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Gypsum scale formation on heated metal surfaces: The influence of polymer type and polymer stability on gypsum inhibition

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ABSTRACT

The deposition of gypsum (i.e. calcium sulfate dihydrate) on brass heat exchanger surfaces in the presence of homopolymers and copolymers containing different functional groups from aqueous solution has been studied. The amount of gypsum deposited on the heat exchanger surface (in the absence of bulk or spontaneous precipitation) is strongly dependent on the polymer architecture and the polymer concentration. Scanning electron microscopic investigations on the deposit show morphological changes to the crystals due to interactive effects of some of the polymers. The effectiveness of the polymers as inhibitors was reduced by thermal treatment (150–240°C), likely due to polymer degradation.

Keywords: Gypsum; Heat exchanger; Polymers; Heat treatment; Crystal morphology

1. Introduction

Crystallization and deposition of sparingly soluble salts or scales on equipment surfaces occur in many industrial processes including boiler, cooling, desalination, geothermal, and oil production. Commonly encountered scales include carbonates, sulfates, and phosphates salts of alkaline earth metals. The problem of scale formation is intensified at higher temperatures because of the peculiar inverse-temperature-solubility profiles of these minerals in water. Among the problems caused by scale deposits are obstruction of fluid flow, impedance of heat transfer, wear of metallic parts, localized corrosion attack, and unscheduled equipment shutdown. In desalination of brackish/sea water by reverse osmosis (RO) membrane-based process, the formation of scale on RO surface often leads to poor quality produced water, increased operating pressure, increased energy costs, and premature membrane replacement.

Calcium sulfate is one of the most commonly encountered scales that occurs in three different crystalline forms: calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$ (gypsum); calcium sulfate hemihydrate, $CaSO_4 \cdot 1/2\ H_2O$ (plaster of Paris); and calcium sulfate anhydrite, $CaSO_4$. In RO and cooling water systems, gypsum is the most commonly formed scale, whereas calcium sulfate hemihydrate and calcium sulfate anhydrite are the most commonly encountered salts in high temperature applications. Over the years, various approaches have been proposed to prevent the precipitation of scale-forming salts in aqueous solutions. Examples include (a) use of ion exchangers to remove hardness ions, (b) decrease in process water pH by controlled addition of acid, (c) addition of chelants or sequestrants causing decrease in supersaturation because of complexation of hardness ions (e.g. Ca, Mg) involved

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in scale formation, and (d) addition of small dosages (few parts per million, ppm) of water soluble additives which have the ability to suppress scale formation. The most commonly used method to control scale formation in industrial water systems involves the addition of additives to the process water. Commonly used additives fall into two types: non-polymeric (e.g. phosphonates, pyrophosphate, phosphonocitrate, etc.) and polymeric (e.g. polyphosphates, polyphosphonates, polycarboxylates, acrylic acid, maleic acid-based copolymers, etc.). Such additives are primarily designed to interact with cations present on the mineral surface. In many cases, the presence of additives may cause modifications of crystal habit of the precipitating particles formed reducing their ability to adhere to the equipment surfaces [1–3].

The influence of low dosages (few ppm) of polymeric and non-polymeric additives on both the rate and crystal modification of gypsum has been investigated by several researchers. Amjad [4] showed that polymeric additives containing carboxyl (–COOH) group such as poly(acrylic acid), poly(maleic acid) (PMA), and poly(itaconic acid) were particularly effective as gypsum growth inhibitors. Oner et al. [5] arrived at similar conclusions after studying the effect of various acrylic acid-based copolymers as gypsum scale inhibitors. Amjad and Hooley [6] 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 (MW) play important roles in imparting inhibitory activity to the polymers.

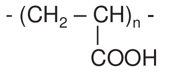
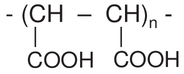
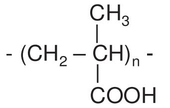
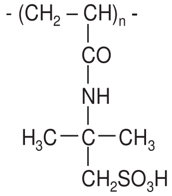
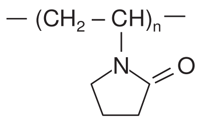
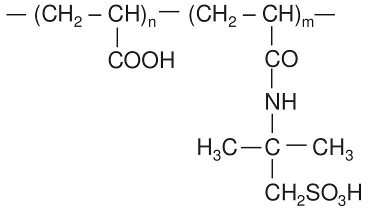
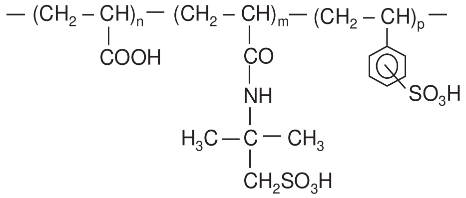
Recently, the performance of carboxymethyl inulin (CMI) with different degree of carboxylation as inhibitors for various scaling systems (e.g. $CaC_2O_4{\cdot}H_2O$, $CaCO_3$, $BaSO_4$) and iron oxide dispersants has been investigated [7–10]. Results of these studies reveal that CMI exhibits good inhibitory and dispersancy activities and its performance strongly depends on the degree of carboxylation. In another study, Zeiher [11] reported that maleic acid-based hybrid polymers also show good inhibitory activity for various scaling systems. Campbell and coworkers in their study showed that poly(aspartic acid) and poly(glutamic acid) are effective $CaC_2O_4.H_2O$ crystal growth inhibitors [12]. In another study, Dogan et al. [13] using the spontaneous precipitation method, investigated the influence of poly(ethylene oxide)–block-poly(methacrylic acid) polymers as gypsum growth inhibitors. Results of their study reveal that inhibition increases with acid content of the copolymer.

