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Effect of surfactants on gypsum scale inhibition by polymeric inhibitors

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ABSTRACT

The inhibition of gypsum precipitation by homo- and copolymers has been examined in aqueous solution. It has been found that polymer performance as gypsum inhibitor depends upon polymer architecture. The influence of surfactants containing different functional group on gypsum inhibition has also been investigated. Inhibition data on the evaluation of surfactants suggest that compared to polymers, surfactants perform poorly as gypsum inhibitors. Results on the impact of cationic surfactant (e.g., cetyltrimethyl ammonium chloride, CTAC) suggest that CTAC exhibits an antagonistic effect on the efficacy of polymers. It has also been found that cationic polymer (e.g., diallyldimethyl ammonium chloride) shows much stronger antagonistic effect than CTAC on the performance of polymers used as gypsum inhibitors. The antagonistic behavior shown by cationic surfactant and cationic polymer on the performance of polymers has been explained in terms of cationic–anionic interactions.

Keywords: Gypsum; Scale; Inhibition; Polymers; Surfactants

1. Introduction

The formation and deposition of insoluble salts on equipment surfaces pose serious operational challenges in the efficient operation of industrial water systems. Depending on the chemistry of the water used, a number of sparingly soluble salts may be formed. Commonly encountered sparingly soluble salts (or mineral scales) in industrial water systems include carbonates, sulfates, fluorides, and phosphate salts of alkaline earth metals. These salts form readily on flow surfaces such as heat exchangers, reverse osmosis (RO) membranes, and other process equipments handling process waters. The formation of these mineral scales reduces heat transfer, decreases the internal diameter of pipes, increases the operating pressure of the pumps, and often results in premature equipment failure. Additionally, scaling is often accompanied by corrosion which leads to damage of metallic parts. In many instances, the removal of scales results in discontinuous operation of the systems. The systems commonly affected by these scales include boiler, cooling, desalination, geothermal, pulp and paper, oil and gas production [1].

Calcium sulfate is one of the most commonly encountered scale deposits and occurs in three different crystalline forms: calcium sulfate dihydrate (gypsum), $CaSO_4{\cdot}2H_2O$; calcium sulfate anhydrite, $CaSO_4$; and calcium sulfate hemi-hydrate, $CaSO_4.{}^1\!/\!_2H_2O$ (plaster of Paris). In cooling water and RO based systems, gypsum is the most commonly encountered calcium sulfate scale whereas calcium sulfate hemi-hydrate and calcium sulfate anhydrite are the most frequently formed salts in high temperature processes

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(e.g., boiler, multi-stage distillation, geothermal). In desalination of brackish/sea waters by RO process, the precipitation and deposition of gypsum on RO membrane leads to poor water quality, increased operating pressure, increased energy costs, and premature membrane replacement [2].

Over the years many approaches have been proposed to control scale formation in industrial water systems. Examples include: (a) decrease of process water pH by the controlled addition of acid, (b) addition of chelants or sequestrants causing decrease of supersaturation because of complexation of hardness ions (e.g., Ca, Mg) involved in scale formation, (c) use of ion-exchangers to remove hardness ions, and (d) use of small amounts (few parts per million, ppm) of water soluble additives, which have the ability to suppress scale formation. The first approach increases the probability of corrosion or deterioration of metallic parts. In the second method, relatively high concentrations of chelants are used to achieve satisfactory results, resulting in higher operating cost. The third method although will eliminate scale formation but will require regeneration of ion exchange resins.

The most commonly used approach involves the addition of water soluble additives (or scale inhibitors) to the process water. Additives commonly used to control scale formation fall into two categories: (a) non-polymeric such as hexametaphosphate, pyrophosphate, phosphonates, phosphonocitrate and (b) polymeric such as polycarboxylates, polyphosphates, polyphosphonates. Such additives are primarily designed to interact with cations present on the mineral surface. In many cases, the presence of scale inhibitors may cause modifications of the crystal habit of the precipitating particles formed reducing their ability to adhere to the equipment surfaces [3,4].

The presence of soluble impurities, such as biocides, cationic polymeric flocculants/coagulants, and metal ions present in cooling waters have been known to impact the performance of polymeric scale inhibitors. Hamdona et al. [5] investigated the kinetics of gypsum precipitation in the presence of divalent metal ions and reported that Mg^{2+} is a better gypsum inhibitor than Fe^{2+} probably due to the formation of $MgSO_4$ ion pairs. In contrast, Weijnen et al. [6] found that 1 mM (63 mg/L) Cu^{2+} or Zn^{2+} (65 mg/L) enhanced crystal growth rate of gypsum. Amjad et al. [7] studied the influence of recirculating water system impurities on the performance of calcium phosphate inhibiting polymers. It was shown that manganese and copper ions are antagonistic to the performance of acrylate-based polymers but the adverse impact is not as great as with Fe^{3+}. Recently, Ahmad et al. [8] investigated the performance of various additives (e.g., sodium salt of aminotris(methylene phosphonate, sodium tripolyphosphate, sodium polyacrylate, a blend of polycarboxylate and phosphonate) as gypsum scale inhibitors. Results of this study reveal that gypsum scale inhibition strongly depends on the concentration and the type of inhibitor tested. Among the various additives tested, polyacrylate exhibits the best performance. In another study by Shih et al. [9] it was reported that trace levels of aluminum ions exhibits significant antagonistic effect on the performance of various gypsum scale inhibitors. Senthilmurugan and his co-workers [10] in their study on the evaluation of maleic acid:acrylic acid and maleic acid:acrylamide copolymers reported that these copolymers are effective gypsum scale inhibitors.

