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Polymer Evaluations as Strontium Sulfate Precipitation Inhibitors for Industrial Systems

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Abstract

In this work, a variety of polymers were evaluated as precipitation inhibitors for strontium sulfate [(SrSO$_4$), celestite] in aqueous solution. The polymers tested include 1) homopolymers of acrylic acid and methacrylic acid of varying molecular weight (MW), 2) acrylic acid based co- and terpolymers containing monomers with different functional groups and 3) natural, bio- and hybrid based polymers The results reveal that polymer performance as a SrSO$_4$ inhibitor is strongly affected by MW, ionic charge of the functional group and polymer dosage. It has been observed that performance of poly(acrylic acid) or PAA is negatively impacted by increasing the strontium sulfate solution supersaturation. Moreover, inhibition of SrSO$_4$ by PAAs suggest an optimum effectiveness at MW ~7,000, with a range of ~1,500 to 345,000 investigated in this paper. Scanning electron microscopic investigations of the SrSO$_4$ crystals grown in the presence of PAA show that structures of these crystals are highly modified. Overall performance reveals the following trend by polymer type: homopolymer > copolymer ≥ terpolymer.

Keywords: strontium sulfate, celestite, precipitation, inhibition, polymer architecture, crystal habit modification

Introduction

Scaling is defined as the formation of sparingly soluble salts on equipment surfaces in many industrial processes including boiler, cooling, geothermal, pulp and paper manufacturing, upstream oil and gas operations, waste water treatment, milk pasteurization, phosphoric acid production, etc. The scales commonly encountered in these processes include sparingly soluble carbonates and sulfates of calcium, barium, and strontium. Although, not as common as calcium carbonate and calcium sulfate scales, barium sulfate (BaSO$_4$) and strontium sulfate (SrSO$_4$) deposits have long plagued oilfield and gas production operations. The deposition of BaSO$_4$ and SrSO$_4$ scale on tubes and vessels can result in production losses, equipment replacement, and cleaning costs.[1] In the North Sea, typical scale problems are related to the formation of BaSO$_4$, SrSO$_4$, and CaCO$_3$. The severity of the problems and the need of novel

solutions are highly dependent on the field operating conditions, which vary from mild scaling tendencies to the extreme.

During the last three decades, reverse osmosis (RO) has become an integral and vital process in the desalination of sea, brackish, and ground waters for potable water and industrial needs. RO applications in the food processing industry are developing broadly to include fruit and vegetable juices, processing of milk, sugar, fats, and meat by-products. The RO membrane separation process also plays a useful role in cleaning industrial effluents including those from pulp and paper, metal recovery from electroplating wastes, and municipal waste water reclamation. In addition, RO processes are used widely in the production of high purity water for pharmaceutical, cosmetics, semiconductor manufacturing, and power industries.

RO membranes typically remove greater than 99% of the dissolved salts, microorganisms, and colloids, and in some cases more than 90% of soluble silica and total organic carbon from the feed stream. A fundamental problem facing RO users today is the persistence of "fouled" membrane surfaces. The term fouling implies the deposition of any material on the surface of the semipermeable membrane. Fouled membranes have a reduced flux and lower operating efficiency which may lead to poor water quality, unscheduled shutdowns, and premature membrane replacement resulting in increased operating cost. The types of scales most commonly encountered in an RO system include calcium carbonate, calcium phosphate, calcium sulfate, colloidal silica, metal silicates, etc. However, deposition of $BaSO_4$ and $SrSO_4$ on the RO membrane surface is also observed due to incompatibility of sea water containing high sulfate with barium and strontium rich formation water. The long term success of an RO system largely depends on three factors: design, pretreatment (including chemical treatment), and operation and maintenance.[2]

The influence of low dosages (few milligram per liter, mg/L) of chemical additives (polymeric or non-polymeric) to prevent or retard sulfate scales of calcium, barium, and strontium in industrial water systems has attracted the attention of academic researchers and industrial technologists. Dogan and coworkers[3] using the spontaneous precipitation technique, investigated the influence of poly(ethylene oxide)-block-poly(methacrylic acid) polymers as calcium sulfate growth inhibitors. Results of their studies reveal that inhibition increases with acid content of the polymer. Amjad[4] showed that polymeric additives containing carboxyl (-COOH) group such as poly(acrylic acid), PAA; poly(maleic acid), PMA; poly(itaconic acid), and poly(aspartic acid) were particularly effective as calcium sulfate growth inhibitors. Amjad and Masler[5] in their study on the evaluation of PAAs as calcium sulfate crystal growth inhibitors showed optimum performance with a ~2,000 MW PAA. Leung and Nancollas[6] and Jones et al.[7] investigated the influence of polyphosphates, polycarboxylates, and phosphonates as inhibitors for $BaSO_4$ precipitation in aqueous solution. Results of these studies suggest that phosphonates exhibit better performance compared to polyphosphates in inhibiting barium sulfate.

