EFFECT OF HEAT TREATMENT ON THE PERFORMANCE OF DEPOSIT CONTROL POLYMERS AS CALCIUM CARBONATE INHIBITORS

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ABSTRACT

The impact of heat treating synthetic polymers upon their performance as calcium carbonate inhibitors in an aqueous system has been investigated. The polymers evaluated were:

- Homopolymers: poly-acrylic acid (P-AA), poly-methacrylic acid (P-MAA), poly-maleic acid (P-MA), and poly(2-acrylamido-2-methylpropane sulfonic acid) or P-SA
- Copolymer: poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid) or P-AA:SA
- Terpolymers: poly-AA:SA:sulfonated styrene (SS) or P-AASASS and poly-AA:SA:non ionic (NI) or P-AASANI

It has been found that all polymers lose calcium carbonate inhibition performance to varying degrees when exposed to thermal treatment (150 to 240°C for 20 hr). Among the homopolymers evaluated, P-MA lost more performance than P-AA. In the case of AA and SA co- and ter-polymers, the calcium carbonate inhibition performance improved after heat treatment. The results have been explained in terms of loss of SA and NI in the co- and ter-polymers, as determined by Fourier Transform Infrared (FT-IR) and nuclear magnetic resonance (NMR) methods, leading to the formation of P-AA.

Keywords: polymer thermal stability, calcium carbonate, precipitation, inhibition, crystal morphology
INTRODUCTION

The precipitation and deposition of scale forming salts especially calcium carbonate (CaCO₃) is a common occurrence in the chemical and related industries. In laundry applications, insoluble inorganic carbonates tend to accumulate on washed fabrics and washing equipment parts, thereby resulting in undesirable fabric encrustation or scaling. Calcium carbonates also pose serious operation problems as insoluble hard scale formation in geothermal processing equipment, heat exchanger and reverse osmosis membrane surfaces, and in other operations where water is processed at conditions exceeding ambient temperatures.

Three fundamental approaches to control CaCO₃ precipitation are (1) adding acid, (2) using complexing/sequestering agents, and (3) using a scale inhibitor. The objective of the first approach or adding acid maintains an unfavorable pH for CaCO₃. However, this is often not attractive because it involves handling a hazardous material and it may accelerate corrosion of involved metallic parts in industrial water systems. The second approach or the use of complexing/sequestering agents is normally not economically practical in recirculating water applications. However, in laundry applications the need for sequestering agent exists because the complexation constant for calcium/magnesium sequestration is very high. The third approach incorporates the addition of low (substoichiometric) concentrations of scale inhibitor(s) that are capable of preventing or drastically reducing the formation of undesirable calcium carbonate scales.

The influence of polymeric and non-polymeric additives as CaCO₃ inhibitors has attracted the attention of academic researchers and industrial technologists. Common non-polymeric inhibitors evaluated include organophosphonates, polyphosphates, polycarboxylic acids, and fulvic acids. It has been reported that these inhibitors when present at low concentrations markedly retard the precipitation of CaCO₃ from supersaturated solutions. A surface adsorption mechanism involving a simple Langmuir adsorption model has been proposed to account for the inhibition of calcium carbonate crystal growth. Among the polymeric inhibitors evaluated include poly(acrylic acid) or P-AA, poly(maleic acid) or P-MA, and co-polymers containing acrylic acid (AA) or maleic acid (MA) and other monomers of different functionality (i.e., -CONH₂, -COOR, SO₃H). Investigations of these and several other mineral scale inhibitors suggest that inhibitor effectiveness depends on the polymer functional groups, polymer composition (e.g., monomer weight ratios), and polymer molecular weight.