Currently, a wide variety of polymers of different composition and MW is commercially available. These polymers are used in water treatment formulations as scale inhibitors and dispersants. It has been reported that various parameters including composition, MW, hydrolytic stability, thermal stability, compatibility with other formulation ingredients, etc., contribute to the performance of polymers [14]. For high-temperature applications such as power plant steam generators, geothermal, and desalination by thermal process, it is important that polymers maintain their efficacy under stressed conditions. During the last three decades, the thermal stability of water soluble polymers has been the subject of numerous investigations. McGaugh and Kottle [15], in their study on polymer thermal stability, showed that poly(acrylic acid) (PAA) forms an intramolecular anhydride at temperatures below 150˚C. At higher temperatures, this anhydride appears as an intermediate in the decarboxylation of PAA. Gurkayanak et al. [16] performed very short degradation tests on a 6000 (6 k) MW, PAA at high temperature and different pH values. Results of their studies show that rate of decarboxylation depends upon various parameters, that is, solution pH, ionic strength, and temperature. Hetper et al. [17] investigated the thermal behavior of sodium, calcium, and magnesium polyacrylates. They found that main decomposition of calcium and magnesium salts occurs in the temperature range of 450–490˚C. It was suggested that thermal degradation of polyacrylates proceeds via side chain and main chain scission, without depolymerization. Masler [18] investigated the thermal stability of several homopolymers used in the boiler. It was demonstrated that under the experimental conditions employed (pH 10.5, 250˚C, 18 h) that PAA, poly(maleic acid), and poly(methacrylic acid) (PMAA); all underwent some degradation. In terms of MW loss, PMAA lost slightly less MW than PAA, which lost considerably less than PMA. In addition, PAA and PMAA had minimal performance changes whereas PMA displayed substantial loss in performance.

The influence of heat exchanger metallurgy (i.e. copper, brass, and stainless steel) on the rate of gypsum scale has been investigated [6]. Results of this study show the following trend (in terms of decreasing order) of the rate of gypsum formation: copper > brass > stainless steel, which is consistent with the thermal conductivity characteristics, that is, copper > brass > stainless steel. In the present work, we selected brass as the substrate to study gypsum scale formation in the absence and presence of inhibitors.

In our earlier papers, we presented results on the performance of various polymers that have been thermally treated at various temperatures, for their effectiveness as scale inhibitors and dispersants [19, 20]. The focus of the present investigation is to study the

Table 1
Polymers tested

Inhibitor	Structure	MW (k)	Acronym
Poly(acrylic acid)	 $-(CH_2-\underset{COOH}{CH})_n-$	~6	A1* (CK7058)
Poly(maleic acid)	 $-(\underset{COOH}{CH}-\underset{COOH}{CH})_n-$	>1	A2**
Poly(methacrylic acid)	 $-(CH_2-\overset{CH_3}{\underset{COOH}{CH}})_n-$	6	A3* (CK766)
Poly(2-acrylamido-2-methylpropane sulfonic acid)	 $-(CH_2-\underset{\underset{\underset{H_3C-\underset{CH_2SO_3H}{C}-CH_3}{NH}}{CO}}{CH})_n-$	~10	A4**
Poly(vinyl pyrrolidone)		<15	A5**
Poly(acrylic acid: 2-acrylamido-2-methylpropane sulfonic acid)	 $-(CH_2-\underset{COOH}{CH})_n-(CH_2-\underset{\underset{\underset{H_3C-\underset{CH_2SO_3H}{C}-CH_3}{NH}}{CO}}{CH})_m-$	<15	B1* (CK775)
Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid:sulfonated styrene		<15	B2* (CK798)

*Carbosperse™ K-700 polymers supplied by The Lubrizol Corporation, Wickliffe, Ohio, USA.

**Experimental.

impact of thermal treatment on the performance of homo- and copolymers as inhibitors for gypsum deposition on heated metal surfaces. This research is a part of our on-going investigation in understanding the role of polymer architecture in inhibiting precipitation of scale-forming minerals, dispersing suspended matter, and stabilizing metal ions in aqueous solutions. The polymers selected in the present study include homopolymers of acrylic acid, maleic acid, methacrylic acid, 2-acrylamido-2-methylproane sulfonic acid, vinylpyrrolidone, and acrylic acid-based copolymers containing comonomers with different functional groups. Table 1 lists the chemical structure, composition, MW, and acronym of the polymers used in the present study.

