

Inhibition of Barium Sulfate Precipitation: Effects of Additives, Solution pH, and Supersaturation

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ABSTRACT

The precipitation of barium sulfate from aqueous solutions at 35°C has been studied by a spontaneous precipitation technique. A variety of polymeric and non-polymeric inhibitors such as poly(acrylic acids) (MW 800 to 20,000), poly(maleic acid), poly(acrylamide), poly(2-acrylamide 2-methyl-propanesulfonic acid), poly(diallyldimethylammonium chloride); polyphosphates (pyro and tripoly); phosphonate (hydroxyethylidene 1,1-diphosphonic acid); citric acid, and benzene polycarboxylic acids, have been examined for their effects on barium sulfate precipitation. The results indicate that the precipitation of barium sulfate is strongly affected by changing the functional group, molecular weight, and concentration of inhibitor. In addition, inhibition data on barium sulfate precipitation suggests an optimum effectiveness with molecular weight of ~2,000 for the poly(acrylic acids) studied in the molecular weight range 800 to 20,000. Scanning electron microscopic investigations of the barium sulfate crystals grown in the presence of poly(acrylic acids) show that structures of these crystals are highly modified. A mechanism based upon surface adsorption of inhibitors on the growing barium sulfate crystals is discussed. The order, in terms of decreasing effectiveness on barium sulfate precipitation, of various precipitation inhibitors studied is poly(maleic acid), poly(acrylic acid), phosphonate, polyphosphate, benzene polycarboxylic acids.

INTRODUCTION

Deposition of scale forming salts on equipment surfaces in many industrial systems such as oil and gas production, desalination, pulp and paper, cooling and boiler, etc. is a well studied problem. Although not as common as calcium carbonate and calcium sulfate scales, barium sulfate deposits have long plagued oil field and gas production operations. In addition, barium sulfate also poses serious problems in production operations where water containing high level (~3,000 mg/L) of sulfate is used as a water flood. The deposition of barium sulfate scale on tubes and vessels can result in plant shutdown, production losses, equipment replacement, and cleaning costs.

Barium sulfate scales once formed on the equipment surfaces are extremely difficult to remove. Typically mineral scaling in oil and gas production is controlled by two methods:

1. Use of inhibitors to prevent formation, and
2. Mechanical removal (scraping, sand blasting, chipping) or chemical removal (use of acids or other specialty formulated cleaners).

It has been demonstrated that precipitation of BaSO₄ is affected by several factors including solution supersaturation, ionic strength, and temperature.

Precipitation inhibitors play an important role in many industrial processes necessitating scale prevention. Examples include calcium carbonate, calcium sulfates and calcium phosphate scales in cooling, boiler, and desalination processes; calcium phosphates in dairy application; and barium sulfate in oil and gas production. The inhibitors used in such processes mostly fall in three classes (a) polyphosphates and phosphate esters, (b) organophosphonates and (c) synthetic organic polymers.

Several studies have discussed the influence of solution pH on the performance of polymeric and non-polymeric inhibitors on the crystal growth of sparingly soluble salts. Griffith, et. al. (ref.1) have shown that the performance of phosphonic acids as CaSO₄ · 2H₂O crystal growth

inhibitors improves with increasing pH, and have attributed this improvement to an increase in the degree of deprotonation of the acids. Leung and Nancollas (ref.2), using a seeded growth technique, arrived at similar conclusions after studying the effect of benzene polycarboxylic acids on the crystal growth of BaSO₄.

Recently, the evaluation of polymers, especially low molecular weight poly(acrylic acids) as scale inhibitors has attracted the attention of several investigators, because these polymers are highly efficient in preventing the deposition of mineral scales on equipment surfaces (refs.3-6). From a practical viewpoint, the use of polymers in controlling scale formation has certain advantages because of their stability even at relatively high temperatures. Furthermore, these polymers provide an economical as well as a relatively easy method of controlling or preventing scale formation.