Polymer thermal degradation is a well studied area. However, there is little information available of practical value to industrial technologists addressing the use of low molecular weight polymers. Polymers used in high temperature applications should be able to sustain high temperature and pressure environments normally associated with boiler and thermal desalination operations. McGaugh and Kottle studied the thermal degradation of P-AA and later the thermal degradation of an acrylic acid-ethylene co-polymer. They used infrared and mass spectrographic analysis to examine the degradation processes that occurred in the temperature regions 25°C to 150°C, 150°C to 275°C, 275°C to 350°C, and above 350°C. Their results suggest that in air (min heating) dry P-AA decomposes by forming an anhydride, probably a six-member glutaric anhydride-type structure at temperature up to 150°C. At 350°C
there is drastic un-measurable change and strong un-saturation absorption. Mass spectrographic analysis showed that carbon dioxide was the major volatile product at 350ºC.

Denman and Salutsky\textsuperscript{14} briefly examined the thermal stability of a sodium poly(methacrylic acid) or P-MAA and a sodium poly(acrylic acid) or P-AA. Under dry conditions they found no change to 316ºC after one (1) hour but some charring at 371ºC. Masler\textsuperscript{15} investigated the thermal stability of several homo-polymers used in the boiler. It was demonstrated that under the experimental conditions employed (pH 10.5, 250ºC, 18 hr) that P-AA, P-MA, and P-MAA all underwent some degradation. In terms of molecular weight (MW) loss, P-MAA lost slightly less MW than P-AA which lost considerably less than P-MA. Additionally, P-AA and P-MAA had minimal performance changes whereas P-MA displayed a substantial loss in performance.

Gurkaynak et al.\textsuperscript{16} performed very short degradation tests on a 6,000 MW P-AA at high temperature and different pH levels. Results of their study show that rate of decarboxylation depends upon various parameters i.e., solution pH, ionic strength, and temperature. Hetper et al.\textsuperscript{17} investigated the thermal behavior of sodium, calcium, and magnesium P-AAs. They found that the main decomposition of the calcium and magnesium salts occurs in the temperature range 450ºC to 490ºC. It was suggested that the thermal degradation of the metal P-AAs proceeds via side chain and main chain scission, without depolymerization. The thermal degradation of calcium and magnesium salts of P-AA has been recently studied by McNiell and Sadeghi.\textsuperscript{18} Results of their study show some similarities to the behavior of the alkali metal salts of P-AA and to that of the alkaline earth metal salts of P-MAA.

Although most studies of polymer degradation have focused on the changes that occur in the solid state, little information is available to the industrial technologists on the performance of polymers that have been subjected to thermal treatment under typical use conditions. In our previous reports\textsuperscript{19, 20} we presented results on the impact of thermal treatment on the performance of polymers as iron oxide dispersants. In the present paper we have studied the role of heat treatment on the efficacy of various polymers with different architectures as calcium carbonate inhibitors. The polymers we selected for evaluation as CaCO\textsubscript{3} inhibitors are summarized below and shown in Table 1:

- Homopolymers: poly-acrylic acid (P-AA), poly-methacrylic acid (P-MAA), poly-maleic acid (P-MA), and poly(2-acrylamido-2-methylpropene sulfonic acid) or P-SA
- Copolymer: poly(acrylic acid:2-acrylamido-2-methylpropene sulfonic acid) or P-AA:SA
- Terpolymers: poly-AA:SA:sulfonated styrene (SS) or P-AASASS and poly-AA:SA:non ionic (NI) or P-AASANI

We also studied the impact of various additives on CaCO\textsubscript{3} crystal morphology. The synthetic polymers above and several natural additives (i.e., fulvic acid, tannic acid, green tea extract) were evaluated in order to understand the influence of phenolic and/or carboxylic acid group(s) on CaCO\textsubscript{3} crystal morphology. Results showing the impact of both natural additives and synthetic polymers on calcium carbonate crystal morphology are included herein.

**EXPERIMENTAL**

The stock solutions of calcium chloride were prepared from reagent grade chemicals and were standardized by atomic absorption spectroscopy. The alkalinity solutions (i.e., sodium bicarbonate and sodium carbonate) solutions were prepared daily. The polymeric inhibitors
used in this study were commercial materials and stock inhibitor solutions were prepared on an active solids basis.