2. Experimental

2.1. Materials

Grade A glassware and reagent grade chemicals were used. The stock solutions of calcium chloride (Fisher Scientific) and sodium sulfate (Fisher Scientific) were prepared in double distilled water and analyzed according to the methods described previously [4]. All polymer solutions were prepared on a dry weight basis. The desired concentrations were obtained by dilution.

2.2. *Thermal treatment of polymer*

A solution of polymer was prepared containing 10% polymer (as active solids) at pH 10.5 using sodium hydroxide to neutralize the polymer. Sodium sulfite was used as an oxygen scavenger. A known amount of polymer was retained for characterization and performance testing. The balance was charged to a stainless tube. The headspace was purged with nitrogen followed by tightening the fittings. The tube was then placed in the oven maintained at the required temperature (either at 150, 200, or 240℃). At 20 h, tubes were removed from the oven, cooled at room temperature, and solution was transferred to vials for polymer characterization and performance testing. The temperature range selected reflects conditions commonly encountered in boiler water treatment.

2.3. *Gypsum deposition protocol*

Gypsum scale formation experiments were carried out by preparing supersaturated solutions of calcium sulfate (35.0×10^{-3} M) in a double-walled, water-jacketed glass cell of about 1000 mL capacity by adding known volume of stock solutions of calcium chloride to sodium sulfate solution. The total volume of calcium sulfate supersaturated solution was 800 mL. In experiments involving the polymer, a known volume of the stock solution of polymer was added to the sulfate solution prior to the addition of calcium chloride solution to avoid precipitation of calcium–polymer salt. The brass tubes, 40 cm long, 1.0 cm outer diameter, were used. These tubes were suspended from the lid of the glass cell and immersed in the supersaturated solution as illustrated in Fig. 1. The total surface area in contact with calcium sulfate solution was typically about 82 cm^2. The new tube was used for each experiment and was chemically cleaned to avoid any surface imperfections and impurities. Scale deposition experiments were initiated by immersing the metal tube in calcium sulfate solution. A temperature differential was provided by circulating hot water, maintained at 67 ± 0.5℃, through the tube, and cold water, 6.0 ± 0.4℃ through the outside of the glass cell. Within ~5 min, a steady state temperature was reached and the bulk solution temperature remained at a constant value. To minimize corrosion of brass metal surfaces during scale formation experiment, an azole-based corrosion inhibitor was used. During the scale deposition experiment solution samples were taken from time-to-time, filtered through 0.22 μm filter paper, and soluble calcium was analyzed by standard EDTA titration method. The amount of gypsum deposited on heat exchanger was calculated from calcium ion concentrations at the beginning of experiment and at known time during the experiment. In addition, the amount of gypsum deposited on heat exchanger was also determined by dissolving gypsum in a known volume of distilled water and analyzing for calcium by EDTA. After the end of the experiments, the solids formed on the outer surface of the metal tube were collected, dried overnight, and were further characterized by scanning electron microscopy (SEM).

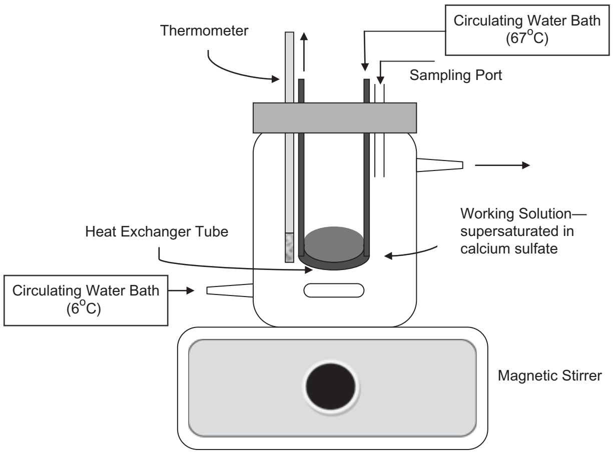


Fig. 1. Experimental set up for gypsum deposition.

3. Results and discussion

Solution species concentrations were calculated by using mass balance, proton dissociation, electroneutrality, and equilibrium constants involving calcium ions with polymers, by iterative procedure using computer program PHREEQC (Version 2). The driving force for gypsum scale formation can be expressed in terms of a Gibbs free energy of transfer, given in Table 2, from a supersaturated to saturated solution at the metal surface by Eq. (1):

$$\Delta G = -RT/2 \ln(IP/K_e) \tag{1}$$

In Eq. (1), IP is the product of free calcium and sulfate ions at time t and K_e is the corresponding solubility product. The ΔG value in Table 2 refers to the initial value, calculated for temperature of 35℃. The poly(acrylic acid) ionization constant and Ca–poly (acrylic acid) complex used in the calculations are