In our previous papers, we have shown that polymer performance as scale inhibitor depends on polymer composition and scaling system being investigated. It was reported that PAAs, compared to co- and terpolymers, are effective inhibitors for calcium carbonate, barium sulfate, and calcium fluoride.[8,9,10] However, for calcium phosphate and calcium phosphonate scales, co- and terpolymers perform better than PAAs.[11,12,13] The present work is a continuation of our efforts in understanding the influence of polymer characteristics (i.e., composition, molecular weight, ionic charge of the functional group, polymerization solvent, etc.) on $SrSO_4$ precipitation in aqueous solution. In addition, scanning electron microscopy and X-ray diffraction techniques were used to characterize $SrSO_4$ crystals grown in the absence and presence of polymers. The goal is to provide water technologists with information that will help facilitate polymer selection based on performance and treatment objectives.

Experimental

Reagents and Materials

Reagent grade chemicals and grade A glassware were used. Stock solutions of strontium nitrate and sodium sulfate were prepared using distilled, CO_2-free water and filtered through 0.22 μm filter paper. The strontium ions concentration was determined by atomic absorption spectrophotometry. The standardization of sodium sulfate was done by ion chromatography. Polymers evaluated in this study were commercial and/or experimental materials and their stock solutions were prepared on dry active solids basis.

Strontium Sulfate Precipitation Protocol

The strontium sulfate precipitation experiments were carried out by adding a known volume of stock solution of sodium sulfate to a known volume of water in a glass bottle. To this sodium sulfate solution, a known volume of stock solution of strontium nitrate was added under continuous stirring. In experiments involving the inhibitor, a known volume of stock solution of inhibitor was added to the sodium sulfate solution prior to the addition of strontium nitrate. The experimental solutions were stored unstirred in a water bath maintained at 25°C. The progress of strontium sulfate (876 mg/L Sr, 960 mg/L SO_4) precipitation in the absence and presence of inhibitors was followed by measuring the conductivity (Orion Star A212 conductivity meter) as a function of time. The conductivity values collected as a function of time were used to calculate inhibition of strontium sulfate precipitation.

Polymer Efficacy

Polymer efficacy as strontium sulfate inhibitor was calculated using the following equation:

$$\text{Percent inhibition (\%I)} = [(C_1 - C_2) / (C_3 - C_2)] \times 100 \qquad (1)$$

Where:

C_1 = conductivity reading at known time
C_2 = conductivity reading at 24 h
C_3 = conductivity reading at 0 h

Strontium Sulfate Crystals Characterization

At the end of precipitation experiments samples were withdrawn and were filtered through 0.22 μm membrane filters and solids were characterized by scanning electron microscope (SEM, Zeiss EVO50) and X-ray diffraction (Bruker D8 Discover).

Results and Discussion

Table 1 lists the homopolymers investigated. As can be seen that polymers vary significantly in terms of MW and functional groups. In all experiments, the calculations for the driving force was done by considering all appropriate equilibria between strontium, sulfate, and inhibitor species in solution using the procedure described previously.[14] A scaling index defined as the ratio of the ion activity product over the thermodynamic solubility product was calculated for each of the potentially forming solid phase, and the calculated values are shown in Table 1. As indicated, the solutions are supersaturated with respect to $SrSO_4$.

Table 1. Homopolymers tested.

Polymer	Structure	Functional Group	MW (k)	Ionic Charge	Acronym
poly(acrylic acid)	$-(CH_2 - CH)_n -$ | COOH	-COOH	2.0	anionic	PA1$_s$[a]
poly(acrylic acid)	$-(CH_2 - CH)_n -$ | COOH	-COOH	6.0	anionic	PA2$_s$[b]
poly(acrylic acid)	$-(CH_2 - CH)_n -$ | COOH	-COOH	2.3	anionic	PA3$_w$[c]
poly(acrylic acid)	$-(CH_2 - CH)_n -$ | COOH	-COOH	7.3	anionic	PA4$_w$[d]
poly(acrylic acid)	$-(CH_2 - CH)_n -$ | COOH	-COOH	120	anionic	PA5$_w$[e]
poly(acrylic acid)	$-(CH_2 - CH)_n -$ | COOH	-COOH	345	anionic	PA6$_w$[f]
poly(methacrylic acid)	CH_3 | $-(CH_2 - CH)_n -$ | COOH	-COOH	30	anionic	PMA1[g]
poly(methacrylic acid)	CH_3 | $-(CH_2 - CH)_n -$ | COOH	-COOH	6	anionic	PMA2[h]