EXPERIMENTAL

Grade A glassware and analytical grade chemicals were used. Stock solutions of barium chloride and sodium sulfate were prepared using distilled water, filtered through 0.22 micron filter paper and analyzed by ion exchange and atomic absorption spectroscopy methods. Sodium pyrophosphate, sodium tripolysphosphate, citric acid, and benzene hexacarboxylic acids were prepared from reagent grade chemicals. The phosphonate used in this study was kindly donated by The Monsanto Company. The polymeric inhibitors used were selected from the range of experimental and commercial polymers supplied by The BFGoodrich Company. Polymer concentrations given herein are on dry polymer basis. All polymers were tested under equal precipitation conditions (i.e., at the same supersaturation and bulk solution pH). Some of the polymers were also tested at different pH values. A Brinkmann pH meter (model 632, Brinkmann Instruments, Westbury, New York) equipped with a pair of glass and calomel electrodes was used to measure pH. The system was calibrated before each set of measurements and checked afterwards against NBS standard buffers.

Supersaturated solutions of barium sulfate for precipitation experiments were prepared by adding a known volume of sulfate stock solution (normally 2 to 5 mL) into the thermostated growth cell maintained at 35°C and containing 180 mL water. Following temperature equilibration, the second component was added in such amount that the final BaSO₄ solution concentration would be 5.00 to 8.00 x 10⁻⁴ M. Precipitation in these solutions was monitored by analyzing aliquots of the filtered (0.22 micron filter paper) solution for barium using the PE6500 ICP / AAS instrument utilizing a 553.6 nm wavelength in the visible region and the nitrous oxide flame. Experiments involving inhibitors were performed by adding the inhibitor solution to the sodium sulfate solution, before the addition of barium chloride solution. The barium sulfate supersaturated solutions' pH values were adjusted to the required value using dilute solutions of sodium hydroxide and/or hydrochloric acid.

The performance of additive as BaSO₄ inhibitor was calculated using the following equation:

$$\text{Percent Inhibition (\%)} = 100 \times [(\text{Ba})_{\text{exp}} - (\text{Ba})_{\text{final}}] / [(\text{Ba})_{\text{initial}} - (\text{Ba})_{\text{final}}] \quad (1)$$

Where

- (Ba)_{exp} = Concentration of barium in the filtrate in the presence of inhibitor at 20 hours.
- (Ba)_{final} = Concentration of barium in the filtrate in the absence of inhibitor at 20 hours.
- (Ba)_{initial} = Concentration of barium at the beginning of the experiment.

Spontaneous precipitation experiments were also made to investigate the influence of inhibitors on the morphology of the precipitated barium sulfate. Sodium sulfate solution, containing the required concentration of inhibitor, and the barium chloride solution were rapidly mixed and allowed to equilibrate for 2 days. The precipitated crystals were studied by scanning electron microscopy.

RESULTS AND DISCUSSION

Performance of Poly (acrylic acids)

Effect of concentration: The experimental conditions and the inhibition results obtained in the presence of inhibitors are summarized in Table 1. The agreement between the results of experiments 7, 8, and 9 respectively, in Table 1 confirms the reproducibility. As can be seen in Table 1, the precipitation of BaSO₄ is highly sensitive to the concentration of PAA in solution. Interestingly, a PAA-1 concentration as low as 2.0 ppm (parts per million) significantly reduces the precipitation of BaSO₄. Table 1 further indicates that at 3.0 ppm concentration, the precipitation is reduced by 78%, and at 6.0 ppm polymer concentration the precipitation reaction is completely inhibited for at least 20 hours.

Table 1
Barium Sulfate Inhibition in the Presence of Poly(acrylic acids) -
The Effect of Polymer Concentration and Molecular Weight.

Inhibitor	MW	Concentration (ppm)	BaSO ₄ inhibition (%)
None	--	0.0	0
PAA-1	800	1.0	19
PAA-1	800	2.0	58
PAA-1	800	2.0	55
PAA-1	800	2.0	60
PAA-1	800	3.0	78
PAA-1	800	6.0	98
PAA-2	1,600	1.0	35
PAA-2	1,600	2.0	75
PAA-2	1,600	3.0	91
PAA-3	2,100	0.50	8
PAA-3	2,100	1.0	46
PAA-3	2,100	1.5	68
PAA-3	2,100	2.0	87
PAA-3	2,100	2.5	93
PAA-3	2,100	3.0	98
PAA-3	2,100	5.0	99
PAA-4	5,100	1.0	30
PAA-4	5,100	2.0	61
PAA-4	5,100	2.5	77
PAA-4	5,100	3.0	85
PAA-4	5,100	5.0	99
PAA-5	10,000	2.0	22
PAA-5	10,000	3.0	45
PAA-6	20,000	2.0	6
PAA-6	20,000	3.0	16