Table 2
Results of gypsum growth experiments

Exp.	Polymer	Acronym	Functional group	Polymer (ppm)	Gypsum (g)
9	None	None	None	0.0	1.67
11	None	None	None	0.0	1.58 (1.49)*
13	Poly(acrylic acid)	A1	–COOH	0.075	1.25
14	Poly(acrylic acid)	A1	–COOH	0.15	0.89
16	Poly(acrylic acid)	A1	–COOH	0.20	0.71
18	Poly(acrylic acid)	A1	–COOH	0.30	0.51
19	Poly(acrylic acid)	A1	–COOH	0.30	0.48
19	Poly(acrylic acid)	A1	–COOH	0.50	0.25
20	Poly(acrylic acid)	A1	–COOH	1.0	0.08
24	Poly(maleic acid)	A2	–COOH	0.30	0.52 (0.47)*
25	Poly(maleic acid)	A2	–COOH	1.0	0.12
26	Poly(methacrylic acid)	A3	–COOH	0.30	1.19
27	Poly(methacryslic acid)	A3	–COOH	1.0	0.34
28	Poly(2-acrylamido-2-methylpropane sulfonic acid)	A4	–SO_3H	0.30	1.55
30	Poly(2-acrylamido-2-methylpropane sulfonic acid	A4	–SO_3H	1.0	1.50
31	Poly(vinylpyrrolidone)	A5	–N– C=O	0.30	1.64
32	Poly(vinylpyrrolidone)		–N– C=O	1.00	1.69
34	Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid)	B1	–COOH, –SO_3H	0.30	0.65 (0.56)*
35	Poly(2-acrylamido-2-methylpropane sulfonic acid: sulfonated styrene	B2	–COOH, –SO_3H, –SO_3H. styrene	0.30	0.88

Total calcium sulfate = 35.0 mM; pH 5.75, brass heat exchanger surface area = 82 cm, Log K_i (PAA) 5.25 [25]; Log K (Ca-PAA) 2.2 [26]; $\Delta G = -0.359$ kJ mo^{-1}. *Obtained by dissolving gypsum deposited on the tube.

shown in Table 2. Since the polymer concentration used in gypsum growth experiments are very low compared to initial calcium ion concentration, no significant impact by Ca–polymer complex on ΔG value is observed.

Table 2 summarizes the experimental conditions and the gypsum growth data. A series of gypsum deposition experiments on heated metal tubes were conducted to evaluate the performance of polymers as scale inhibitors as a function of dosage, time, and the thermal treatment. Typical calcium concentration–time profiles for duplicate experiments on brass tubes in the absence of a polymer are presented in Fig. 2. It is evident that gypsum deposition on heated metal surface begins after an initial induction time, β, during which there is a negligible change in the bulk calcium concentration. The time at which a decrease in calcium concentration was first detected was taken as the β. It can be seen in Fig. 2 that, following an induction period (~18 min), gypsum scale formation takes place on the heated brass surface. The reproducibility of the scale formation experiments is illustrated by the excellent agreement (±6%) between the results of experiments 9 and 11. In order to observe the effect of gypsum scale formation on heated brass tube, temperature readings were also recorded as a function of time. The temperature–time profile for gypsum

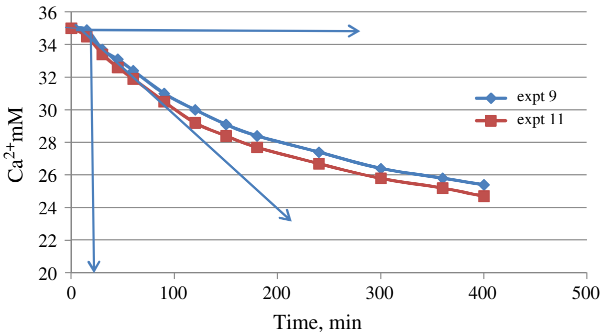


Fig. 2. Plot of Ca^{2+} concentration as a function of time in the absence of polymer.

growth experiment suggests that, as the concentration of calcium decreases (or the amount of gypsum deposited on the heat exchanger increases), the calcium sulfate solution temperature in the double-walled glass cell decreases. For example, temperature readings obtained at 1.5, 3, 5, and 7 h are 30, 27, 25, and 24°C, respectively, compared to 35°C obtained in the beginning of experiment. The observed decrease in solution temperature with increasing gypsum deposit reflects the thermal loss of the heat exchanger. To verify that spontaneous precipitation did not occur in the reaction cell during the scale deposition experiment, unfiltered samples were also analyzed for calcium ion and were found to be within ±0.5% of the filtered sample.

3.1. Polymer performance

Using the experimental protocol described above, a series of gypsum growth experiments were carried out in the presence of a variety of synthetic polymers (i.e. homo- and copolymers) containing different functional groups, i.e. anionic (–COOH, –SO_3H), neutral (pyrrolidone). For performance comparison experiments were also carried out in the presence of polymers that were subjected to thermal treatment at various temperatures.