Key: [a]CK752; [b]CK732; [c]CK7028; [d]CK7058; [e]CK7600N; [f]CK702; [g]K765; [h]CK766; supplied by The Lubrizol Corporation, Wickliffe, OH; Saturation Ratio = SR = Log IAP/K_{sp} = 1.68 at the pH of the working solution.

Polymers Performance

Water technologists use a variety of additives to control scaling, corrosion, suspended matter and microbiological growth in industrial systems. The additives selection largely depends on various factors including water chemistry, system metallurgy, system operating conditions and compatibility with other formulation components. Typical deposit control additives include polyphosphates, phosphonates, homopolymers of acrylic acid, maleic acid, aspartic acid, and acrylic acid or maleic based co- and terpolymers. The results reported here had good reproducibility (±6%).

Homopolymers

Dosage effect. To study the impact of polymer dosage on $SrSO_4$ precipitation, a series of experiments were carried out in the presence of varying dosages of poly (acrylic acid). Figure 1 presents conductivity vs. time profiles for experiments conducted in the presence of varying dosages (0 – 3 mg/L) of $PA3_w$ [poly(acrylic acid), polymerized in water, MW 2,300). It can be seen that a measurable lag in time (as illustrated by arrow in Figure 1) is observed. The polymer inhibits if it delays the onset of precipitation. This delay is known as induction time or β. The conductivity vs. time profiles also shown in Figure 1 suggests that β is greatly prolonged by increasing $PA3_w$ concentration. For example, β values obtained in the presence of 0.5, 0.75, and 1.0 mg/L of $PA3_w$ are 30, 155, and 462 min respectively, compared to < 2 min observed in the absence of $PA3_w$. It is worth noting that increasing the $PA3_w$ concentration by threefold i.e., 1.0 to 3.0 mg/L results in complete inhibition of $SrSO_4$ for at least 24 h. It is interesting to note that several researchers in their studies on the evaluation of polyelectrolytes as $SrSO_4$, $CaSO_4.2H2O$ and $CaCO_3$, crystal growth inhibitors showed that precipitation is preceded by an induction time.[15,16,17]

Figure 2 presents percent inhibition (%I) data as a function of $PA3_w$ dosage calculated according to equation (1). It is evident that %I increases with increasing polymer dosage. For example, %I values obtained in the presence of 0.5, 1.0, and 1.5 mg/L are 10, 30, and 53 % respectively. The data presented in Figure 2 also shows that increasing the dose two fold i.e., from 1.5 to 3.0 mg/L results in >90% inhibition.
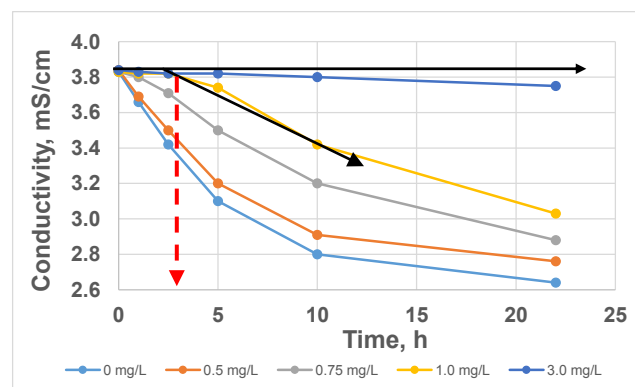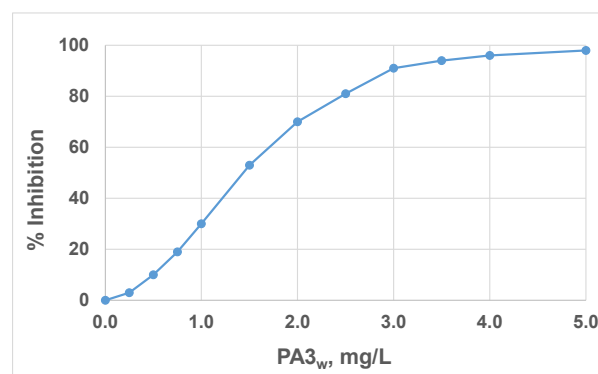
Figure 1. Plots of conductivity vs. time for $SrSO_4$ precipitation in the presence of varying concentrations of $PA3_w$.