Surfactants are used in a variety of applications including laundry detergents, agrochemicals, pharmaceuticals, petroleum, mineral ores, personal care, paints, coatings, fuel additives, and photographic films. The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. Surfactants are generally classified into four groups: (a) anionic, (b) non-ionic, (c) amphoteric, and (d) cationic. In laundry detergents, surfactants are used to aid in the removal of oily soil and in the suspension of solids in a washing liquid. In hard water (water containing multivalent cations), anionic surfactants tend to form insoluble salts with metal ions, and then they are no longer available to participate in the cleaning process. Cationic surfactants are generally used in textile as a fabric softener. In cooling water systems surfactants are frequently used to emulsify oil, to enhance the penetration of biocides, and to disperse biological masses [11]. Surfactants are also used as a component of RO membrane cleaning formulations [12].

The interactions of hardness ions and cationic surfactants with anionic surfactants have been investigated. Results of this study show that anionic surfactants such as sodium dodecyl sulfate and sodium octylbenzene sulfonate form insoluble salts with calcium ions in aqueous solutions depending upon experimental conditions such as concentrations, surfactant molar ratios, and temperature [13]. In another study on the compatibility of anionic surfactants with cationic surfactants, it was shown that using the phase diagram it is possible to formulate homogeneous and stable compositions [14].

In our previous investigations, we reported the influence of surfactants on the performance of polymers as calcium phosphate inhibitors and as dispersants for iron oxide particles [15,16]. It was shown that cationic surfactants exhibit antagonistic influence on the performance of scale inhibitors and dispersants. The results presented in this paper are a part of our broader research efforts to understand the impact of surfactants of different ionic charge on the performance of various gypsum scale inhibitors. The surfactants evaluated include: (a) anionic, i.e., sodium lauryl sulfate, sodium xylene sulfonate, (b) non-ionic, i.e., octyl phenol ethoxylate, (c) amphoteric, i.e., cocamidopropyl betaine, and (d) cationic, e.g., cetyl trimethyl ammonium chloride. The polymers tested include: (a) homopolymers of acrylic acid, methacrylic acid, maleic acid, itaconic acid, aspartic acid, 2-acrylammido-2-methylpropane sulfonic acid, 2-ethyloxazoline, vinylpyrrolidone, (b) copolymers of acrylic acid:acrylamide, acrylic acid:2-acrylamido-2-methylpropane sulfonic acid, acrylic acid:hydroxyl propylacrylate, maleic acid:sulfonated styrene, and (c) terpolymer of acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:t-butylacrylamide. In addition, experiments were also carried out to study the influence of commonly used polymeric cationic flocculant/coagulant (e.g., polydiallyldimethyl ammonium chloride) on the performance of gypsum scale inhibiting polymers.

2. Experimental

Reagents grade chemicals and grade A glassware were used. Stock solutions of calcium chloride and sodium sulfate were prepared using distilled water, filtered through 0.22 micron filter paper and analyzed as described previously [17]. The polymeric materials (gypsum inhibitors) and surfactants tested were commercial and experimental materials. Surfactants and inhibitors stock solutions were prepared on a dry weight basis. The desired concentrations of the surfactants and inhibitors were obtained by dilution. Table 1 lists the surfactants, polymeric coagulant/flocculant, and gypsum inhibitors tested.

The gypsum precipitation experiments were carried by adding known volume of stock solution of sodium sulfate to known volume of water in a 100 mL bottle. To this sodium sulfate solution was added with continuous stirring a known volume of stock solution of calcium chloride. In experiments involving the additive, a known volume of stock solution of inhibitor and/or surfactant was added to the sodium sulfate solution prior to the addition of calcium chloride. The pH of calcium sulfate solutions was adjusted to 7.0 with dilute HCl and/or NaOH solutions and the calcium sulfate solutions were stored in water bath maintained at 66°C to simulate heat exchanger temperature encountered in cooling water systems. At the end of experiment solution pH was also measured and found to be 6.85 ± 0.05. At known time, solution was filtered through 0.22 micron filter paper and solution calcium was determined by standard EDTA titration method.

