence of inhibitor at 20 h; $(Ca)_{final}$ is the Concentration of calcium in the filtrate in the absence of inhibitor at 20 h; $(Ca)_{ini}$ is the Concentration of calcium at the beginning of the experiment.

At the end of experiments solids samples of precipitates were collected for characterization by x-ray diffraction method and by scanning electron microscopy.

3. Results and discussion

3.1. Performance of polymers

Using the precipitation technique described above, a series of experiments were carried out as function of polymer dosage and polymer composition. Fig. 1 presents plots of calcium concentration as a function of time in the presence of 0.0 parts per million (ppm) of poly(maleic acid), P-MA. It can be seen that gypsum precipitation in the absence of P-MA is preceded by an "induction time" or φ. The time at which a decrease in the solution calcium concentration was first detected was taken as φ. Results on the experiments carried out in the presence of 2.0 ppm of P-MA and copolymer of maleic acid:sulfonated styrene, P-MA:SS, are illustrated in Fig. 1. It can be seen that φ value strongly depends on polymer architecture. For example, φ values obtained in the presence of 2.0 ppm of P-MA and 2.0 ppm of P-MA:SS are >700 min and 72 min, respectively compared to 52 min obtained in the absence of polymer. The data presented in Fig. 1 clearly show that substituting partly maleic acid with bulkier and hydrophobic sulfonated styrene, results in decreased φ value. Fig. 1 also presents calcium concentration-time profile for experiment carried out in the presence of non-carboxyl containing monomer i.e., poly(acrylamide), P-AM. It is evident from Fig. 1 that polymer devoid of carboxyl group is an ineffective gypsum inhibitor. It should be noted similar observations were also observed for non-ionic polymer i.e., poly(2-ethyloxazoline, and cationic polymer i.e., poly(diallyldimethyl ammonium chloride).

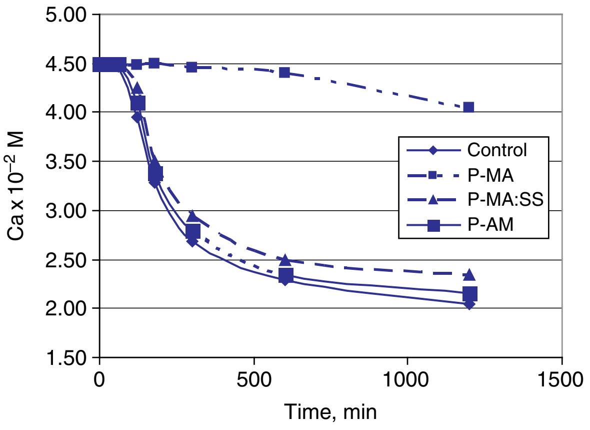


Fig. 1. Calcium sulfate precipitation in the absence and presence of 2.0 ppm of poly(maleic acid), P-MA; copolymer of maleic acid: sulfonated styrene, P-MA:SS, and poly(acrylammide), P-AM. Plots of calcium concentration as a function of time.

3.2. Effect of polymer dosage

The influence of polymer composition on gypsum inhibition has been the subject of several investigations. Ahmad et al. in their study on the influence of sodium polyacrylate reported that addition of low levels of polymer to gypsum supersaturated solution affects induction time [17]. Results of this study also reveal that with increasing temperature or supersaturation, the induction time decreases and the growth rate increases. Similar observations were also noted by Amjad and Hooley in their seeded growth study on the evaluation of homo- and copolymers as gypsum crystallization inhibitors [11]. Oner et al. in another study on the evaluation of block polymers as gypsum inhibitors reported that gypsum inhibition strongly depends on polymer composition, charge, and molecular weight [18].

The impact of dosage on the performance of homo- and copolymers was investigated. Fig. 2 presents inhibition data at 20 h, calculated according to Eq. (1), for experiments carried out in the presence of varying polymer dosages. There are two points worth noting: a) gypsum inhibition increases with increasing polymer concentration and b) homo-polymer i.e., P-AA exhibits better inhibitory activity compared to copolymers of acrylic acid:vinyl acetate and acrylic dimethylitaconate. The lower % inhibition values obtained for copolymers compared to P-AA may be attributed to poor adsorption of copolymers on gypsum crystallites and/or possible interference by various groups i.e., vinyl acetate and dimethylitaconate. It is clear from the data presented in Fig. 2 that polymer architecture strongly influences