Figure 2. Plots of % inhibition vs. PA3w dosages at 24 h.

Polymerization solvent effect: Synthetic polymers are produced by various methods including precipitation, solution, suspension, emulsion, and bulk. All of these polymerization methods have the advantage of heat and viscosity control during the polymerization. The choice of polymerization process depends on several considerations including technology alternatives, product performance, application requirements and economics. Solution polymerization is the primary method for manufacturing scale and deposit control polymers. Polymers used in water treatment are typically produced in an organic solvent and/or water.

To understand the impact of polymerization solvent on PAA performance, several experiments were carried out under similar experimental conditions. It can be seen (Figure 3) that PAAs made in water (i.e., $PA3_w$ and $PA4_w$) inhibited $SrSO_4$ precipitation better than PAAs made in an organic solvent (i.e., $PA1_s$, $PA2_s$). It is interesting to note that PAAs made in organic solvent have been reported to exhibit better tolerance toward high hardness water compared to PAAs made in water.[18] Moreover, it has also been shown that PAAs made in organic solvent exhibit better performance as $CaCO_3$ and $CaSO_4.2H_2O$ compared to PAAs made in water.[19]

Polymer molecular weight effect: In recent years, many studies have been undertaken concerning the influence of MW on the precipitation of scale forming salts. Studies of polymers as scale inhibitors have shown that polymer performance in industrial water treatment is strongly affected by polymer MW. For carboxylic acid containing polymers (i.e., PAAs) it appears that precipitation inhibition is greatest for MW below 20,000 with the optimum MW being dependent on the particular polymer composition and the salt being inhibited.[20]

The strontium sulfate inhibition data collected under similar experimental conditions at 24 h for PAA_s and PAA_w with MW ranging from 2,000 to 345,000 are presented in Figure 4. It is evident that PAAs (made in organic solvent and water) and poly(methacrylic acids), PMAA, performance strongly depends on polymer MW. As illustrated, PAA (water polymerized) performance initially increases with increasing MW, reaches a maximum at a MW ~ 7,000 and decreases thereafter with increasing MW. As noted in Figure 4, similar MW dependence as shown by PAA is also observed for PMAA. It is worth pointing out that Amjad and Masler[5] in their study on the evaluation PAAs (MW 800 to 12,000) as $CaSO_4 \cdot 2H_2O$ (gypsum) crystal growth inhibitors showed optimum performance at ~2,000 MW. Amjad[21] in another study on the performance of PAA in controlling gypsum scale formation on heat exchanger surfaces, reported that the MW of PAA plays an important role in the inhibition of gypsum crystal growth from aqueous solution. The amount of gypsum deposited on heat exchanger surface was found to be higher when treated with a 240,000 MW PAA, than when treated with a 2,100 MW PAA.

The phenomenon of markedly decreasing PAA performance with increasing MW as observed in the study, may be due to several factors, causing different rates and degrees of adsorption/desorption of PAA molecules on the precipitating $SrSO_4$ particles, coiling/uncoiling of the polymer molecule, branching and the type of end group on the polymer. Adsorption studies are currently underway in our laboratories to better understand the role of polymer MW in inhibiting the precipitation of sparingly soluble salts from aqueous solutions.
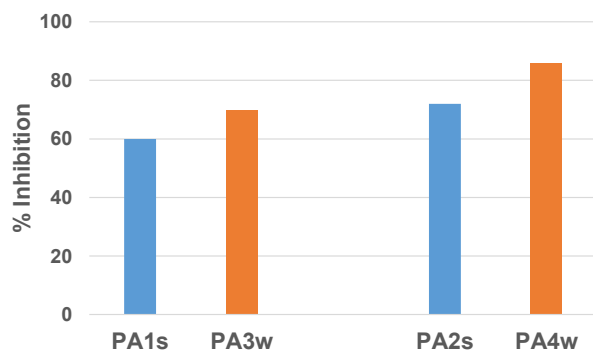

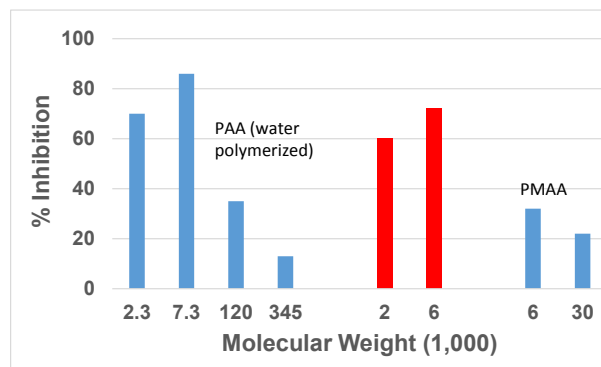Figure 3. Effect of polymerization solvent on the performance of PAA.