Conditions: 5.00 x 10⁻⁴ M BaSO₄, pH 7.00, 35°C

Effect of Molecular Weight (MW): In recent years considerable attention has been given to the use of water soluble polymers, added to water at very low dosages, which are capable of either preventing or drastically retarding the formation of mineral scales. Studies have shown that one of the factors determining the effectiveness of a polymer is its MW. Amjad (refs. 7-9) in studies on the influence of PAA in retarding the crystal growth of calcium sulfate dihydrate, calcium fluoride and calcium phosphate, reported that MW of the PAA plays an

important role. Smith and Huilin (ref. 10) in their study on the effect of MW (1,200 to 8,000) of PAAs on calcium sulfate precipitation reported that high MW PAAs were the least effective and the effectiveness increased as the MW of the polymer decrease. Libutti, et al. (ref. 3) in their study on the evaluation of PAAs as antiscalants for cooling water application showed that the rate of fouling of heat exchanger by CaCO₃ increases with an increase in MW in the range of 2,000 to 100,000. Based upon results of similar MW polyelectrolytes, Smith and Alexander (ref. 11) reported that poly(acrylic acids) were more effective than poly(methacrylic acids) in inhibiting the precipitation of calcium sulfate solution from supersaturated solutions.

The effect of PAA MW on the precipitation of BaSO₄ was studied. Results summarized in Table 1 show that at constant temperature and polymer concentration, the BaSO₄ inhibition value increases with decreasing MW (from 20,000 to 2,100), reached a maximum at an MW about 2,000 and thereafter decreases with decreasing MW (from 2,000 to 800). Result of a recent study on the effect of copolymers of acrylic acid and 2-hydroxy-3-(allyloxy)-1 propane sulfonic acid as CaCO₃ inhibitors suggested optimum effectiveness with a MW ~3,000 copolymer (ref. 12). It is also interesting to note that Amjad and Masler (ref. 13) in their study on the evaluation of PAAs as CaSO₄ · 2H₂O crystal growth inhibitors showed optimum performance with a MW ~2,000 PAA. The effect of polymer molecular weight on the precipitation of BaSO₄ observed in the present investigation is thus consistent with observations made for the other sparingly soluble salts (refs. 7, 8, 14).

Effect of Supersaturation

The results on the influence of solution supersaturation (i.e., BaSO₄ = 5.00 to 8.00 X 10⁻⁴M) in the presence of PAA-4 are summarized in Table 2. It can be seen (Table 2) that as the solution supersaturation is raised, there is a concomitant marked decrease in the barium sulfate inhibition. At a given temperature and polymer concentration, the relationship between the supersaturation and the BaSO₄ inhibition can roughly be expressed quantitatively by an empirical equation:

$$(\% \text{ inhibition})^{-1} = a [\text{BaSO}_4] + b \quad (2)$$

Where “a” and “b” are constants.

Table 2
Barium Sulfate Inhibition in the Presence of PAA-4.
The Effect of Solution Supersaturation.

[BaSO ₄] x 10 ⁴ M	BaSO ₄ Inhibition (%)
5.00	87
6.00	28
7.00	16
8.00	9

Conditions: 35°C, pH 7.0, 3.0 ppm polymer

Effect of Solution pH

The influence of pH on the effect of several phosphonic acids as gypsum crystal growth inhibitors has been reported. Results of this seeded growth study show that an increase in the pH of the crystal growth medium over a pH 4 to 9 range brings about an improvement in inhibitor performance that runs parallel to the phosphonic acid titration (ref.1).

The effect of solution pH on the precipitation of BaSO₄ in the presence of PAA4 (3.0 ppm) was studied. The results clearly demonstrated the ineffectiveness of PAA-4 at pH 2.0 and 4.0. It should be noted under similar experimental conditions at pH 5.0, 6.0, 7.0, and 8.0, that inhibition values obtained for PAA-4 at 3.0 ppm were 34%, 49%, 62%, and 87%, respectively. The poor

inhibitory performance exhibited by PAA-4 at pH <4 may be explained by insignificant deprotonation of carboxylic acid group.