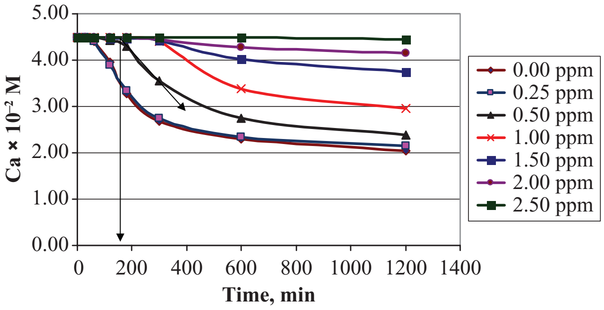


Fig. 1. Plots of calcium concentration as a function of time in the presence of varying dosages of poly(maleic acid), P1.

The sulfate ion was determined by ion chromatography (Dionex DX500). The solids collected on the membrane filters were analyzed by scanning electron microscopy (SEM, Model Zeiss EVO50) and by X-ray diffraction spectrometry (Model Rigaku Geigerflex). The results presented in this study had reproducibility (±5% or better).

Additive (polymer and/or surfactant) performance as gypsum inhibitor was calculated using the following equation:

$$\text{Percent inhibition } (\%) = \left[(\mathrm{Ca})_e - (\mathrm{Ca})_f\right] / \left[(\mathrm{Ca})_i - (\mathrm{Ca})_f\right] \times 100 \tag{1}$$

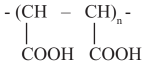
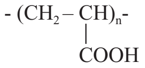
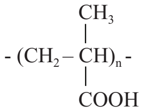
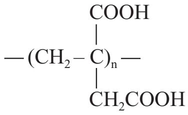
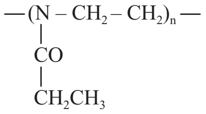
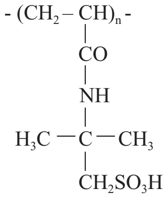
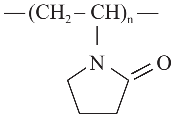
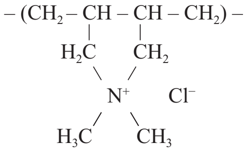
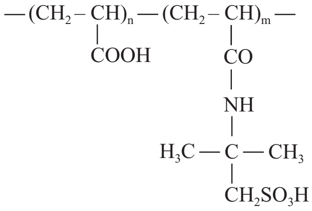
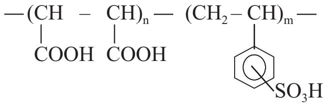
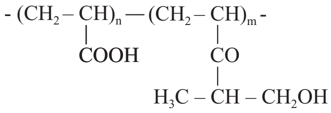
where: $(\mathrm{Ca})_e$ = concentration of calcium in the filtrate in the presence of inhibitor at known time. $(\mathrm{Ca})_f$ = concentration of calcium in the filtrate in the absence of inhibitor at 24 h. $(\mathrm{Ca})_i$ = concentration of calcium at the beginning of the experiment.

3. Results and discussion

3.1. Performance of Polymers

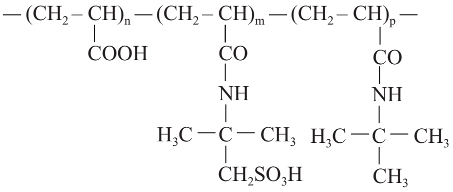
Using the experimental procedure described above, a series of gypsum precipitation experiments were carried out under similar experimental conditions (i.e., 1,800 mg/L Ca, 4,300 mg/L SO_4, pH 7.0, 66°C) and in the presence of varying concentration of poly (maleic acid), P1. Plots of total calcium concentration as a function of time are given in Fig. 1. It can be seen in Fig. 1 that gypsum precipitation in the absence of inhibitor is preceded by an induction period, α. The α in the precipitation experiments is the time period between the mixing of the calcium chloride and sodium sulfate solutions to attain gypsum supersaturation and first measurable decrease in calcium ion concentrations as illustrated in Fig. 1. The data shown in Fig. 1 reveal that the presence of trace amount of P1 resulted in an increase in α value, followed by gypsum precipitation at a rate comparable to the rate of