**Polymer Heat Treatment**

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 added as an oxygen scavenger. A known amount of polymer solution was retained for characterization and performance testing. The balance was charged to a stainless steel 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 150ºC (84 psig), or 200ºC (241 psig) or 240ºC (470 psig)]. After 20 hr, tubes were removed from the oven, cooled to room temperature, and the solutions transferred to vials for characterization and performance testing.

**Polymer Characterization**

Polymer MWs were determined by using gel permeation chromatography (GPC) according to the procedure described previously. Nuclear magnetic resonance (NMR) spectra of polymers before and after thermal treatment were obtained on a Brubaker AV-500 NMR spectrometer at 500.13 MHz for spectra detection. Attenuated total reflectance infrared of all samples were acquired on a Nicolet Magna 560 Fourier Transform Infrared (FT-IR) spectrometer, equipped with the Pike MIRacle.

**Calcium Carbonate Inhibition**

The CaCO₃ precipitation experiments were done in 100 mL glass bottles. The CaCO₃ supersaturated solutions (100 mL total volume) were prepared in glass bottles by adding known volumes of alkalinity (sodium carbonate and sodium bicarbonate) and hardness (calcium chloride) solutions to yield a solution containing 560 mg/L calcium, 630 mg/L bicarbonate, 30 mg/L carbonate (all expressed as mg/L CaCO₃) and varying inhibitor concentrations. The pH of the calcium carbonate supersaturated solution was 8.30. The solutions were stored in a water bath maintained at 67ºC. After 24 hr, a known volume of the supersaturated calcium carbonate solution was filtered (0.22 micron) and the filtrate analyzed by ICP-atomic absorption method. The CaCO₃ solids collected on the membrane filters were analyzed by x-ray diffraction (Rigaku Geigerflex) and Zeiss EVO50 scanning electron microscope (SEM)

Polymer efficacy as CaCO₃ inhibitor was calculated using the following equation:

\[
\text{Inhibition (\%)} = \left( \frac{[\text{Ca}]_{\text{sample}} - [\text{Ca}]_{\text{control}}}{[\text{Ca}]_{\text{initial}} - [\text{Ca}]_{\text{control}}} \right) \times 100
\]

Where:

- \([\text{Ca}]_{\text{sample}}\) = concentration of Ca in the filtrate in the presence of inhibitor at 24 hr
- \([\text{Ca}]_{\text{control}}\) = concentration of Ca in the filtrate in the absence of inhibitor at 24 hr
- \([\text{Ca}]_{\text{initial}}\) = concentration of Ca in the solution at 0 hr
Polymer-Calcium Interaction

Polymer compatibility with calcium ions was measured by monitoring solution turbidity. The test set-up used a constant water bath, double walled-glass reaction cell, and a Brinkmann (Westbury, New York) PC 910 Colorimeter with 420 nm filter (for transmittance measurements).

The polymer-calcium compatibility experiments were performed in 125-mL glass bottles placed in double-walled glass cell maintained at 25°C. The test solutions were prepared by adding known volumes of (a) stock polymer solution and (b) water volume in the glass bottles. After allowing the polymer solution to equilibrate at the required temperature for at least 30 minutes, the solution pH was adjusted to 9.00 using dilute HCl or dilute NaOH solutions followed by adding a known volume of CaCl₂ stock solution to the test solution. The solution pH was then quickly re-adjusted to 9.00. The bottles were capped and continuously stirred with stirring bars. At a known time (typically 40 minutes) transmittance readings were taken using a fiber optic probe. Duplicate/triplicate experiments were run to check the reproducibility of the compatibility data. In order to avoid faulty signals, extreme care was taken to eliminate air bubbles in the solutions, especially in the vicinity of the fiber optic probe.

The additives used in this study were commercial synthetic polymers and natural materials as characterized in Table 1.