Effect of Polymer Composition

Precipitation data for several homopolymers including PAA, PMA (polymaleic acid), PSA (poly2-acrylamido-2-methylpropane sulfonic acid), PAM (polyacrylamide) and PDADMAC (polydiallyldimethylammonium chloride) are summarized in Table 3. The results reveal that polymers which are devoid of carboxyl groups (i.e., PAM, PSA, PDADMAC) do not significantly inhibit BaSO₄ precipitation. Table 3 shows that PAA-1 is less effective an inhibitor than PMA of similar molecular weight. For example, inhibition values obtained for PMA and PAA-1 at 2.0 ppm polymer concentration are 97% and 58%, respectively, compared to 0% in the absence of polymer. On the basis of inhibition values for PAA-1 (MW 800, Table 1) at 2.0 ppm polymer concentration, it appears that effectiveness of PMA is due to the presence of highly charged-dicarboxylate icons. This is consistent with the results of a study reported by Coffey (ref. 15), which showed that the best inhibitors for BaSO₄ precipitation were those that imparted the most negative electrophoretic mobility to the BaSO₄ particles. Similar observations have also been reported in recent kinetic studies involving the effect of polycarboxylic acids on the crystallization of dicalcium phosphate dihydrate (ref. 16) and calcium carbonate (ref. 17).

Table 3
Barium Sulfate inhibition in the Presence of Homopolymers, Polyphosphates, Phosphonate, Citric Acid, and Benzene Hexacarboxylic Acid

Inhibitor	BaSO ₄ inhibition (%)
PAA-1	58
PAA-3	87
PMA	97
PAM	2
PSA	4
PDADMAC	1
PYP	22
TPP	78
HEDP	98
BHCA	15
CA	6

Conditions: 5.00 X 10⁻⁴ M BaSO₄, pH 7.00, 35°C, 2.00 ppm inhibitor

Results presented in Table 3 clearly indicate that inhibition of BaSO₄ precipitation at constant pH, temperature, and polymer concentration is a function of polymer functional group. The order in terms of inhibitor effectiveness is as follows:

PMA > PAA >> PAM ≈ PSA ≈ PDADMAC ≈ control (no polymer).

It is noteworthy that in the case of CaF₂ seeded growth in the presence of inhibitors (ref. 8) the order of effectiveness suggested was as follows:

PAA > PSA > PAM ≈ PDADMAC.

Effect of Polyphosphates, Phosphonates, and Carboxylic Acids

Inhibition of crystal growth of a number of sparingly soluble salts by pyrophosphate (PYP) has been the subject of numerous investigations (refs. 18, 19). In biological calcification processes, PYP ion has been found to be an effective crystal growth inhibitor for calcium phosphate and calcium oxalate systems. Another class of compounds that have proved to be effective in

inhibiting calcification of mineral scale formation is the organic phosphonates. These inhibitors are characterized by relatively inert P-C-P and P-C-N-P linkages, which substitute for hydrolysable P-O-P bond of PYP.

The influences of polyphosphates such as PYP and TPP as BaSO_4 precipitation inhibitors are summarized in Table 3. As shown in Table 3, the precipitation in the presence of 2.0 ppm PYP BaSO_4 precipitation is reduced by 22%. Table 3 shows that TPP inhibited precipitation to a greater degree than PYP under similar experimental conditions. Results of BaSO_4 inhibition (Table 3) for polyphosphates suggest that the inhibition by polyphosphates decreases as the chain length decreases. It is interesting to note that similar inhibiting effect of these polyphosphates has been reported for the crystallization of calcium phosphate dihydrate (ref. 20) and hydroxyapatite (ref. 21).

The effects of diphosphonate (HEDP), benzene hexacarboxylic acid (BHCA), benzene 1, 3, 5-tricarboxylic acid (BTCA), and citric acid (CA) on the precipitation of BaSO_4 were also studied by a series of experiments summarized in Table 3. Based upon the inhibition data (Table 3) the order in terms of decreasing effectiveness for non-polymeric inhibitors is as follows:

HEDP > TPP >> BHCA > PYP > CA.