Figure 4. SrSO₄ inhibition by PAAs. Effect of molecular weight.

Supersaturation effect: The degree of supersaturation or saturation index for strontium sulfate is defined as the ratio of observed ion activity product to the solubility product:[22]

$$\text{Saturation Index (SI)} = [Sr][SO_4] / K_{sp} = IAP / K_{sp} \qquad\qquad (2)$$

Where:
   IAP = ion activity product
   K_{sp} = solubility product

Saturation Index can be interpreted as follows:

   SI < 1, the water is under saturated, $SrSO_4$ will not precipitate
   SI = 1, the water is saturated or in equilibrium and $SrSO_4$ will not tend to form or dissolve
   SI > 1, the water is supersaturated and $SrSO_4$ will tend to form

To study the impact of supersaturation on $SrSO_4$ precipitation, a series of experiments were carried out in the presence of 2.0 mg/L of $PA3_w$. Results presented in Figure 5 clearly show that inhibition of $SrSO_4$ precipitation decreases with increasing supersaturation.

2.0 mg/L polymer, 25°C, 24 h
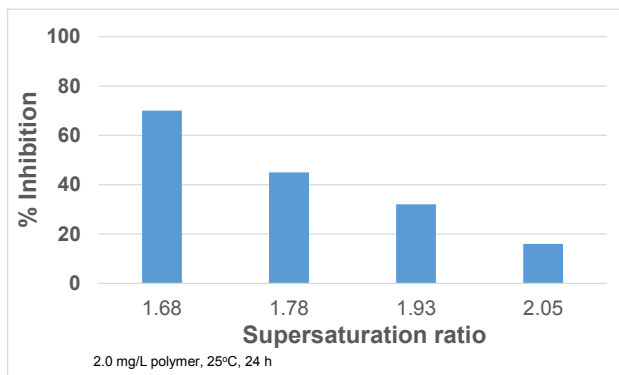
Figure 5. Effect of strontium sulfate supersaturation on $PA3_w$ performance.

Figure 6. Strontium sulfate inhibition in the presence of $PA3_w$ and at different supersaturation.
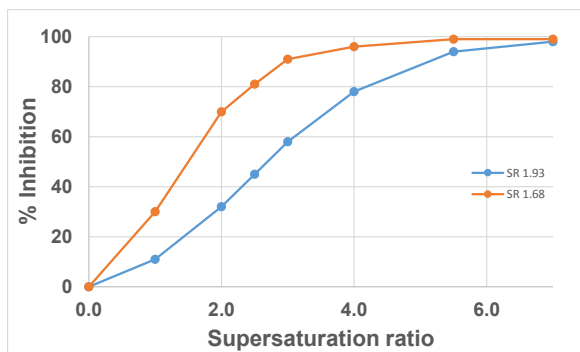
Results presented in Figure 6 show inhibition data collected in the presence of varying dosages of $PA3_w$ at two different saturation indices, (1.68, 1.93, expressed as Log IAP/K_{sp}). It can be seen that %I values strongly depends on the $SrSO_4$ supersaturation ratios. For example, % inhibition values obtained in the presence of 2 mg/L of $PA3_w$ at 1.68 SI is 70% compared to 32% obtained for solution at 1.93 SI. Furthermore, to achieve ~70% inhibition at 1.93 SI vs. 1.68 SI, it takes almost double the dosage of PA3w.