RESULTS AND DISCUSSION

Calcium Carbonate Inhibition by Synthetic Polymers

Polymer Dosage. The assessment of synthetic polymer effectiveness as a CaCO₃ inhibitor was done by precipitation experiments at similar initial calcite supersaturation and in the presence of varying polymer concentrations. Figure 1 details the %inhibition vs. polymer dosage profile for a 5k MW solvent polymerized P-AA (HP1). As seen in Figure 1, the addition of a relatively small amount of HP1 (without heat treatment) exhibits significant CaCO₃ precipitation inhibition. Figure 1 shows that a 1.0 ppm (parts per million) HP1 dosage yields 35% CaCO₃ inhibition and increasing the HP1 dosage three fold to 3.0 ppm increases the inhibition value by approximately 2 fold (to 67%). As noted in Figure 1, increasing the HP1 dosage from 3.0 to 5.0 ppm results in a modest increase in the CaCO₃ inhibition to 75%.

Polymer Heat Treatment.

Homo-polymers: The influence of polymer heat treatment on CaCO₃ inhibition was investigated by conducting a series of experiments under standard test conditions. Figure 2 compares the performance of homo-polymers prior to and after heat treatment at 200°C. It is evident from Figure 2 that exposure of aqueous solutions of carboxylic acid containing homo-polymers (i.e., P-AA, P-MAA, and P-MA) to heat treatment has varying effects on polymer performance. For example, heat treatment of HP1, HP2, and HP3 has no negative impact on the performance of these polymers suggesting that there is not a significant loss of either carboxylic acid groups or MW. It is worth noting that the CaCO₃ inhibition performance of P-AA made in different solvents (i.e., HP1 in organic and HP2 in water) and with phosphinate end groups (i.e., HP3) does not appear to be impacted by heat treatment. Only a modest performance loss was observed for HP5 (P-MAA) compared to P-AA. However, the P-MA (HP4) containing two carboxylic acid groups on the adjacent carbons lost a small (≈12%)
amount of its CaCO$_3$ inhibition. This suggests that poly-maleic acid (HP4) experienced more degradation than either the poly-acrylic acid (HP1) or poly-methacrylic acid (HP5).

Masler$^{15}$ in his investigation on the effect of thermal treatment (250$^\circ$C, 18 hr, pH 10.5) of several homo-polymers reported that P-MAA lost slightly less MW than P-AA, which lost considerably less MW than P-MA. Furthermore, the decarboxylation of P-AA was less than that for P-MAA which decarboxylated less than P-MA. In addition, it was reported that P-MA lost about 40% of its CaCO$_3$ inhibitory activity after heat treatment. By contrast, P-AA and P-MAA lost only 5 to 8% of their CaCO$_3$ inhibition thus suggesting that carboxyl content plays an important role in polymer performance. The CaCO$_3$ inhibition data presented in Figure 2 suggest that there was negligible loss of either inhibitory activity or carboxyl content for HP1 and HP5 under the experimental conditions (200$^\circ$C, 20 hr, pH 10.5) used in this study.

Figure 2 also presents CaCO$_3$ inhibition data for P-SA (HP6) before and after thermal treatment. P-SA (HP6) at 3 ppm exhibits poor (<5%) CaCO$_3$ inhibition performance suggesting that the SO$_3$H group present in HP6 compared to COOH in HP1 (P-AA) shows weak interaction with calcium. However, after heat treating HP6 the CaCO$_3$ inhibition increases about 10 fold (from 3% to 36%). This significant increase in CaCO$_3$ inhibition for HP6 shown in Figure 2 may be attributed to the conversion of P-SA to P-AA during the heat treatment process.

The influence of polymer MW on precipitation of scale-forming salts has been the subject of numerous investigations.$^{4,10,12}$ Results of these studies reveal that 2,000 MW P-AAs provide optimum CaCO$_3$ inhibition. The poor performance we observed for heat treated HP6 (36%) compared to HP1 (67%) is consistent with previous studies on the influence of polymer MW on CaCO$_3$ inhibition. 