3.2. Homopolymers

3.2.1. Polymer dosage

Calcium concentration–time profiles for gypsum growth experiments made in the presence of varying dosages of poly(acrylic acid), A1 (MW 2 k), are presented in Fig. 3. As shown, the crystallization reaction in the presence of 0.075 ppm is preceded by induction period ($\beta = 68$ min) compared to 18 min obtained in the absence of A1. Fig. 3 further indicates that an increase in A1 concentration from 0.075 to 0.15 and 0.20 ppm results in a prolongation of β from 68 to 165, and 270 min, respectively. As illustrated in Fig. 3 at 1.0 ppm A1 concentration gypsum growth is completely inhibited for at least 7 h. It is worth noting that initial rate (10^4 M/min) of gypsum scale deposition decreases with increase in A1 concentration. For example, initial rate observed in the presence of 0.075, 0.15, and 0.20 ppm is 0.48, 0.16, and 0.08 (10^4 M/min), respectively, compared to 0.60 (10^4 M/min) obtained in the absence of A1. It is interesting to note that similar dependence of induction time and growth rate with increasing polymer concentration as observed in the presence study has also been previously reported [5].

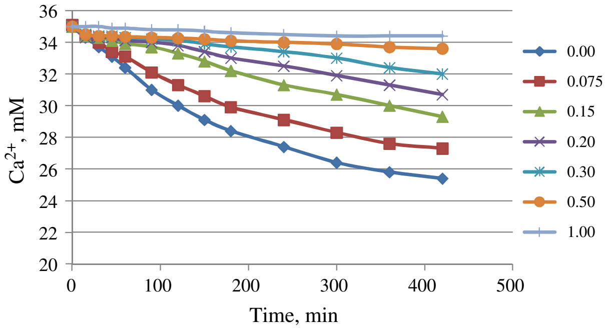


Fig. 3. Gypsum deposition on heat exchanger surfaces. Plot of Ca^{2+} concentration as a function of time and at varying poly(acrylic acid) dosages (ppm).

It has been previously reported [4] that influence of polymeric and non-polymeric additives as gypsum growth inhibitors falls into two categories: those additives that affect the induction period and those that show no significant effect on the induction period preceding the gypsum crystal growth. The calcium–time profiles for the first type were observed for the better additive while profiles for the second type were obtained for less effective additives. In both cases, the decrease in calcium ion concentration from solutions with increasing reaction time was found to follow the second order rate law [6]. To accommodate both types of behavior, in the present study, we have selected, for polymer performance, the amount of calcium remaining in solution after 7 h. When expressed as a function of the total calcium ion present at the beginning of the scale formation experiment, the difference between initial and 7 h residual calcium ion concentrations becomes a measure of the amount of the gypsum scale deposited on the heated metal surface. The choice of 7 h is arbitrary and, although the selection of different growth time would lead to a change of absolute amount of gypsum scale deposited, it would not affect the relative ranking of polymer effectiveness.

In Fig. 4, the amount of gypsum (g) deposited in 7 h on the heated metal tube is plotted as a function of A1 dosage. As can be seen, the amount of gypsum deposited strongly depends on A1 dosage. For example, amount of gypsum deposited in the presence of 0.075 and 0.20 ppm is 1.25 and 0.71 g, respectively compared to 1.67 g obtained in the presence of 0.0 ppm of A1 dosage. As illustrated in Fig. 4, increasing the A1 dosage by a factor of 5 (i.e. from 0.20 to 1.0 ppm) results in ∼9-fold decrease in gypsum growth. As indicated in the experimental section the amount of gypsum deposited was also determined by dissolving gypsum scale deposited on heat exchanger in the known volume of distilled water and analyzed by EDTA titration. Results presented in Table 2 (exp.

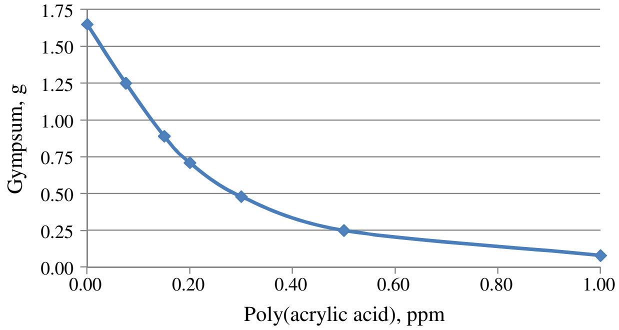


Fig. 4. Gypsum growth in the presence of varying dosages of poly(acrylic acid).

11, 24, 34) show good agreement (±6%) between the results obtained by two methods.

3.2.2. Polymer composition

To evaluate the performance of homopolymers containing different functional groups, that is, –COOH, –SO_3H, pyrrolidone, etc., a series of experiments were carried in the presence of 0.30 ppm of various homopolymers such as poly(maleic acid), A2; poly(methacrylic acid), A3; poly(2-acrylamido-2-methylpropane sulfonic acid), A4; and (polyvinylpyrrolidone), A5. Fig. 5 presents the amount of gypsum deposited in 7 h for various homopolymers. The data suggest that all polymers containing –COOH group show good to excellent performance in inhibiting gypsum scale formation. For example, the mass of gypsum deposited on heated metal tube in the presence of 0.30 ppm A1, A2, A3 is 0.48, 0.52, and 1.19 g, respectively, compared to 1.67 g obtained in the absence of polymer. As illustrated in Fig. 5 under similar experimental conditions, the amount of gypsum deposited in the presence of non-carboxyl containing homopolymer such as A4, poly(2-acrylamido-2-methylpropane sulfonic acid), and A6, (poly vinylpyrrolidone), is 1.55 and 1.64 g, respectively. It is also worth noting that increasing the A4 and A5 dosage from 0.30 to 1.0 ppm, does not exhibit any significant influence on the mass of gypsum formed. As noted in Fig. 5 under similar conditions increasing the A1, A2, and A3 concentration from 0.30 to 1.0 ppm, results in significant decrease in the mass of gypsum deposited on the heat exchanger.