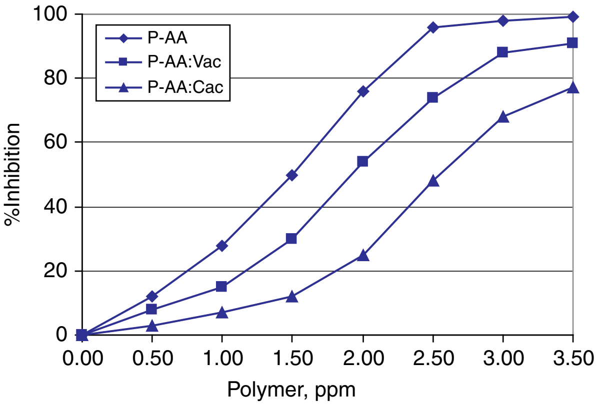


Fig. 2. Plots of gypsum inhibition (%) as a function of dosage for homo- and copolymers.

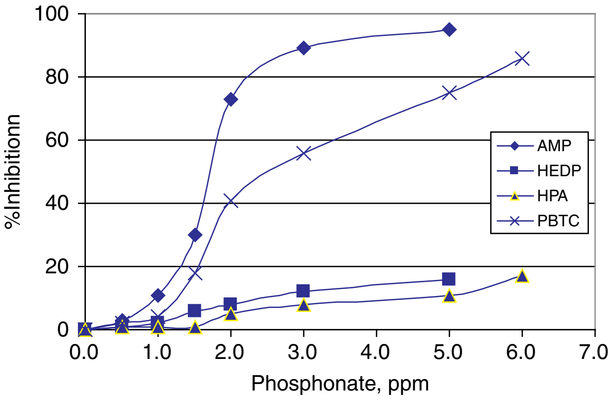


Fig. 3. Plots of gypsum inhibition (%) in the presence varying dosages of various phosphonates.

polymer performance as gypsum inhibitor. It should be noted that similar observations regarding the influence of polymer architecture have been reported in earlier investigations [11,15,18].

3.3. Performance of phosphonates

Several authors have studied the influence of phosphorous containing compounds such as polyphosphates and phosphonates on gypsum crystallization in aqueous systems. Results of these studies reveal that performance of these compounds depends not only on the precipitation conditions but also on the structure of phosphorous containing compounds [3,19–21]. In order to study the influence of various phosphonates on gypsum precipitation, a series of precipitation experiments were carried in the presence of varying concentration of phosphonates such as aminotris(methylene phosphonic acid), AMP; 1-hydroxyethylidine 1–1, diphosphonic acid, HEDP. Fig. 3 presents %I versus phosphonate concentration profiles for AMP and HEDP. For example, %I values obtained in the presence of 2.0 ppm for AMP and HEDP were 73% and 8%, respectively. Liu and Nancollas, in their seeded growth study on the evaluation of various phosphonates as gypsum inhibitors, also made similar observations regarding the poor inhibitory action of HEDP [21]. It is worth noting that where as HEDP showed poor inhibitory activity compared to AMP for gypsum precipitation HEDP has been reported to be an excellent inhibitor for strontium fluoride and calcium carbonate [22,23]. Thus, the performance of phosphonates as precipitation inhibitors depends on the type of the sparingly soluble salts being inhibited.

The effect of carboxyl and/or hydroxyl group present in the phosphonates i.e., hydroxyphosphono acetic acid, HPA, and 2-phosphonobutane 1,2,4, tricarboxylic acid, PBTC, on gypsum inhibition was also investigated. Fig. 3 presents inhibition data collected in the presence of varying concentrations of phosphonates. It can be seen that in the presence of 2.0 ppm of phosphonates, HPA compared to PBTC exhibits poor performance (<5% inhibition) as gypsum inhibitor. For example, %I values obtained in the presence of 2.0 ppm of HPA and PBTC are 5% and 41% respectively, compared to 73% obtained for AMP. The data presented in Fig. 3 also reveal that increasing the phosphonate concentration by three fold i.e., from 2.0 ppm to 6.0 ppm increases %I for HPA from 5% to 17% compared to 41% and 85% obtained for PBTC. The poor performance shown by HPA may be attributed to low molecular weight and/or poor adsorption of HPA on gypsum crystallites. Based on the data presented, the ranking of phosphonates in terms of decreasing effectiveness is: AMP >> PBTC > HEDP ~ HPA > control (no phosphonate).