Table 1
List of synthetic polymers and surfactants tested

Inhibitor	Structure	Mol. Wt.	Ionic Charge	Acronym
poly(maleic acid)	 $-(\underset{\mathrm{COOH}}{\mathrm{CH}}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	<1,000	Anionic	P1[a]
poly(acrylic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-$	~6,000	Anionic	P2[b]
poly(methacrylic acid)	 $-(\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{COOH}}{\mathrm{CH}}})_n-$	~6,000	Anionic	P3[c]
Poly(itaconic acid)	 $-(\mathrm{CH_2}-\overset{\mathrm{COOH}}{\underset{\mathrm{CH_2COOH}}{\mathrm{C}}})_n-$	~10,000	Anionic	P4[a]
Poly (aspartic acid)	 $-(\underset{\mathrm{COOH}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CO}-\mathrm{NH})_n-$	<20,000	Anionic	P5[a]
Poly(2-ethyl-2-oxazoline)	 $-(\underset{\underset{\mathrm{CH_2CH_3}}{\mathrm{CO}}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2})_n-$	~5,000	Non-ionic	P6[d]
Ppoly(2-acrylamido-2-methylpropane sulfonic acid)	 $-(\mathrm{CH_2}-\underset{\begin{array}{c}\mathrm{CO}\\ \mathrm{NH}\\ \mathrm{H_3C-C-CH_3}\\ \mathrm{CH_2SO_3H}\end{array}}{\mathrm{CH}})_n-$	~10,000	Anionic	P7[a]
Poly(vinyl pyrrolidone)		<20,000	Non-ionic	P8[a]
Poly(diallydimethyl ammonium chloride)		<20,000	Cationic	P9[a]
Poly(acrylic acid: 2-acrylamido-2- methylpropane sulfonic acid)	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-(\mathrm{CH_2}-\underset{\begin{array}{c}\mathrm{CO}\\ \mathrm{NH}\\ \mathrm{H_3C-C-CH_3}\\ \mathrm{CH_2SO_3H}\end{array}}{\mathrm{CH}})_m-$	<15,000	Anionic	P10[e]
Poly(maleic acid:sulfonated styrene) (P-MA:SS)		<10,000	Anionic	P11[a]
poly(acrylic acid: hydroxypropyl acrylate) P-AA:HPA	 $-(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}})_n-(\mathrm{CH_2}-\underset{\begin{array}{c}\mathrm{CO}\\ \mathrm{H_3C-CH-CH_2OH}\end{array}}{\mathrm{CH}})_m-$	~7,000	Anionic	P12[a]

(continued)

Table 1 (continued)

Inhibitor	Structure	Mol. Wt.	Ionic Charge	Acronym
poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid: t-butyl acrylamide)		<15,000	Anionic	P13[a]
Sodium Lauryl Sulfate, SLS	$CH_3(CH_2)_{11}SO_4{}^-\ Na^+$	288	Anionic	S1[f]
Sodium xylene sulfonate, (SXS)	$(CH_3)_2C_6H_3SO_3{}^-\ Na^+$	208	Anionic	S2[f]
Octyl phenolethoxylate (OPE)	$C_{14}H_{22}O(C_2H_4O)_n$	624 (average)	Non-ionic	S3[g]
Cocamidopropyl Betaine, (CAPB)	$CH_3(CH_2)_{10}CONH(CH_2)_3N^+(CH_3)_2COO^-$	342	Anionic/Cationic	S4[h]
Cetyltrimethyl ammonium chloride (CTAC)	$CH_3(CH_2)_{14}CH_2N^{+\cdot}(CH_3)_3Cl^-$	320	Cationic	S5[i]

Key: [a]Experimental, Carbosperse^{TM} [b]K-732; [c]K-766; [e]K-775;[d]PCI; Fisher Scientific; [g]Dow Chemicals [h]Pilot Chemicals; [i]Aldrich. Carbosperse^{TM} polymers supplied by Lubrizol Advanced Materials, Inc., Cleveland, Ohio.

crystallization in the absence of P1. It is evident that 0.25 ppm of P1 does not exhibit any inhibitory influence on both, α value and the rate of gypsum precipitation. However, increasing the concentration of P1 by twofold, i.e., from 0.25 to 0.50 ppm resulted in significant increase in α value. For example, the α values obtained in the presence of 0.25 and 0.50 ppm of P1 were 55 and 185 min, respectively compared to 50 min obtained in the absence of P1. The data presented in Fig. 1 also show that the α value increases with increasing P1 concentration and gypsum precipitation is completely inhibited for at least 24 h in the presence of 2.50 ppm of P1. It is worth noting that similar influence on α and rate of gypsum precipitation by phosphonates and polymers has been reported [18–20].