Co- and Terpolymers

The impact of polymer architecture on the inhibition of various scale forming salts has been the investigated by various researchers.[11,23,24] Results of these studies reveal that polymer containing bulkier and/or hydrophobic monomers show good to excellent performance as calcium phosphate and calcium phosphonate inhibitors. Table 2 lists the co- and terpolymers evaluated. As noted, the polymers vary significantly in terms of composition, monomer type, and molecular weight. Excellent examples of substitution of –H in PAA with SA (2-acrylamido-2-methyl sulfonic acid) monomer containing sulfonic acid ($-SO_3H$) are presented in Figure 7. It is evident that compared to $PA4_w$, PASA1 (AA:SA, 74:26, MW <15k) and PASA2 (AA:SA, 60:40, MW >10k) show mediocre performance as $SrSO_4$ inhibitors. Figure 7 also presents inhibition data on the terpolymers, PASS (AA:SA:sulfonated styrene, MW <15k). The results show that polymers containing two or three types of monomers exhibit lower performance compared to polymer containing only one monomer (i.e., $PA4_w$). It is worth noting that whereas co- and terpolymers show poor performance as SrSO4 inhibitors, these polymers have been reported to exhibit excellent inhibitory activity for calcium phosphate scale and iron oxide dispersancy.[25] Thus, it is clear the performance of polymer as scale inhibitor strongly depends on the scaling system being inhibited. Figure 7 also shows inhibition data on poly(2-ethyloxazoline), PEOX. It is evident that PEOX containing a neutral functional group is an ineffective $SrSO_4$ inhibitor. It is worth pointing out that whereas PEOX shows poor performance as $SrSO_4$ inhibitor, this polymer has been reported to exhibit good inhibitory activity for silica scale.[26]

Natural, Bio, and Hybrid Polymers

In the last two decades there has been a need for "green' (i.e., environmentally friendly) additives to control corrosion and/or scale in industrial water systems. It has been reported that a biodegradable polymer i.e., poly(aspartic acid), PAS, exhibits performance comparable to PAA.[27] Recently, the performance of a hybrid polymer i.e., carboxymethyl inulin (CMI) as an inhibitor for $CaCO_3$, $BaSO_4$, and CaC_2O_4 has been reported.[28,29,30] Results of these studies reveal that CMI shows good inhibitory for various scales.   Figure 8 presents inhibition data on lignosulfonate (LS), PAS, CMI-15, and CMI-25 (where -15 and -25 denotes degree of carboxylation). It can be seen that compared to $PA4_w$, hybrid and biodegradable polymers show poor performance as $SrSO_4$ inhibitors. It is interesting to note that LS containing $-SO_3H$, and $-OH$ (phenolic) groups are ineffective $SrSO_4$ inhibitors. The observed difference in performance may be attributed to several factors including non-ionic functionality in CMI, MW, degree of adsorption/desorption, etc.

Table 2. Co- and terpolymers tested.

Polymer	Structure	Functional Group	MW (k)	Ionic Charge	Acronym
poly(acrylic acid:2-acrylamido-2-methyl propane sulfonic acid	$-(CH_2-CH)_n-(CH_2-CH)_m-$ COOH CO NH $H_3C-C-CH_3$ CH_2SO_3H	-COOH -SO$_3$H	<15k	negative	PASA1[a]
poly(acrylic acid:2-acrylamido-2-methyl propane sulfonic acid	$-(CH_2-CH)_n-(CH_2-CH)_m-$ COOH CO NH $H_3C-C-CH_3$ CH_2SO_3H	-COOH -SO$_3$H	>10k	negative	PASA2[b]
poly(acrylic acid:2-acrylamido-2-methyl propane sulfonic acid:sulfonated styrene	$-(CH_2-CH)_m-(CH_2-CH)_n-(CH_2-CH)_y-$ COOH CO NH SO$_3$H $H_3C-C-CH_3$ CH_2SO_3H	-COOH -SO$_3$H -styrene	<15	negative	PASS[c]
Poly(2-ethyloxazoline)	$-(N-CH_2-CH_2)_n-$ CO CH_2CH_3	-C-N-C CO-	5	neutral	PEOX[d]

Key:[a]CK775; [b]CK776; [c]CK798 supplied by The Lubrizol Corporation, Wickliffe, OH; [d]Polymer Chemistry Innovations, Tucson, AZ.

Table 3. Natural, bio, and hybrid polymers evaluated.

Polymer	Structure	Functional Group	MW (k)	Ionic Charge	Acronym
poly(aspartic acid)	O OH C O CH C (NH CH$_2$)$_n$	-COOH	<10	negative	PAS[a]
lignosulfonate	cellulosic with phenolic and sulfonic groups	-OH -SO$_3$H	2.8	neutral negative	LS
carboxymethyl inulin	inulin with 15% degree of carboxylation	-saccharide -COOH	3.5	neutral negative	CMI-15
carboxymethyl inulin	inulin with 25% degree of carboxylation	-saccharide -COOH	4.5	neutral negative	CMI-25