Effect of Inhibitors on BaSO_4 Crystal Morphology

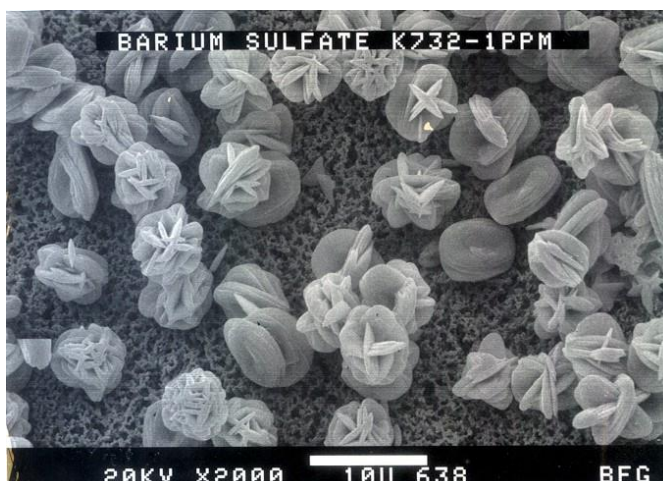
It has been shown that the presence of low levels of scale inhibitors influences not only the growth rate and morphology of the crystals, but also the nature of the hydrated phase which forms (ref. 22-25). This may be of particular importance in industrial water systems since the presence of certain inhibitors may influence the nature of the scaling mineral. In the present work the influence of polymeric and non-polymeric inhibitors on the morphology of growing BaSO_4 crystals was also studied. Figures 1(a) and 1(b) show BaSO_4 crystals grown in the absence and presence PAA-3, respectively and indicated 1.0 ppm PAA-3 results in highly modified crystals. The observed change in morphology may be explained in terms of surface adsorption of PAA on the growing BaSO_4 crystals.

Figure 1
Barium Sulfate Crystals in the Absence and Presence of PAA-3

(a) Control (No Inhibitor)



(b) In the Presence of 1 ppm PAA-3



Mechanism of Barium Sulfate Inhibition

The results discussed in this paper on BaSO₄ precipitation by a number of polymeric and non-polymeric inhibitors containing varying functional groups can be categorized into the following two types:

1. Those such as anionic charged low MW PAAs, PMA, and phosphorus-containing inhibitors (i.e., PYP, TPP, and HEDP) that exhibit marked inhibitory activity on BaSO₄ precipitation.
2. Those cationic, neutral or anionic charged inhibitors, such as poly(diallyldimethyl ammonium chloride), poly(acrylamide), poly(2-acrylamido 2-methyl propane sulfonic acid), citric acid, and benzene poly(carboxylic acids), which show poor inhibitory influence on BaSO₄ precipitation.

The marked influence of BaSO₄ precipitation inhibitors observed in the present investigation may be attributed to one or more of the following factors:

- Inhibitor may change the ionic strength.
- Inhibitor may form stable complex with barium and/or sulfate ion and reduce supersaturation and hence the effective solubility of the BaSO₄.
- Inhibitor may be adsorbed on the precipitating crystal surface and inhibit growth.

Under the experimental conditions employed in the present investigation an adsorption process appears to offer a more feasible explanation because the inhibitor concentrations used were so small that the formation of barium inhibitor complex and/or a concomitant increase in ionic strength would not reduce the supersaturation. An adsorption mechanism is also indicated in many systems by an appreciable modification of crystals grown in the presence of inhibitors.

SUMMARY

Results of precipitation experiments made in the presence of low levels of PAAs and PMA clearly indicate that these polymers exhibit an excellent inhibitory property. In terms of MW dependence it has been found that the amount of BaSO₄ precipitated decreases with decreasing MW (from 20,000 to 2,100) of PAA reaching a maximum at MW ~2,000, and thereafter increases with decreasing MW (from 2,100 to 800). Results also indicate that polymer composition greatly affects BaSO₄ precipitation. In addition, it has also been found that phosphorous containing compounds show excellent inhibitory activity.

Overall, the order in terms of decreasing effectiveness of the inhibitors studied is as follows:

Polymeric: PMA > PAA > > PAM ≈ control
Non polymeric: HEDP > STPP > PYP.

Scanning electron microscopic investigations of the BaSO₄ crystals grown in the presence of PAA show that these crystal structures are highly modified.

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