**Co- and ter-polymers**: Figure 3 shows comparative inhibition data on several co- and ter-polymers. As illustrated, both the co- and ter-polymers in the absence of thermal stress exhibit mediocre (<50%) CaCO$_3$ inhibition. However, polymer heat treatment (200$^\circ$C, 20 hr), causes varying degrees of performance changes. For example, % CaCO$_3$ inhibition values obtained for the P-AA:SA co-polymer (CP7) before and after heat treatment were 49% and 55%, respectively. The slight CaCO$_3$ inhibition improvement for heat treated CP7 may be attributed to changes in MW and conversion of SA to COOH.

Figure 3 illustrates CaCO$_3$ inhibition data for ter-polymers (i.e., TP8, and TP9) and indicates mediocre (<60%) performance in the absence of heat treatment. However, both TP8 and TP9 exhibit significantly higher CaCO$_3$ inhibition values after heat treatment as shown below:

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>TP8</th>
<th>TP9</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>54%</td>
<td>59%</td>
</tr>
<tr>
<td>200$^\circ$C @ 20 hr</td>
<td>67%</td>
<td>72%</td>
</tr>
</tbody>
</table>

As shown in Table 1, the primary structural difference between TP8 and TP9 is the third monomer (i.e., NI for TP8 and SS for TP9). From the Figure 3 data, it is clear that subjecting the ter-polymers (i.e., TP8 and TP9) to heat treatment increases their CaCO$_3$ inhibition values more than for the co-polymer (CP7). The observed increase in performance between the two ter-polymers and CP7 may be attributed to difference in molecular weights (<10k for ter-polymers vs. <40k for the co-polymer). It is worth noting that the CaCO$_3$ inhibition values for
both ter-polymers increased after heat treatment whereas previous studies have shown that the calcium phosphate inhibition and iron oxide dispersancy values decreased after heat treatment (200°C, 20hr). The performance differences observed in the present study compared to earlier investigations clearly shows that the functional groups present in ter-polymers play important roles in preventing the precipitation of different scale forming salts (i.e., CaCO$_3$, calcium phosphate).

**Effect of Temperature.** The influence of temperature on the thermal stability of polymers was also investigated at several levels: 150°C, 200°C, and 240°C. The performance data presented in Figure 4 illustrate excellent thermal stability for the two P-AAs (HP1 and HP2). However for P-MA (HP4), the situation is markedly different as shown in Figure 4 wherein increasing the temperature from 150°C to 200°C to 240°C results in gradual and then significant decrease in CaCO$_3$ inhibition values. The drop in inhibitory activity may be attributed to MW loss and greater decarboxylation with increasing solution temperature.

Figure 4 also shows a comparison of the ter-polymers that have the same baseline performance before heat treatment. However, as the polymers are exposed to progressively higher temperatures (i.e., 150°C, 200°C, and 240°C) marked increases in CaCO$_3$ inhibition values are observed. As noted in Figure 4, increasing solution temperature from 200°C to 240°C results in CaCO$_3$ inhibition improvement (>10%) for each of the ter-polymers. The performance data presented in Figure 4 suggest that essentially all of SA and non-ionic monomers present in TP8 and TP9 are degraded to form P-AA or a co-polymer of AA and SS.

**Calcium-Polymer Interactions**

It has been reported that a polymer’s ability to complex hardness ions (i.e., Ca, Mg) is affected by polymer MW. Higher-MW polymers typically exhibit better complexing ability than the low MW polymers. However, polymers that complex hardness ions can, if not properly dosed, form insoluble calcium salts that exhibit inverse solubility with temperature.