[a]experimental

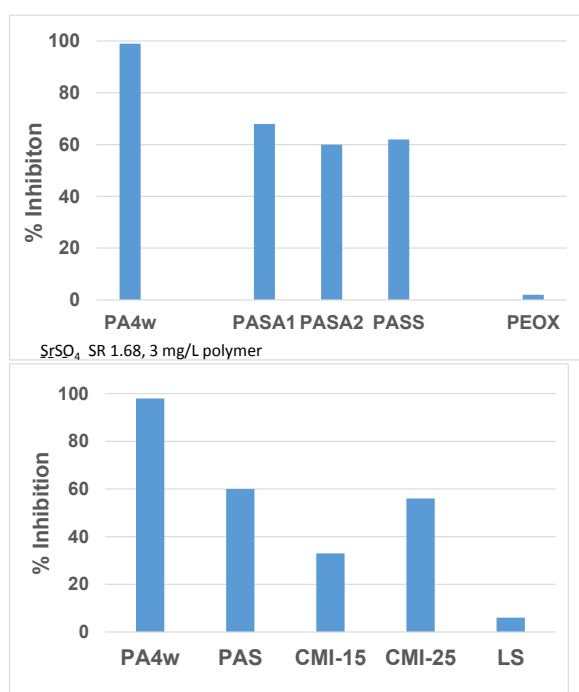Figure 7. Strontium sulfate inhibition by homo-, co-, and terpolymers.

Figure 8. Performance of natural, bio-, and hybrid polymers as strontium sulfate inhibitors.

$SrSO_4$ SR 1.68, 3 mg/L polymer

Strontium Sulfate Crystal Morphology Characterization

The change of crystal habit, size, and modifications brought about by the poly(acrylic acid) addition, were examined through scanning electron microscopy (SEM) and X-ray diffraction technique. Figure 9 A and 9B show XRD spectra of $SrSO_4$ crystals formed in the absence and presence of $PA3_w$. As illustrated, spectra confirmed the formation of $SrSO_4$ (celestite) as the only phase present.
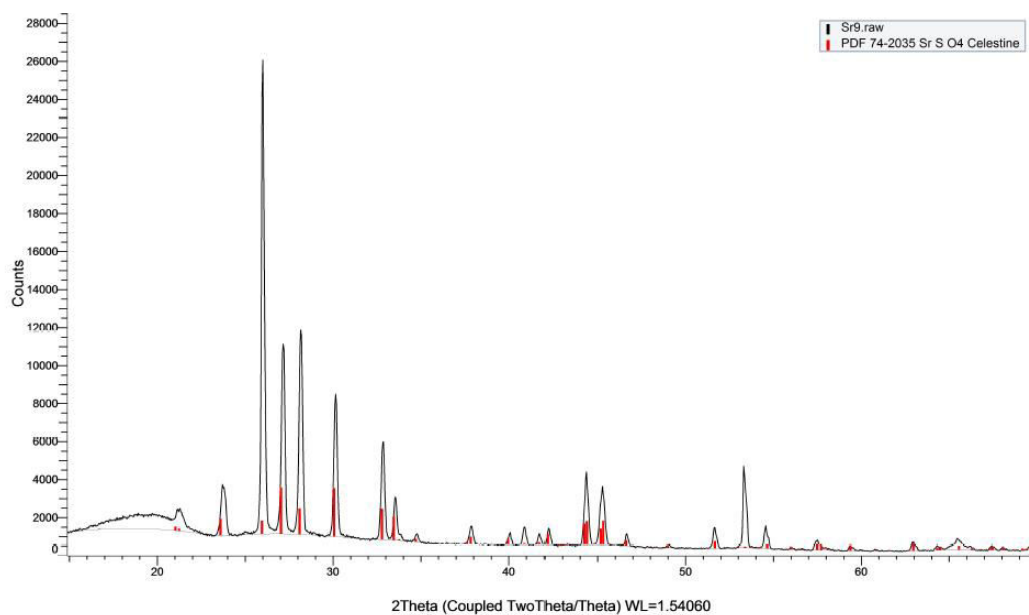
(A)
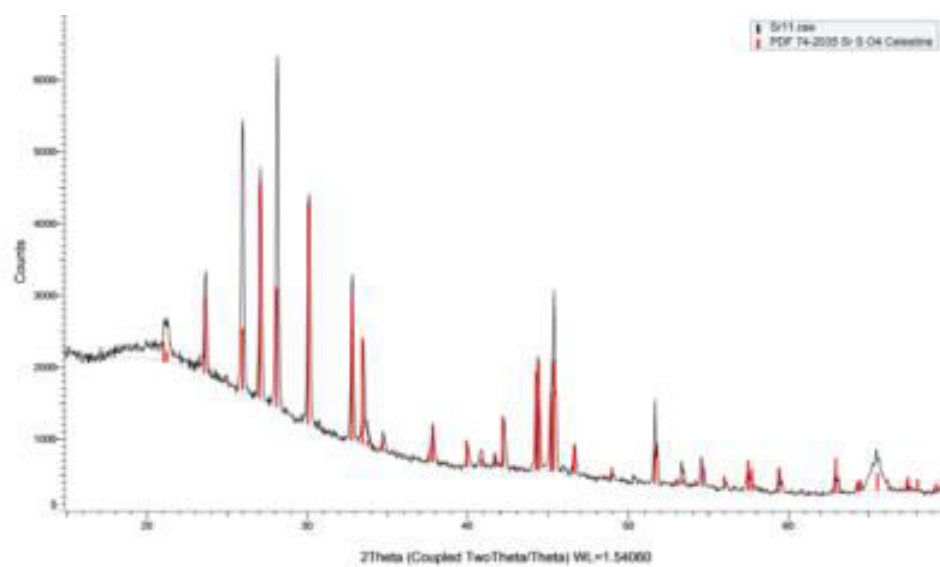
(B)

