KINETIC AND MORPHOLOGICAL INVESTIGATION
ON THE PRECIPITATION OF CALCIUM CARBONATE
IN THE PRESENCE OF INHIBITORS

Z. Amjad, PhD and R. W. Zuhl
Noveon, Inc.
9911 Brecksville Road
Cleveland, OH 44141

ABSTRACT

Control of calcium carbonate precipitation especially under highly stressed conditions continues to pose serious operational challenges to the water technologist. Scarcity of good quality water and stringent environmental regulations are the driving forces leading to high cycles in cooling water systems. In this paper, the pH-stat method has been used to study the precipitation of calcium carbonate in aqueous solutions with varying degrees of calcite supersaturation in the presence of inhibitors. Results are discussed in terms of rate of retardation of calcium carbonate precipitation by phosphonates, polymers, and phosphonate/polymer blends, and the influence of inhibitors on induction period (lag time preceding the precipitation). The impact of inhibitors on calcium carbonate crystal morphology has been investigated by scanning electron microscopy (SEM) and x-ray diffraction.

Keywords: calcium carbonate, precipitation, inhibitors, kinetic, crystal morphology

INTRODUCTION

Calcium carbonate (CaCO₃) is one of the most commonly encountered scale deposits and occurs in different crystalline forms: calcite, aragonite, vaterite, calcium carbonate monohydrate, and calcium carbonate hexahydrate. The precipitation and stabilization of these polymorphs depends upon the precipitation conditions, i.e., degree of supersaturation, pH, ionic medium, and concentration and type of impurities. The precipitation and deposition of CaCO₃ continues to pose serious operational problems in industrial water systems. The formation of these deposits reduces heat transfer and internal diameter of pipes, increasing the operating pressure of pumps, and enhances the probability of corrosion damage. In soda-based laundry detergents, the free calcium ion concentration in the washing liquid is reduced by the precipitation of CaCO₃. A disadvantage of such detergents is that part of CaCO₃ is deposited on the textile surfaces and on exposed parts of washing machines.

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Model compound studies examining the molecular relationship to growth inhibition have yielded interesting results in precipitation reactions. Miura, et al.\textsuperscript{6} reported that phosphates adsorbed to CaCO\textsubscript{3}, but pyrophosphate and tripolyphosphate were better inhibitors than orthophosphate. Amjad\textsuperscript{7} examined calcite growth inhibition in the presence of benzene polycarboxylic acids and reported that more highly carboxylated benzenes are better inhibitors (at the same solution concentration) than less carboxylated benzenes. A Langmuir type adsorption model has been proposed to describe the inhibition of CaCO\textsubscript{3} crystal growth by carboxyl containing ions.\textsuperscript{7}

Major progress has been made toward the understanding of phosphonate solution and precipitation chemistry as well as how this relates to fouling problems in industrial water systems. Ashcraft\textsuperscript{8} studied the influence of various factors on the performance of AMP, HEDP, and PBTC in the presence of soluble iron. Ashcraft’s study showed PBTC to be superior to AMP and HEDP in the presence of high calcium ion presumably due to the greater solubility of Ca-PBTC salt. The precipitation of Ca-phosphonate salts can (a) directly cause heat exchanger fouling and (b) indirectly cause severe CaCO\textsubscript{3} scaling due to the decrease in phosphonate concentrations.

During the last two decades investigations of polymeric inhibitors to prevent or retard CaCO\textsubscript{3} scaling have attracted the attention of academic and industrial researchers. Common inhibitors evaluated include poly(acrylic acid), P-AA; poly(maleic acid), P-MA; and co-polymers containing acrylic acid or maleic acid and other monomers with different functionality (i.e., -CONH\textsubscript{2}, -COOR, SO\textsubscript{3}H). Investigations of these and several others mineral scale inhibitors suggest that inhibitor effectiveness depends on the functional groups in the inhibitor molecule, polymer composition, and molecular weight.\textsuperscript{9-11}

To understand the interaction of various functional groups with CaCO\textsubscript{3}, the influence of phosphonates, a variety of polymers with different functional groups, and phosphonate/polymer blends as precipitation inhibitors for CaCO\textsubscript{3} in aqueous solution were studied. This study also presents results on the effect of various inhibitors on the crystal morphology of CaCO\textsubscript{3}.

**EXPERIMENTAL**

The stock solutions of calcium chloride and magnesium chloride were prepared from reagent grade chemicals and were standardized by atomic absorption spectroscopy. The sodium bicarbonate and sodium carbonate solutions were prepared on the day of each experiment. Phosphonates and polymeric inhibitors used in this study were commercial materials and stock solutions of these additives were prepared on an active solids basis. Tables 1 and 2 identify the phosphonates and polymeric inhibitors evaluated in this work. As can be seen from Table 2, the polymers evaluated contain a variety of monomers and functional groups (i.e., carboxylic acid, sulfonic acid, sulfonated styrene, maleic acid). Table 3 summarizes the water chemistry used in the precipitation experiments.