The performance of phosphonates as inhibitors for calcium carbonate system has been reported. Results of this study reveal that performance of phosphonates depends on the concentration of phosphonates present in the calcium carbonate ($CaCO_3$) supersaturated solution [8]. For example, performance trend observed in the presence of 5.0 ppm phosphonates for $CaCO_3$ system (at 180x saturation) is HEDP ≥ AMP >> PBTC. However, at higher concentration of phosphonates (i.e., 40 ppm) the performance trend observed is: PBTC >> HEDP ≥ AMP. The improved performance of PBTC at high $CaCO_3$ saturation has been attributed to better tolerance of PBTC to calcium ions. Thus, for cooling water systems operating at high cycles of concentration PBTC is a better inhibitor for $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ than HEDP.

3.4. Performance of polymer/phosphonate blends

To study the impact of phosphonate on the performance of polymers, a series of precipitation experiments

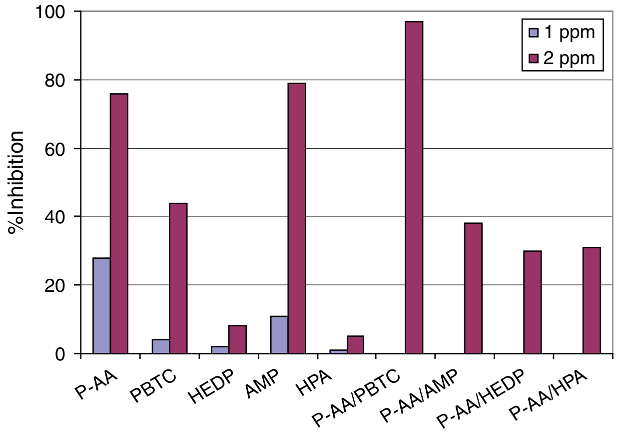


Fig. 4. Plots of gypsum inhibition in the presence of varying dosages of phosphonates, poy(acrylic acid), P-AA, and P-AA/phosphonates.

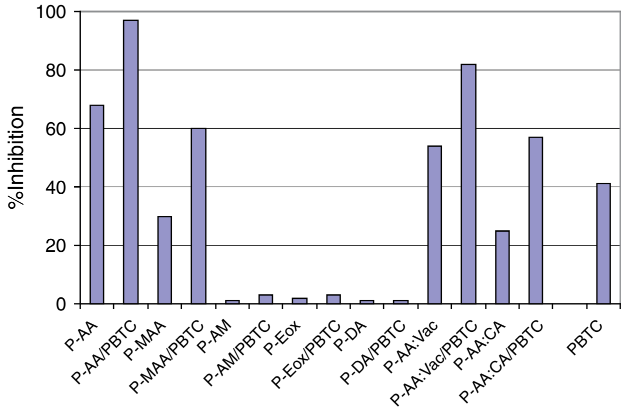


Fig. 5. Plots of gypsum inhibition (%) in the presence of 2.0 ppm of various polymemrs and polymers/PBTC blends (1:1).

were carried out in the presence of 2.0 ppm of phosphonates, P-AA, and P-AA/phosphonates (1:1 ratio). It is evident from Fig. 4 that P-AA/PBTC blend shows synergistic effect in inhibiting gypsum precipitation from aqueous solution. For example, %I values obtained in the presence of 2.0 ppm of P-AA and PBTC are 68% and 41% respectively, compared to 98% obtained in the presence of 2.0 ppm of P-AA/PBTC blend (1.0 ppm of P-AA + 1.0 ppm of PBTC). It is evident from the data presented in Fig. 4 that the P-AA/PBTC blend performs better than P-AA and PBTC tested individually at 2.0 ppm concentration. It is worth noting that experiments carried out in the presence of P-AA and P-AA/AMP P-AA/HEDP, and P-AA/HPA blends do not show any significant synergistic effect in inhibiting the precipitation of gypsum from aqueous solution.

Fig. 5 presents gypsum inhibition data collected in the presence of 2.0 ppm of various homo- and copolymers, PBTC, and polymer/PBTC (1:1 ratio) blends. It can be seen that polymers containing carboxyl group exhibit synergistic effect in inhibiting gypsum precipitation. It is interesting to note that polymers that are devoid of carboxyl group i.e., poly(acrylamide), poly(2-ethyloxazoline), poly(diallydimethylammonium chloride) do not show any synergistic influence in inhibiting gypsum precipitation. Thus, it is clear from the data presented in Fig. 5 that carboxyl group present in the polymers interacts with calcium ion present on gypsum crystallites and thus plays an important role in preventing gypsum precipitation from aqueous solution.