The calcium ion compatibility of several polymers exposed to thermal stress (200°C for 20 hr) was studied using a standard test method (1,000 mg/L Ca, pH 9.0, 25°C). The compatibility data presented in Figure 5 indicate that thermal treatment of P-AAs (i.e., HP1, HP2, and HP3) does not significantly impact the compatibility of these polymers with calcium ion. The data in Figure 5 also show that all SA-containing co- and ter-polymers are affected by thermal treatment; all co-and ter-polymers with the exception of TP9 became significantly less tolerant to Ca. For example, Ca ion tolerance value obtained for CP7 (P-AA:SA) before thermal stress is greater than 100 ppm polymer per 1,000 mg/L Ca compared to about 1 ppm polymer per 1,000 mg/L calcium after thermal stress (200°C for 20 hr); the thermal degraded CP7 becomes a P-AA and the poor compatibility is consistent with a high molecular weight water polymerized P-AA. The relative calcium ion compatibility improvement (after vs. before thermal treatment) of TP9 vs. TP8 may be attributed to the thermal stability of SS in the TP9.

**Polymer Characterization**

**Molecular Weight.** It is generally recognized that polymer MW has profound effects on polymer performance in domestic, biological, and industrial applications. For example, low (between 2k and 10k) MW polymers are effective precipitation inhibitors and dispersing agents
for particulate matter whereas high (>100k) MW polymers are poor precipitation inhibitors but may be effective flocculants.

All polymers (synthetic and natural) degrade as a result of exposure to elevated temperature and pressure. The extent of degradation depends upon several factors including temperature, duration of heat treatment, and polymer architecture. The polymers used in the present study lost molecular weight as a result of their thermal degradation. Figure 6 depicts the “% molecular weight loss” for homo-, co-, and ter-polymers. The data show that there is small loss of MW for the four homo-polymers (i.e., HP1, HP2, HP3, and HP5) after heating at 200ºC. Figure 6 also shows that ter-polymers (i.e., TP8 and TP9) lost less MW than the co-polymer (CP7); the MW loss obtained for ter-polymers was about 11% compared to 22% loss for the co-polymer. As discussed earlier, the gain in the ter-polymer performance as a result of heat treatment is far greater (≈50%) than the observed (≈10%) loss in MW. This suggests that the increase in performance of ter-polymers as CaCO$_3$ inhibitors is due to degradation of the non-contributing functional group(s) i.e., SO$_3$H and non-ionic rather than the cleavage of the polymer backbone.

**FT-IR Spectroscopy.** Before and after thermal treatment (at 200ºC) FT-IR spectra of HP1, CP7, TP8, TP9 are presented in Figures 7, 8, 9, and 10, respectively. Figure 10 includes FT-IR spectra for TP9 before as well as after both 4 and 20 hr of thermal treatment at 200 ºC. In all cases, poly(acrylic carboxylate) salt carbonyl, which is near 1,565 cm$^{-1}$ shifted to a 7-8 cm$^{-1}$ lower frequency after thermal stress. The reason(s) for this is not fully understood, but may reflect a change in pH caused by the heat treatment.

For those samples containing SA (i.e., Figures 8, 9, and 10), the amide carbonyl band near 1,655 cm$^{-1}$ diminishes and eventually disappears during heat treatment, as the amide functionality is oxidized. As the amide carbonyl diminishes, a complementary carboxylate salt band near 1,565 cm$^{-1}$ grows; this band is indistinguishable from the carboxylate salt band observed in poly(acrylate) salt type products (i.e., HP1). As the SA component is degraded, the primary sulfonate salt asymmetric SO$_3$ stretch band near 1,195 cm$^{-1}$ shifts to an approximately 15 cm$^{-1}$ higher frequency. The position of asymmetric SO$_3$ stretch band near 1,047 cm$^{-1}$ is essentially unchanged. However, the relative intensity of this band is somewhat less in heat-treated samples than in the untreated samples.

The spectra in Figure 10 indicate that the majority of the thermal degradation occurred after only 4 hr. Furthermore, the greater thermal stability of TP9 compared to TP8 is evident by comparing the spectra in Figures 10 and 9, respectively.