The CaCO\textsubscript{3} precipitation experiments were done in a 250 mL double-walled Pyrex\textsuperscript{®} glass cell thermostatted by water circulated from a constant temperature bath. The working solution was stirred with a Teflon\textsuperscript{®} coated stirring bar. The solution pH was measured by a combination electrode. The CaCO\textsubscript{3} super-saturation conditions used in this study were determined by using common ion computer modeling\textsuperscript{12} and appropriate volume of bicarbonate/carbonate
solutions were combined to create supersaturated conditions. The supersaturated solutions (223 mL total volume) were prepared in the reaction cell by adding a known volume of stock solutions containing sodium carbonate, sodium bicarbonate, and inhibitor. After equilibrating the solutions at 50°C for 30 minutes, a known volume of stock solution of calcium chloride and magnesium chloride was added. The pH of the CaCO₃ supersaturated solutions was quickly (typically <20 sec) adjusted to 9.00 and kept constant by the automatic addition of 0.2 M NaOH solution. The uptake of NaOH was also recorded on a strip chart recorder. At the end of precipitation experiments the solutions were filtered and filtrate analyzed for calcium and magnesium by atomic absorption method. The CaCO₃ solids collected on the membrane filters were analyzed by x-ray diffraction and scanning electron microscopy.

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

\[
\text{Inhibition (\%) = } \frac{[\text{Ca}]_{\text{sample}} - [\text{Ca}]_{\text{control}}}{[\text{Ca}]_{\text{initial}} - [\text{Ca}]_{\text{control}}} \times 100
\]  \hspace{1cm} (1)

Where:

\[
[\text{Ca}]_{\text{sample}} = \text{concentration of Ca in the filtrate in the presence of inhibitor at 1 hr}
\]

\[
[\text{Ca}]_{\text{control}} = \text{concentration of Ca in the filtrate in the absence of inhibitor at 1 hr}
\]

\[
[\text{Ca}]_{\text{initial}} = \text{concentration of Ca in the solution at 0 hr}
\]

Because CaCO₃ precipitation reaction in the absence of inhibitor is essentially completed in less than 10 minutes, we chose a 1-hr precipitation period as the basis for comparing results. It should be noted that the use of a different precipitation period would lead to a change in absolute inhibition values. However, changing the precipitation time should not affect the findings and conclusions regarding the performance of phosphonates and phosphonate/polymer blends as CaCO₃ inhibitors.

RESULTS AND DISCUSSION

Figure 1 illustrates the pH-stat apparatus used in the present study. Using this method, a large number of experiments were conducted to study and record CaCO₃ precipitation from supersaturated solution as a function of time. The experiments reported here had good reproducibility (±7%). Figure 2 shows the amount of NaOH required (added) as a function of time to maintain a constant pH in calcite saturated (ranging from 125x to 223x) solutions (without inhibitors) as CaCO₃ forms. As illustrated in Figure 2, a measurable lag (delay) or induction time occurs (hereafter called β) in the development of precipitate. The determination of β is illustrated in Figure 2. It is evident from Figure 2 that the β value decreases as the calcite saturation is increased. For example, the β value obtained for the 125x calcite saturation is 48 seconds compared to 20 seconds obtained for 223x calcite saturation.

Effect of Phophonates

The effect of AMP, HEDP, and PBTC on the precipitation of CaCO₃ was investigated at various calcite super-saturations and as a function of phosphonate concentration. Figure 3 shows the uptake of 0.2 M NaOH vs. time profiles for various dosages of HEDP at 223x calcite super-saturation. It is evident from Figure 3 that β values are greatly prolonged by increasing
HEDP concentrations. Figure 4 plots induction time ($\beta$) vs. phosphonate dosages for AMP, HEDP, and PBTC. As indicated, low dosages (<10 mg/L) all phosphonates show less than 1-minute induction times. However, as phosphate dosages are gradually increased (up to 20, 40, and 50 mg/L), PBTC starts differentiating itself. For example, at 50 mg/L phosphate dosages, the $\beta$ values obtained for AMP and HEDP are 3.5 and 6 minutes, respectively compared to 41 minutes for PBTC.

Figure 5 shows CaCO$_3$ inhibition data as a function of phosphonate dosage at 223x calcite saturation. It is worth noting that none of the phosphonates even at 40 mg/L dosage are able to completely prevent CaCO$_3$ precipitation at 223x calcite saturation. Several experiments were carried out at higher phosphate dosages (i.e., 50 and 60 mg/L), but complete inhibition was not obtained. It should be pointed out that under high calcium and phosphonates concentrations as used in these experiments, it is likely that HEDP, AMP, and PBTC are precipitated as calcium salts. From a practical application perspective, in order to control CaCO$_3$ precipitation under high calcite saturation, these phosphonates need to be blended with high performance scale inhibitors and dispersants in order to prevent their precipitation with calcium ions.