Figure 9: X-ray diffraction spectra of $SrSO_4$ crystals formed in the absence (A) and in the presence of 1.0 ppm of PA3w.

The effect of 0 and 1.0 mg/L PA3$_w$ on the morphology of SrSO$_4$ crystals is shown in Figure 10. It can be seen that crystal grown in the presence of polymers are smaller and modified Figure 10 B) compared to SrSO$_4$ formed in the absence of PA3w (Figure 10 A).
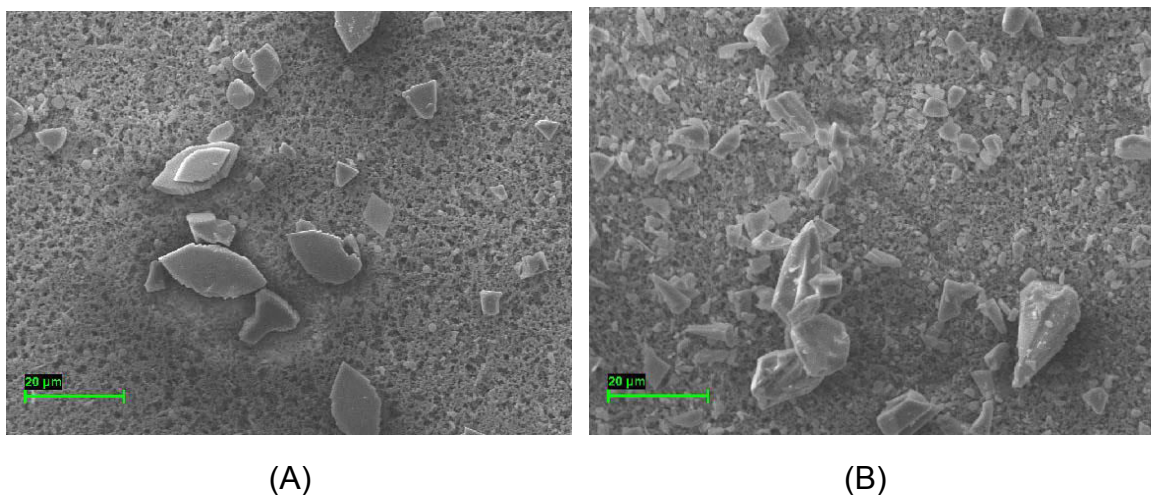

(A)   (B)

Figure 10: Scanning electron micrographs of SrSO$_4$ crystals grown in the presence of 0 ppm polymer (A) and 1.0 ppm PA3w (B).

Summary

The results presented show that strontium sulfate (SrSO$_4$) inhibition strongly depends on polymer composition, solution supersaturation, and polymer dosage. In general, increasing the polymer dosage results in increased inhibition of strontium sulfate precipitation in an aqueous solution. Under the experimental conditions employed polymers containing carboxylic acid (-COOH) group exhibit better performance compared to polymers made with monomers containing different functional groups.

The results on the performance of poly(acrylic acids0, PAAs, with varying molecular weight (MW) in the range 2,000 to 345,000 suggest optimum performance is achieved with ~7,000. Additionally, it has also been observed that PAAs made in water show superior performance compared to PAAs made in organic solvent. Under the experimental conditions employed, the homopolymers perform better than co-, ter- and hybrid polymers.

Scanning electron microscopic investigations reveal that the presence of PAA decreases the crystal size of SrSO$_4$. Furthermore, EDX spectra of the crystals confirmed the formation of SrSO4 (celesite).

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