In order to understand the impact of monomers containing different functional groups; (a) anionic, i.e., –COOH, $-SO_3H$, (b) non-ionic, i.e., ethyloxazoline, pyrrolidone and (c) cationic, i.e., poly(diallyldimethyl ammonium chloride), a series of precipitation experiments were carried in the presence of 1.50 ppm of homopolymers. Results calculated according to Eq. (1) are depicted in Fig. 2. It can be seen that among the homopolymers evaluated (i.e., poly(maleic acid), P1; poly(acrylic acid), P2; poly(methacrylic acid), P3; poly(itaconic acid), P4; poly(aspartic acid), P5; poly(2-ethyloxazoline), P6; poly(2-acrylamido-2-methylpropane sulfonic acid, P7), poly(vinylpyrrolidone), P8; poly(diallyldimethyl ammonium chloride), P9; polymers containing the anionic group, i.e., carboxyl group (–COOH) exhibit good (>37% *I*) performance compared to (<3%) for non-carboxyl containing polymer, P7, poly(2-acrylamido-2-methylpropane sulfonic acid). It is worth noting that increasing the P7 concentration from 1.5 to 7.5 ppm only results in ~10% inhibition, thus indicating that $-SO_3H$, compared to –COOH, does not significantly adsorb on gypsum crystallites. The inhibition data presented in Fig. 2 also reveal that polymers containing non-ionic group (P6, P8) and cationic group (P9) are ineffective (<3% *I*) inhibitors for gypsum. The excellent performance exhibited by P1, P2, P4, and P5 as gypsum inhibitors is consistent with earlier studies on the influence homopolymers as precipitation inhibitors for calcium fluoride [21], calcium carbonate [22], and barium sulfate [23]. The poor performance exhibited by poly(methacrylic acid), P3, may be attributed to poor adsorption of P-MAA on gypsum crystallites.

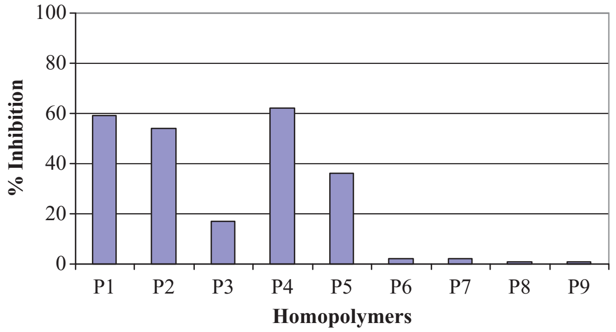


Fig. 2. Gypsum inhibition in the presence of 1.50 ppm of homopolymers.

Fig. 3 presents inhibition data collected in the presence of 2.0 ppm of copolymers in which monomers containing –COOH group in P1 and P2 have been replaced with monomers containing $-SO_3H$, i.e., acrylic

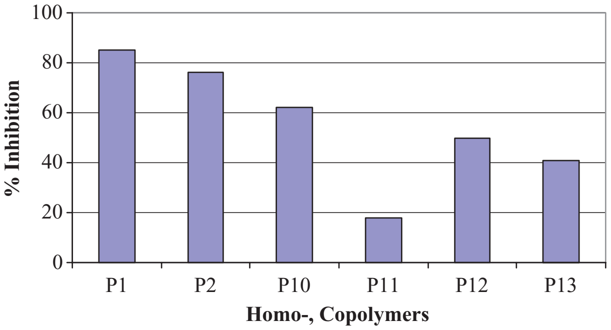


Fig. 3. Gypsum inhibition in the presence of 2.0 ppm of homo- and co-polymers.

acid:2-acrylamido-2-methylpropane sulfonic acid, P10; maleic acid:styrene sulfonic acid, P11; –COOR, i.e., hydroxylpropyl acrylate, P12; and substituted acrylamide, $-CONH_2$, i.e., acrylic acid:t-butylacrylamide, P13; exhibit poor (<20%) to good (>60%) inhibition. For example, % *I* values obtained for P1 and P2 are 85% and 76% respectively, compared to 62%, 18%, 50%, and 41% for P10, P11, P12, and P13, respectively. It is worth noting that although, these copolymers show poor to good performance as gypsum inhibitors, however, these copolymers have been reported to be excellent inhibitors for calcium phosphate, calcium phosphonate, iron (III) stabilization agents, and iron oxide dispersants [7,24–26]. Thus, it is clear from the data presented in the present investigation that polymer architecture plays an important role in inhibiting precipitation of various sparingly soluble salts.

3.2. Surfactant performance

Recently, El-Shall et al. [27] have examined the effect of a commercial non-ionic surfactant on the filterability of gypsum crystals. It was reported that the presence of a small amount of soluble impurities alters the growth rate and habit of formed crystals. Mahmoud et al. [28] in their study on the evaluation of surfactants reported that whereas cetyltrimethylammonium bromide (CTAB) decreased the induction time and increased the growth efficiency, while addition of sodium xylene sulfonate sulfate (SXS) increased the induction time and decreased the growth efficiency compared with the baseline (without additives).

In order to investigate the effect of surfactants, i.e., sodium lauryl sulfate (SLS), SXS, octylphenol ethoxylate (OPE), cocamidoprpyl betaine (CAPB) and cetyl trimethyl ammonium chloride (CTAC), a series of precipitation experiments were carried out under similar experimental conditions. Fig. 4 presents performance data collected in the presence of 2.0 ppm of various surfactants. Results presented in Fig. 4 clearly show that all surfactants do not exhibit any inhibitory influence on the gypsum precipitation. For example, %*I* values obtained for surfactants containing various function groups are <5% compared to 76% obtained for P2. Results presented in Fig. 4 also reveal that increasing the surfactant concentration by fivefold, i.e., from 2.0 to 10.0 ppm does not exhibit any significant influence on gypsum precipitation. It is clear from the data presented in Figs. 2 and 4 that additives containing $-SO_3H$ groups (i.e., P7, SXS) are poor inhibitors for gypsum precipitation.