3.2.3. Copolymers

The influence of polymer composition at a constant dosage of 0.30 ppm was investigated using the brass metal tubes. Results presented in Table 2 and shown in Fig. 6 reveal that at constant polymer dosage the amount of gypsum deposited is a function of polymer composition. For example, the mass of gypsum deposited in the presence of 0.3 ppm of B1 copolymer of (acrylic acid: 2-acrylamido-2-methylpropane sulfonic, SA) and B2 copolymer of (acrylic acid: SA: sulfonated styrene, SS) is 0.65 and 0.86 g, respectively. For comparison, gypsum growth data for two homopolymers, namely A1 and A4, are also presented in Fig. 6. The data suggest that replacing acrylic acid with non-carboxyl containing comonomers, that is, SA and SS, results in relatively poor performance of copolymers. It is worth noting that whereas copolymers investigated in the present study show mediocre performance as gypsum inhibitors, these polymers, however, have been reported to exhibit excellent performance for calcium phosphate [21] and calcium phosphonate [22] systems and as dispersants for iron oxide particles [23]. Thus, it is clear that polymer performance as scale inhibitor and/or dispersants strongly depends

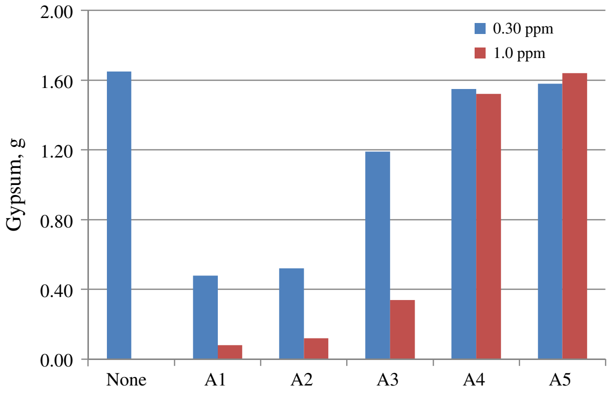


Fig. 5. Mass of gypsum deposited on heat exchangers in the absence (none) and in the presence (0.30 ppm) of homopolymers.

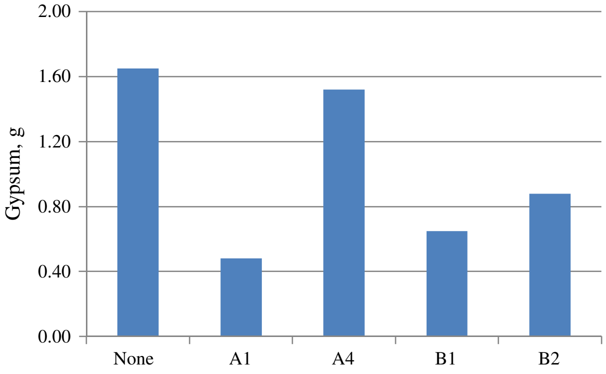


Fig. 6. Gypsum growth (g) on heat exchanger surface in the absence (none) and in the presence of 0.30 ppm polymers.

not only on the polymer architecture but also on the type of scales being inhibited.

3.3. Influence of heat treatment on polymer performance

Fig. 7 presents mass of gypsum deposited in the presence of 0.3 ppm of homo- and copolymers. It is evident that homopolymers, that is, A1, A2, A3, before heat treatment, provided relatively effective gypsum inhibition. Furthermore, in the case of A1 and A3, the mass of gypsum deposited on metal tubes for both heat treated and no heat treated homopolymers are very similar. This indicates that heat stress (exposure of aqueous solutions of these homopolymers to 200˚C, 20 h) exhibits insignificant effect (<8% change in gypsum mass) on the inhibitory activity of the polymers. The data presented in Fig. 7 for homopolymers containing –COOH group suggest that A1 and A3 do not undergo significant decarboxylation under the test conditions. For A2, homopolymer of maleic acid, results presented in Fig. 7 reveal that A3 performance decreases with thermal exposure presumably due to decarboxylation.

The performance differences, before and after heat treatment of A1, A2, A3 polymers, as observed in the present investigation are thus consistent with previously reported studies on the thermal stability of poly (acrylic acid), poly(methacrylic acid), and poly(maleic acid) in alkaline pH [18,20,24].