Rahman et al. using the seeded growth technique investigated the influence of ethylenediamine tetra (methylene phosphonate), ENTMP, P-AA, and P-AA/ENTMP blend on the crystal growth of calcium fluoride [24]. It was shown that although P-AA and ENTMP were effective crystal growth inhibitors, but the combined retarding effect of their mixtures was less than the sums of those of the components. It was proposed that molecular interference between the adsorbates facilitating diffusive access of calcium and fluoride ions to growth sites through the disrupted adsorption layer. Recently, Amjad and Zuhl reported that performance of phosphonates such as AMP, HEDP, and PBTC (2-phosphonobutane 1,2,4-tricarboxylic acid) as calcium carbonate inhibitors could be improved by incorporating a high performance deposit control polymer in the formulation [8]. It was also shown that both polymer and phosphonate exhibit marked influence on the crystal morphology of calcium carbonate. Thus, it is clear that influence of phosphonate on the performance of polymer as precipitation inhibitor depends not only on the type of inhibitors but also on the scaling system being inhibited.

In order to check the performance of various ratios of P-AA/PBTC blend, a series of precipitation experiments were carried out in the presence of 2.0 ppm of P-AA/PBTC blends. Results presented in Fig. 6 clearly show that P-AA/PBTC blend performance strongly depends on the ratio of P-AA and PBTC. For example, %I values obtained in the presence of 2.0 ppm of P-AA are 68% compared to 41% obtained in the presence of 2.0 ppm of PBTC. As noted in Fig. 5 performance of P-AA/PBTC blends increases with decrease in P-AA concentration and maximum %I value is reached at 1:1 ratio and further decrease in P-AA concentration (from 1.0 ppm to 0.25 ppm) does not exhibit any significant influence on the performance of P-AA/PBTC blends. Fig. 6 also presents inhibition data for poly(aspartic acid), PAsp, PBTC, and P-Asp/PBTC blends. Interestingly, similar improved performance of P-Asp/PBTC

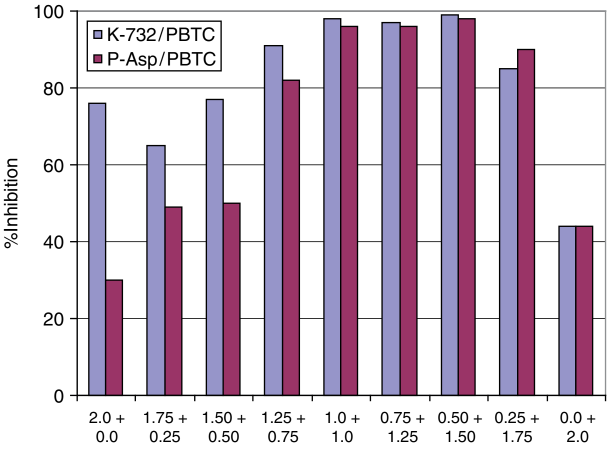


Fig. 6. Plots of gypsum inhibition (%) in the presence of 2.0 ppm of P-AA/PBTC blends of varying composition.

blends is observed. Thus, it is clear that the presence of PBTC strongly influences the performance of carboxyl containing polymers.

To investigate the influence of inhibitor dosage, a series of gypsum precipitation experiments were carried out in the presence of varying dosages of P-AA, PBTC, and P-AA/PBTC (1:1 ratio) blend. Results of these experiments are presented in Fig. 7. There are two points worth noting: a) %I value increases with increasing inhibitor concentration and b): positive influence by PBTC on P-AA performance is observed at very low concentration i.e., >1.5 ppm, of P-AA/PBTC blend. As noted in Fig. 7, increasing the blend concentration from 1.0 ppm to 2.0 ppm results in ~ 3 fold increase (from 30% to 98% inhibition) in blend performance.

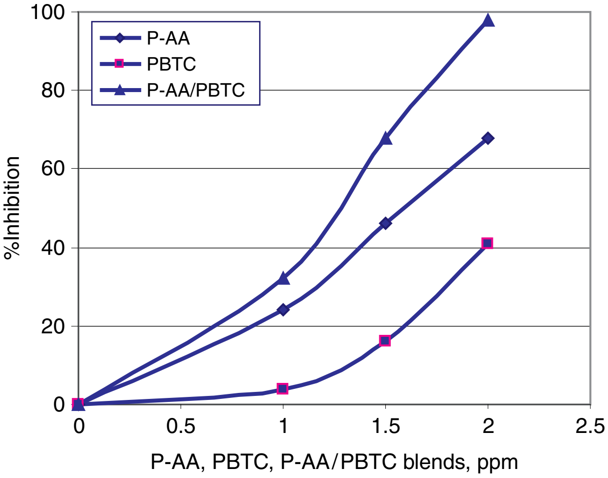


Fig. 7. Plots of gypsum inhibition (%) in the presence of varying dosages of P-AA, PBTC, and P-AA/PBTC blend (1:1).