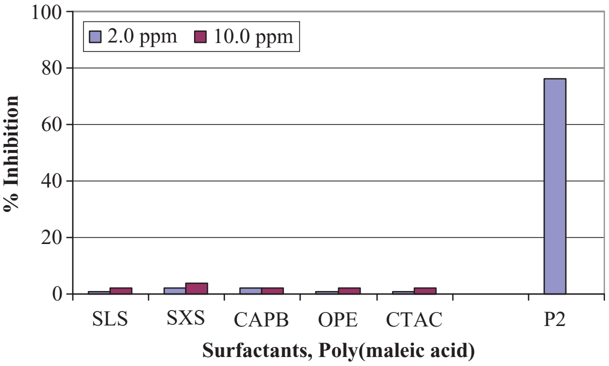


Fig. 4. Gypsum inhibition in the presence of surfactants (2.0 and 10.0 ppm) and 2 ppm of P2.

As indicated in Fig. 4 that surfactants with varying functional groups, i.e., ionic, non-ionic, cationic, amphoteric are ineffective gypsum inhibitors. Additionally, results presented in Figs. 2 and 3 reveal that polymer performance as gypsum inhibitor depends on the type of the functional group present in the polymer. In view of above results that anionic polymers strongly inhibit gypsum precipitation, a series of experiments were carried out to study the effect of surfactants on the performance of poly(acrylic acid acid), P2. Results presented in Fig. 5 show that in the presence of 2.0 ppm P2, addition of 5.0 ppm of ionic, non-ionic, and amphoteric surfactants, i.e., SLS, SXS, EOPO, OPE, CAPB does not exhibit any significant influence on the performance of P1. However, as noted in Fig. 5 addition of 5.0 ppm of CTAC exhibits antagonistic effect on the performance of P2. For example, %*I* values obtained in the presence of 2.0 ppm of P2 are 76% compared to 59% obtained in the presence of 2.0 ppm P2 and 5.0 ppm CTAC. The negative influence shown by CTAC on P2 may be attributed to poor compatibility and/or complex formation between cationic surfactant with anionic polymer, P2.

In order to check the effect of CTAC concentrations on the performance of P2, a number of precipitation experiments were carried out in the presence of 2.0 ppm of P2 and varying concentrations of CTAC. Results are illustrated in Fig. 6. It can be seen that

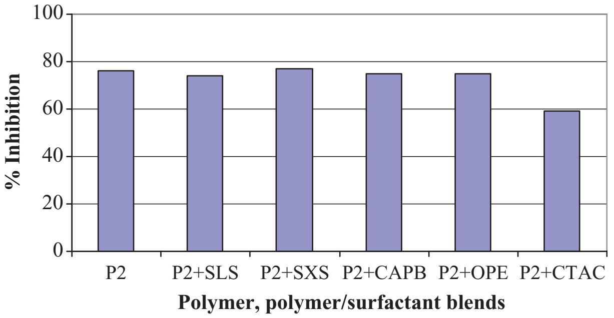


Fig. 5. Gypsum inhibition in the presence of poly(acrylic acid), P2, 2.0 ppm, and P2/surfactant blends (2.0 ppm/5.0 ppm).

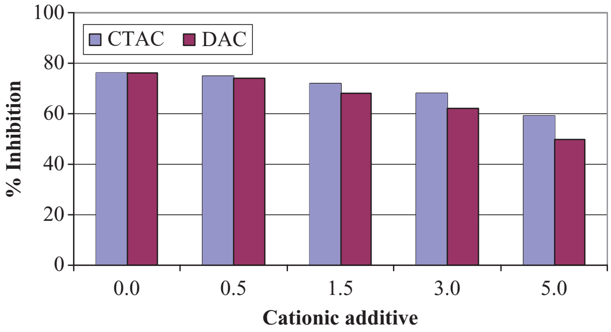


Fig. 6. Gypsum inhibition in the presence 2.0 ppm of poly (acrylic acid), P2, and varying dosages of cationic surfactant and cationic polymeric flocculant.

addition of low levels, i.e., 0.50 ppm of CTAC does not show any significant influence on the performance of P2. As noted in Fig. 6 increasing the CTAC by threefold, i.e., 0.50–1.50 ppm, results in ~5% decrease in %*I* value and further increase in CTAC from 1.5 to 5.0 ppm shows ~20% decrease in %*I* value. The data presented in Fig. 6 clearly show that addition of low concentrations of CTAC exhibits marked antagonistic effect on the performance of P2.