The influence of heat treatment on the performance of non-carboxyl containing polymer, that is, 2-acryalamido-2-methylpropane sulfonic acid, A4, as gypsum scale inhibitor, is presented in Fig. 7. It is evident that heat treated A4 performs better than the non-heat treated A4. For example, mass of gypsum obtained in the presence of 0.3 ppm of heat treated A4 is 1.15 g compared to 1.55 g obtained in the presence of non-heat treated A4. The observed increase in A4 performance with heat treatment reflects loss of –CONH– group or the formation of –COOH in A4. It is worth noting that whereas A1 compared to A4 exhibits poor performance as iron oxide dispersant, exposure of A4 to heat treatment results in loss of dispersancy activity thus supporting the generation of –COOH group in A4 [18,20,24]. In earlier study, it was shown that performance of A4 as calcium carbonate inhibitor improves for thermally treated polymer versus non-thermally treated A4 [24]. In addition, it was also reported that poly(acrylic acid) and poly(maleic acid), in general, are less tolerant (tendency to form insoluble salt with Ca ion) to calcium ion compared to copolymers such as B1 and B2, thus supporting the degradation of SA to –COOH group [24].

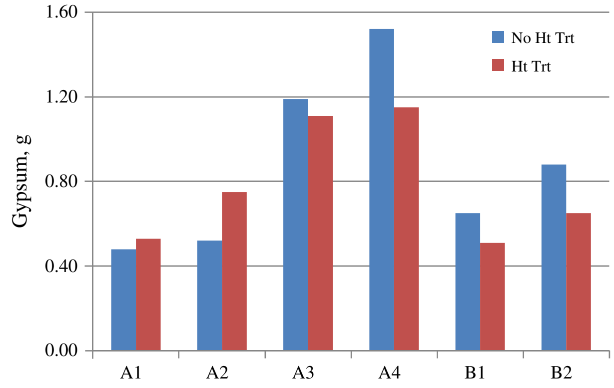


Fig. 7. Gypsum growth on heat exchanger surface in the presence of 0.3 ppm polymer with and without heat treatment (200˚C, 20 h).

Comparative gypsum inhibition data on two copolymers, that is, acrylic acid: 2-acryalamido-2-methylpropane sulfonic acid (B1) and acrylic acid: 2-acrylamido-2-methylpropane sulfonic acid:sulfonated styrene (B2) are presented in Fig. 7. As illustrated, copolymers, compared to A1, in the absence of heat treatment shows good inhibitory activity. However, when these copolymers are exposed to heat treatment (200˚C, 20 h), mass of gypsum deposited decreases reflecting the formation of additional –COOH group during thermal treatment. The marked increase in B1 and B2 performance clearly indicates that 2-acrylamido-2-methylpropane sulfonic acid present in B1 and B2 underwent serious degradation upon exposure to heat treatment thus leading to the formation of poly (acrylic acid). The formation of poly(acrylic acid) due to SA monomer degradation in homo- (A4) and copolymers (B1, B2) upon heat treatment has been previously confirmed by NMR and FT-IR spectroscopy [19,20].

3.4. Effect of temperature

The influence of temperature on the thermal stability of polymers was also investigated at several levels: 150, 200, and 240˚C. The performance data presented in Fig. 9 illustrate excellent thermal stability for poly (acrylic acid), A1. However, for poly(maleic acid), A2, the situation is markedly different as presented in Fig. 8 wherein increasing the temperature from 150 to 200 to 240˚C results in gradual and significant decrease in the performance of A2 as gypsum growth inhibitor. The observed drop in inhibitory activity may be attributed to MW loss and greater decarboxylation with increasing solution temperature.

Fig. 8 also presents a comparison of the copolymers performance as a function of heat treatment. It is evident that as the polymers were exposed to

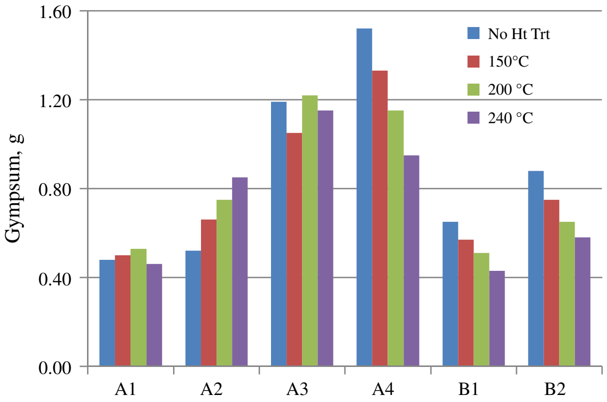


Fig. 8. Gypsum growth on heat exchanger surface in the presence of 0.3 ppm of homo- and copolymers exposed to different temperatures.