**Calcium Carbonate Crystal Morphology**

The influence of natural and synthetic additives (polymeric and non-polymeric) on the formation of various CaCO$_3$ inhibition polymorphs has been the subject of numerous investigations. Sarig and Kahana$^{22}$ reported inhibition of crystal growth of calcite by poly(glutamic acid) due to structural matching of polymeric anions and cations in calcite crystal. According to Dallas et al.,$^{23}$ sulfonated poly(styrene) and poly(styrene-divinyl benzene) polymers are suitable substrates for the growth of CaCO$_3$ monohydrate. Kitano$^{24}$ reported that organic additives capable of chelating calcium, favored the formation of Mg-rich calcite in the presence of Mg$^{2+}$. Borman et al.$^{25}$ found a strong inhibition of CaCO$_3$ formation by Ca$^{2+}$-binding polysaccharides.
As discussed above, we have investigated the efficacy of several polymers as CaCO$_3$ inhibitors. The polymers were tested at varying dosages resulting in a wide range (0% to >80%) of CaCO$_3$ inhibition performance values. Table 2 summarizes the composition of various CaCO$_3$ polymorphs formed in the presence and absence of additives as determined by x-ray diffraction data (XRD). Figure 11 (A-D) show scanning electron micrographs (SEMs) of CaCO$_3$ precipitated in the absence and presence of additives. As shown by XRD data (Table 2) and illustrated in Figure 11A, the preferred CaCO$_3$ polymorph formed in the absence of additive is calcite, the thermodynamically more stable polymorph. Figure 11 (B, C) presents SEMs of CaCO$_3$ crystals formed in the presence of 1.0 and 3.0 ppm HP1. It can be seen (Figure 11B, Table 2) that calcite is the predominant phase formed in the presence of 1.0 ppm HP1. However, as the HP1 concentration is increased from 1.0 to 3.0 ppm, the polymorph formed is essentially vaterite. Figure 11D shows the SEM of CaCO$_3$ formed in the presence of 3.0 ppm TP9.

The effect of heat treated co- and ter-polymers on CaCO$_3$ morphology was also investigated. As shown in Table 2, the predominant polymorph formed in the presence of non-heat treated polymers is calcite with traces of vaterite and aragonite. Furthermore, the relative amount of aragonite increases in the presence of heat treated ter-polymer (TP9).

Regarding the influence of natural inhibitors (FA, TA, and GTE), it has been found that in all cases calcite is the only polymorph observed thus suggesting that both phenolic and/or carboxylic acid groups play important roles in the formation of calcite. It is worth mentioning that in the presence of carboxylic acid containing inhibitor (i.e., HP1), the polymorph formed even at high inhibitor concentration, was still vaterite (Table 2).

**SUMMARY**

The data presented in this paper suggest that polymeric (homo-, co, and ter-polymers) inhibitors exhibit different influence on the precipitation of CaCO$_3$ from supersaturated solutions. It has been found that under the conditions employed in the present study neither homo-, or co- and ter-polymers prevent the precipitation of CaCO$_3$. It has also been observed that heat treatment of polymers exhibit varying effects on the inhibitory power of polymers.

The XRD data on crystal formed during precipitation in the presence of inhibitors reveal that crystal morphology strongly depends upon polymer architecture. It has been found that homo-polymers at low concentrations favor the formation of calcite, thermodynamically most stable polymorph whereas in the presence of heat treated ter-polymers the mixture of calcite, vaterite, and aragonite is formed.

**ACKNOWLEDGEMENTS**

The authors thank Noveon’s Pam Lane and Valerie Woodward for assistance with calcium analyses and scanning electron microscopy for crystal morphology study. Thanks also to Noveon, Inc. for support to carry out the research and present the findings at the NACE International’s CORROSION/2007.
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Table 1. Additives Evaluated