3.3. Effect of cationic polymer on inhibitor performance

Cationic polymers are extremely important materials used to clarify the wastewaters via processes known as coagulation and flocculation [29]. Wastewaters requiring treatment come from a wide range of sources including food processing, industrial manufacturing, and wastewater generated from during the extraction and refining of petroleum. Cationic polymers commonly used to treat wastewater include homopolymer of diallyldimethylammonium chloride, polyethyleneimmine, and copolymers of acrylic acid:acrylamide. These polymers neutralize the charge of the colloidal particles in the water to form large particles. In most cases these large particles (flocks) are removed via settling in a clarifier and are recollected as sludge. Occasionally, clarifier upsets cause the residual polymer to carryover. It has been reported [7,16] that low levels of cationic polymer, if present in the recirculating water, can interact with the highly anionic charged polymers commonly used as scale control agents and dispersant in water treatment formulations.

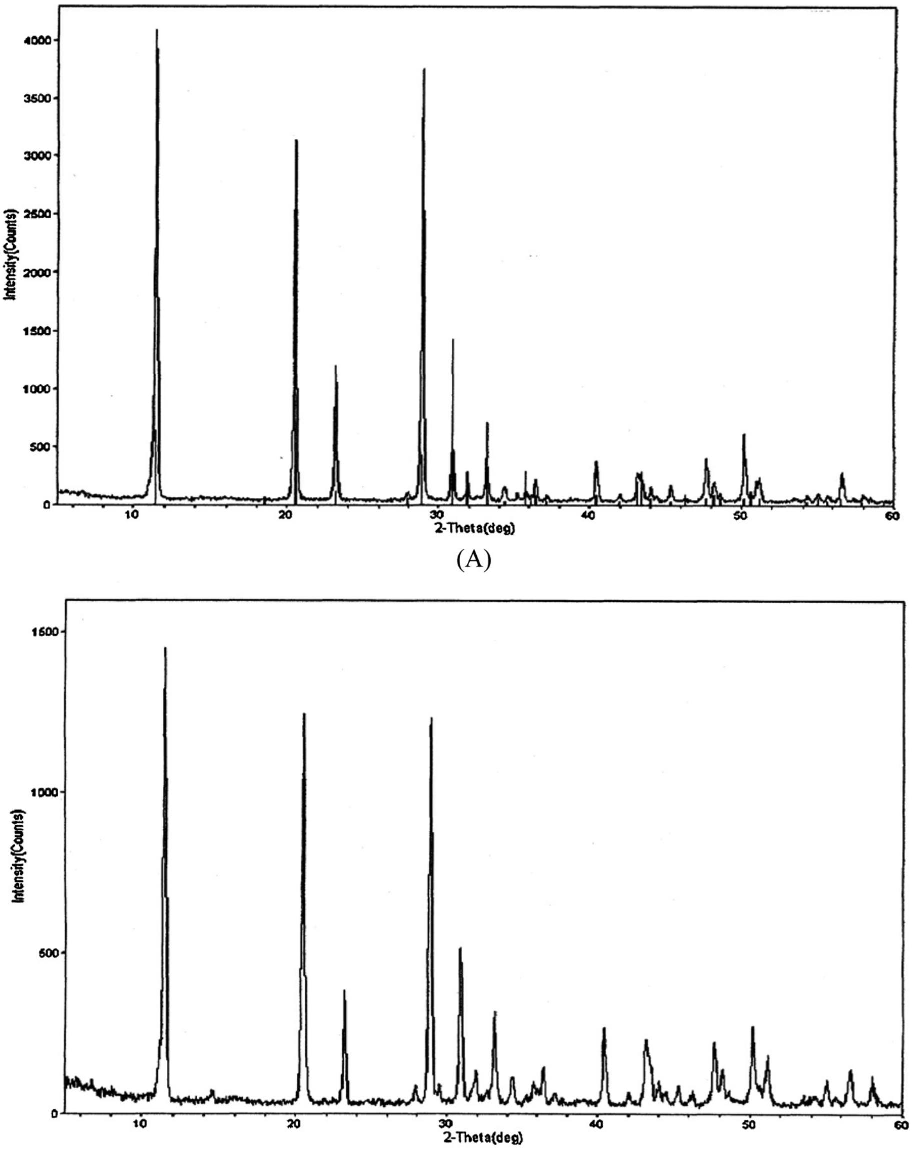
The results of gypsum precipitation experiments carried out in the presence of varying concentration of cationic polymer, poly(diallyldimethyl ammonium chloride), DAC, and 2.0 ppm of P2 are presented in Fig. 6. It can be seen that addition of small concentration, i.e., 1.5 ppm of DAC exhibits small (5%) antagonistic effect on the performance of P2 and increasing the DAC concentration from 1.5 to 3.0 ppm results in almost twofold decrease in P2 performance. The data clearly show that under similar experimental conditions DAC compared to CATC exhibits stronger antagonistic effect on the performance of P2. The observed negative influence shown by DAC may be attributed to higher cationic charge thus resulting in precipitation of anionic poly(acrylic acid), P2.