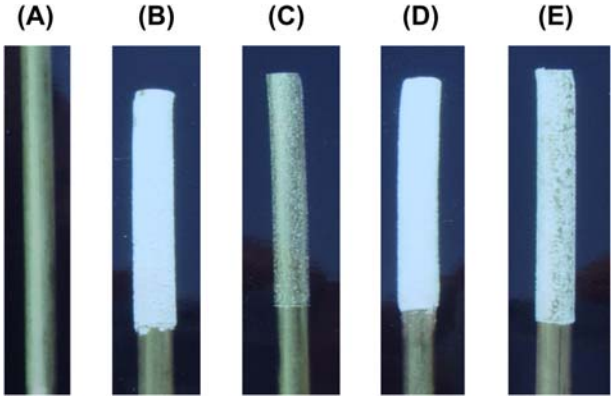


Fig. 9. Gyspum deposits on heat exchanger surface: (A) brass tube; (B) in the absence of polymer at 7 h; (C) in the presence of 0.5 ppm A1; (D) in the presence of 0.5 ppm) A4 (before heat treatment); and (E) in the presence of 0.5 ppm A4 after heat treatment.

progressively higher temperature (i.e. 150, 200, and 240˚C), marked decreases in mass of gypsum deposited are observed. As noted in Fig. 9, increasing solution temperature from 200 to 240˚C results in significant decrease (>10%) in the mass of gypsum deposited suggesting that essentially all of SA monomer present in B1 and B2 are degraded to form poly (acrylic acid) or a copolymer of acrylic acid: sulfonated styrene.

3.5. Characterization of gypsum grown in the absence and presence of polymers

Previous studies have shown that presence of trace amounts of scale-inhibitors influences not only the growth rate but also the morphology of scale forming minerals. In some cases, such as calcium oxalate, calcium sulfate, calcium carbonate, and calcium phosphate, the presence of inhibitors also affects the nature of phase that forms [1,4,24]. Fig. 9 presents photographs of gypsum grown on heat exchanger surface in the absence and presence of polymers. It can be seen in Fig. 9B that brass tube is essentially covered with gypsum crystals after 7 h. For comparison, Fig. 9A shows the photograph of brass tube at the beginning of experiment. The significant influence of 0.5 ppm of A1 is presented in Fig. 9C. The effect of heat treatment on the performance of A4 is clearly illustrated in Fig. 9D and E, respectively.

The morphology of gypsum crystals grown in the absence and presence of A1 was also investigated by scanning electron microscopy. It can be seen that gypsum crystals grown in the presence of 0.5 ppm of A1 (Fig. 10B), compared to gypsum crystals grown in the absence of A1 (Fig. 10A), are highly modified.

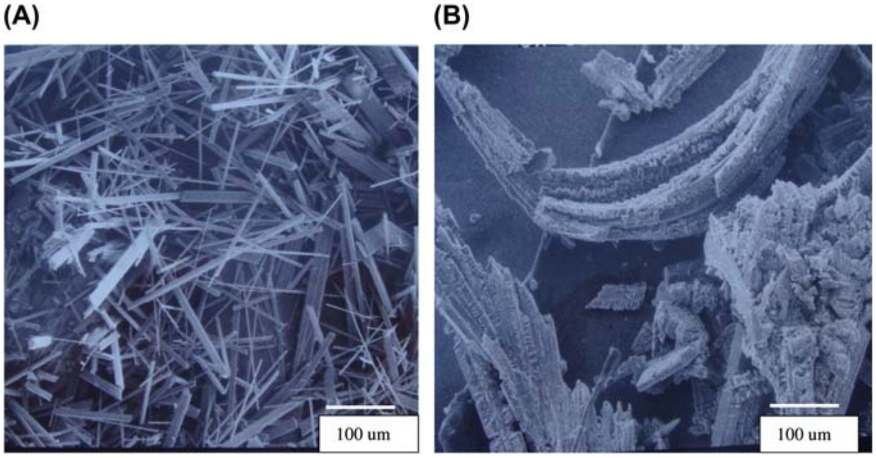


Fig. 10. Scanning micrographs of gypsum crystals grown in the absence (A) and in the presence of 0.5 ppm A1.

Summary

The deposition of gypsum on brass heat exchangers in the presence of various homopolymers and copolymers has been investigated. The results indicate that performance of polymers as inhibitors depends on both the polymer architecture and polymer concentration. In general, carboxyl acid (–COOH) containing homopolymers, that is, poly(acrylic acid), A1; poly (maleic acid), A2; perform better than the non-carboxyl group containing polymers, that is, 2-acrylamide-2-methylpropane sulfonic acid, A4, and poly(vinyl pyrrolidone, A5. On the other hand, performance of copolymers depends on the nature of functional group present in the copolymer. The performance data also reveal that homopolymers containing –COOH group perform better than –COOH containing copolymers.

The results on the thermal stability indicate that all polymers undergo some degradation under conditions employed in the present study. For polymers before heat treatment, homopolymers (i.e. A1, A2) provide significantly better gypsum inhibition than the copolymers. Interestingly, A4 shows poor performance before heat treatment. However, after heat treatment A4 performance increases presumably due to the degradation of 2-acrylamido-2-methylpropane sulfonic acid (SA) to acrylic acid. Similar increased performance of copolymers (B1, B2) containing SA has been observed after heat treatment of copolymers.

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