3.5. Mechanism of gypsum inhibition

Over the years various approaches have been proposed to prevent the precipitation of sparingly soluble salts (or scale) from aqueous solutions. These techniques include: a) physical such as magnetic, electric, or the use of sonic waves and b) chemical such as acid addition, ion exchange, or scale inhibitor [25–27]. Currently, a wide variety of non-polymeric (i.e., polyphosphates and phosphonates and polymeric (i.e., poly(acrylic acid), poly(maleic acid), and acrylic/maleic acid based copolymers) to inhibit the precipitation of sparingly soluble or scale forming salts. Inhibition phenomena of scale formation do not require chemical reactions and originate from various physical processes including adsorption of inhibitor on crystallites, nucleation, and crystal growth processes. The fundamentals of inhibition processes especially from their quantitative aspects are not fully understood [28].

The results discussed above show that trace quantities of additives (polymeric and non-polymeric) markedly reduce the precipitation of calcium sulfate dihydrate. The influence of these additives on the precipitation process may be explained in terms of three effects: a) direct complexation of additive with crystal lattice ions in solution; b) adsorption of additive on the gypsum crystal surface; and c) additive may change the ionic strength of the calcium sulfate dihydrate solution and hence the effective solubility of calcium sulfate dihydrate. It is generally agreed that inhibition of scale formation is via the adsorption of additives on the crystal surface, which blocks the active growth sites. After the adsorption phase, several processes including reduction of crystal growth rate, delaying nucleation, crystal modification, etc., may take place. The marked effects of inhibitors on rate of gypsum crystal growth and crystal modification have been previously reported [15,21]. Under the experimental condition used in the present study the marked reduction in gypsum precipitation must be attributed surface adsorption rather than calcium-additive complex formation (the percentage of calcium complex, even at highest inhibitor concentration, accounts to less than 5% of total calcium) or the concomitant increase in ionic strength of the calcium sulfate supersaturated solution in the presence of inhibitors. The synergistic effect observed in the case of polymer/PBTC blend may be explained by considering that PBTC, being small molecule compared to polymer, adsorbed initially on gypsum crystallites followed by adsorption of polymer, thus reducing the chance for desorption of PBTC. To better understand the mechanistic aspects of gypsum inhibition, studies are currently underway to investigate the effects of polymer, phosphonates, and polymer/phosphonate blends on the induction time and rate of gypsum growth. Results of these investigations will be presented in a future paper.

Characterization of gypsum crystals formed in the presence of polymers and phosphonates was carried out by XRD and SEM. The data reveal that crystal structure has not been altered and only the morphology is changed and this is confirmed by the variation in the intensity values and no change in 'd' and 'Θ' compared to that of control (no polymer). The XRD results obtained in the present study are consistent with earlier investigations on the performance of synthetic and natural additives as gypsum precipitation inhibitors [15,29,30].

4. Conclusions

The results presented in this paper support the following conclusions regarding the performance of phosphonates and polymers of varying composition, molecular weight, and functional groups under test conditions commonly encountered in industrial water systems:

1) Homopolymers e.g. poly(acrylic acid), poly(maleic acid), poly(aspartic acid), poly(itaconic acid) containing carboxyl group exhibit excellent performance in inhibiting gypsum precipitation in aqueous system.
2) Homopolymers containing non-ionic monomers e.g., 2-ethyloxazoline, acrylamide and cationic monomer, e.g., diallyldimethyl ammonium chloride, are ineffective gypsum scale inhibitors.
3) Incorporation of bulkier co-monomers containing non-ionic and/or anionic groups (e.g., vinyl acetate, carbitol acrylate, sulfonated styrene) in the polymer significantly decreases the inhibitory activity of the polymer.
4) Polymer concentration is critical to the performance of gypsum inhibiting polymer. An increase in polymer concentration results in a significant increase in the inhibition of gypsum precipitation.
5) Among the various phosphonates (e.g., aminotris(methylene phosphonic aciod, AMP; 1-hydroxyethylidine 1,1-diphosphonic acid, HEDP; 2-hydroxyphosphono acetic acid, HPA; 2-phosphonobutane 1,2,4-tricarboxylic acid, PBTC) investigated, AMP shows the best performance as gypsum precipitation inhibitor.
6) Addition of phosphonates to homo- and copolymers containing carboxyl group exhibit unexpected synergistic performance with only PBTC. Under similar experimental conditions no synergistic effects were observed with polymer/phosphonate (AMP, HEDP, HPA) blends.

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