3.4. Gypsum crystals characterization

The results discussed above show that trace quantities of certain additives markedly reduce the precipitation of gypsum from aqueous solution. 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 particle surface; and (c) additive may change the ionic strength of the gypsum solution and hence the effective solubility of calcium phosphate.

Under the experimental conditions employed in the present investigation, the marked reduction in gypsum must be attributed to surface adsorption factor rather than calcium-additive complex formation (the percentage of calcium complex, even at the highest inhibitor concentration, accounts to less than 5% of total calcium) [30,31] or the concomitant increase in ionic strength of the supersaturated solution in the presence of additives.

Characterization of gypsum scale crystals was carried out by XRD and SEM for understanding the mechanism of scale inhibition. The XRD spectra of gypsum crystals formed in the absence and presence of 1.5 ppm of poly(acrylic acid) are illustrated in Figs. 7(a) and 7(b), respectively. From gypsum crystals (control, no inhibitor, Fig. 7(a)), the structure is proved to be $CaSO_4 \cdot 2H_2O$. The '*d*' and 'Θ' values of gypsum are in conformity with the reported values. It is interesting to note that in the presence of poly(acrylic acid)



(A)

(B)

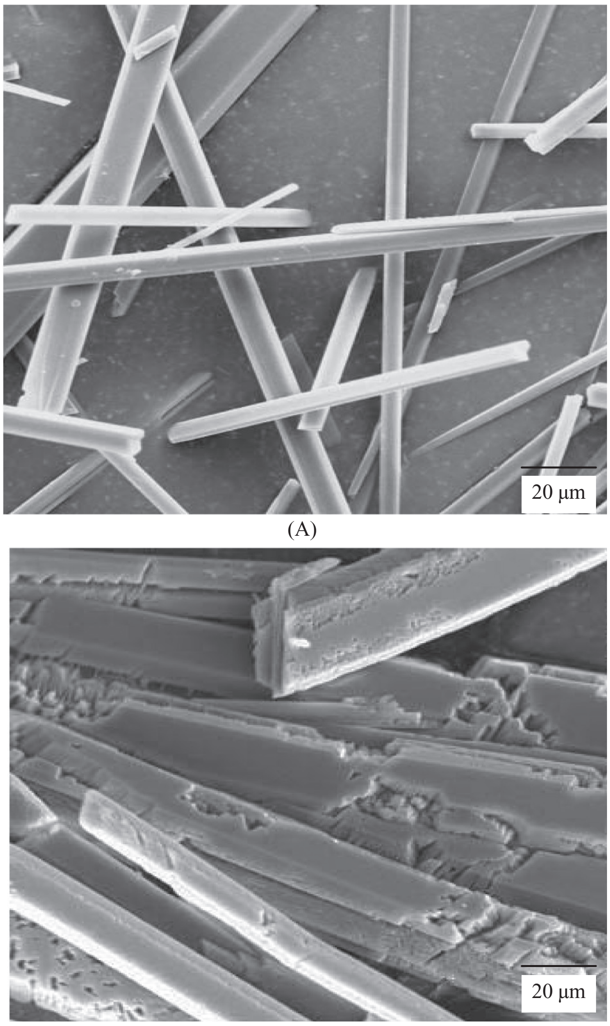
Fig. 7. XRD spectra of gypsum crystal grown in the absence (A) and in the presence (B) of 1.5 ppm of poly(acrylic acid), P2.

the crystal structure has not been altered (Fig. 7(b)) 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 the control.

The electron micrographs of uninhibited and inhibited gypsum scales are presented in Figs. 8(a) and 8(b). As illustrated in Fig. 8(b) gypsum crystals grown in the presence of poly(acrylic acid) are highly modified compared with those grown in the absence of poly(acrylic acid). It is worth noting that gypsum crystals modification as observed in the present study has also been reported by Senthilmurugan et al. [10] in their study on the evaluation of maleic acid copolymers as gypsum scale inhibitors. Additionally, crystal modification by polymeric inhibitors has also been reported for calcium carbonate [32], calcium fluoride [21], and barium sulfate [23].

4. Conclusions

The results presented show that gypsum inhibition strongly depends upon polymer dosage and polymer architecture. In general, polymers containing carboxyl group exhibit better performance compared to polymers containing non-ionic groups. Under the experimental conditions employed surfactants containing different groups (i.e., ionic, non-ionic, amphoteric, cationic, etc.) are ineffective gypsum inhibitors. It has also been



(A)

(B)

Fig. 8. Scanning electron micrographs of gypsum crystals grown in the absence (A) and in the presence (B) of poly(-acrylic acid), P2.

observed that addition of low levels of cationic surfactant and cationic polymeric flocculant exhibit an antagonistic influence on the performance of anionic polymers used as gypsum inhibitors.

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