<table>
<thead>
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<th>Additive</th>
<th>Type*</th>
<th>Acronym</th>
<th>Mol. Weight</th>
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<tr>
<td>Tannic Acid</td>
<td>Natural material</td>
<td>TA</td>
<td>N/A***</td>
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<tr>
<td>Fulvic Acid</td>
<td>Natural material</td>
<td>FA</td>
<td>N/A</td>
</tr>
<tr>
<td>Green Tea Extract</td>
<td>Natural material</td>
<td>GTE</td>
<td>N/A</td>
</tr>
<tr>
<td>GRK732 **</td>
<td>Solvent polymerized P-AA</td>
<td>HP1</td>
<td>≈5,000</td>
</tr>
<tr>
<td>GRK7058 **</td>
<td>Water polymerized P-AA</td>
<td>HP2</td>
<td>≈5,000</td>
</tr>
<tr>
<td>BS161</td>
<td>P-AA with phosphinate groups</td>
<td>HP3</td>
<td>≈2,000</td>
</tr>
<tr>
<td>BC200</td>
<td>P-MA</td>
<td>HP4</td>
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</tr>
<tr>
<td>GRK766 **</td>
<td>P-MAA</td>
<td>HP5</td>
<td>5,000</td>
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<td>Poly-SA</td>
<td>HP6</td>
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<tr>
<td>GRK776</td>
<td>P-AA:SA copolymer</td>
<td>CP7</td>
<td>&gt;10k &amp; &lt;40k</td>
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<td>AC3100</td>
<td>P-AA:SA:NI terpolymer</td>
<td>TP8</td>
<td>&lt;10,000</td>
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<tr>
<td>GRK781 **</td>
<td>P-AA:SA:SS terpolymer</td>
<td>TP9</td>
<td>&lt;10,000</td>
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* Key to polymer type abbreviations (in table above):

<table>
<thead>
<tr>
<th>AA = acrylic acid</th>
<th>MAA = methacrylic acid</th>
<th>MA = maleic acid</th>
<th>SS = sulfonated styrene</th>
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<tr>
<td>SA = sulfonic acid or 2-acrylamido 2-methylpropane sulfonic acid</td>
<td>NI = non ionic monomer</td>
<td></td>
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</tbody>
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** Good-Rite® K-700 polymer supplied by Noveon, Inc.
*** N/A = not available

Table 2. - XRD Data for Calcium Carbonate Polymorphs formed in the Presence of Inhibitors

<table>
<thead>
<tr>
<th>Polymer*</th>
<th>Functional Group</th>
<th>Polymer (ppm)</th>
<th>Calcite (%)</th>
<th>Aragonite (%)</th>
<th>Vaterite (%)</th>
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<tr>
<td>None</td>
<td>None</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HP1</td>
<td>COOH</td>
<td>1.0</td>
<td>100</td>
<td>0</td>
<td>0</td>
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<tr>
<td>HP1</td>
<td>COOH</td>
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<td>HP1</td>
<td>COOH</td>
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* See Table 1 above for key to acronyms
** After heat treatment at 200ºC
*** NI = non ionic monomer
Figure 1. Calcium Carbonate Inhibition by Poly(acrylic acid)

Figure 2. Effect of Heat Treatment on Calcium Carbonate Inhibition by Homo-polymers
Figure 3. Effect of Polymer Heat Treatment on Calcium Carbonate Inhibition by Co- & Ter-polymers

Figure 4. Effect of Heat Treatment on Calcium Carbonate Inhibition by Polymers
Figure 7
HP1 FT-IR Spectra before and after Heat Treatment

Figure 8
CP7 FT-IR Spectra before and after Heat Treatment
Figure 9
TP8 FT-IR Spectra before and after Heat Treatment

TP8 before heating (solid line)
TP8 after 200°C for 20 hours (dotted line)

Figure 10
TP9 FT-IR Spectra before and after Heat Treatment

TP9 before heating (solid line)
TP9 after 200°C for 4 hours (dashed line)
TP9 after 200°C for 20 hours (dotted line)
Figure 11
Scanning Electron Micrographs of CaCO$_3$ Precipitated in the Absence and Presence of Polymers

A: Control (no polymer)  
B: In the Presence of 1 ppm HP1

C. In the Presence of 3 ppm HP1  
D. In the Presence of 3 ppm TP9