To study the effect of phosphonates on calcium carbonate precipitation at low to medium calcite saturation (150x and 180x) a series of experiments were performed in the presence of AMP, HEDP, and PBTC. Figure 6 shows the plots of CaCO$_3$ inhibition as a function of phosphate dosages for AMP, HEDP, and PBTC. It can be seen that at 180x calcite saturation, none of the phosphonates completely inhibited CaCO$_3$ precipitation. It is worth noting the CaCO$_3$ inhibition data for low phosphate dosages (<10 mg/L) indicate much poorer performance for PBTC compared to AMP and HEDP. However, as illustrated in Figure 6, all three phosphonates at 20 mg/L dosages provide similar performance. Furthermore, when the phosphate dosage is increased to 40 mg/L, PBTC exhibits better performance than both HEDP and AMP.

Figure 7 shows induction time vs. calcite saturations for PBTC at 10 mg/L. Similar induction times vs. calcite saturation trends were also observed for AMP and HEDP.

**Effect of Polymers**

Polymers such as poly(acrylic acid), poly(maleic acid), poly(aspartic acid) and acrylic-, maleic acid–based co- and ter-polymers are known to inhibit the precipitation of CaCO$_3$. It is generally agreed that homo-polymers compared to co- and ter-polymers are better CaCO$_3$ precipitation inhibitors. The better performance offered by these homo-polymers has been attributed to the presence of carboxyl group. On the other hand, it has been reported that homo-polymers are not effective inhibitors compared to co- and ter-polymers in preventing the precipitation of Ca-HEDP and Ca-AMP salts. In addition to scale inhibition, terpolymers are known for their excellent performance as particulate matter (especially iron oxide) dispersants.

The efficacy of various homo-, co-, and ter-polymers as CaCO$_3$ inhibitors was evaluated at various polymer dosages. Figure 8 presents results on percent CaCO$_3$ inhibition in the presence of 30 mg/L polymer dosages. It can be seen that HP1 (P-AA) performs better than HP2 (P-MA). Among co-polymers, CP2 (AA:SA) exhibits better CaCO$_3$ inhibition than CP1 (AA:MA). In addition, as illustrated in Figure 8, TP2 is a better inhibitor than TP1. This
difference in performance may be attributed to different molecular weight and polymer composition.

**Effect of Polymer/HEDP Blend.** Figure 9 shows the CaCO\(_3\) inhibition for several polymer/HEDP (3:1) blends at 30 mg/L dosages and 180x calcite saturation and indicate the following order of effectiveness:

\[
\text{TP2/HEDP} > \text{TP1/HEDP} > \text{HP1/HEDP} > \text{CP1/HEDP}
\]

All of the polymer/HEDP blends provide better CaCO\(_3\) inhibition than HEDP alone. TP2/HEDP blend provides the best performance. Although the data are not presented herein, it is noteworthy that a TP2/HEDP/AMP (3:0.5:0.5) blend did not show any synergistic CaCO\(_3\) inhibition compared to the TP2/HEDP (3:1) blend.

**Effect of Polymer/PBTC Blend.** Figure 10 presents CaCO\(_3\) inhibition data for three (3) polymer/PBTC (3:1) blends (incorporating high performance polymers [i.e., TP1, TP2, and CP1] as components) at various dosages (10 to 40 mg/L) and 180x calcite saturation. The data clearly show that polymers impact CaCO\(_3\) scale inhibition performance in different ways and that the TP2/PBTC blend is the most effective.

**Kinetic Aspects of CaCO\(_3\) Precipitation and Inhibition**

As discussed above in this study we have investigated the influence of a variety of polymers, phosphonates, and polymer/phosphonate blends by a pH-stat method for their performance as CaCO\(_3\) inhibitors. Several concentrations of each inhibitor were tested giving results ranging from no inhibition to induction times of 3 to >300 minutes. To determine the impact of inhibitors on the kinetics of precipitation we have used the initial rate of precipitation as calculated from the uptake of NaOH vs. time profiles for various inhibitors. The precipitation rates relative to the absence of inhibitor were calculated using the following equation:

\[
\text{Relative Inhibition} (%) = (1 – R_i/R_o) \times 100\% \quad (2)
\]

Where:

- \(R_o\) : precipitation rate in the absence of inhibitor
- \(R_i\) : precipitation rate in the presence of inhibitor

Figure 11 shows plots of relative inhibition (1-R/R_o) as a function of phosphonate dosage. It can be seen that PBTC at concentrations below 10 mg/L is a poor inhibitor. For example at a 5-mg/L phosphonate concentration, the relative inhibition (%) values obtained for AMP and HEDP are 22% and 31%, respectively compared to 7% obtained for PBTC. However, as the phosphonate concentration is increased tenfold (i.e., from 5 to 50 mg/L), PBTC performs better than AMP and HEDP. This observed difference in PBTC performance may be attributed to better Ca-PBTC salt solubility as compared to Ca-AMP and Ca-HEDP salts.

Figure 12 presents induction time (\(\beta\)) and relative inhibition (%) data for 40 mg/L dosages of several inhibitor systems. There are two points worth mentioning. First, the \(\beta\) value obtained at PBTC is 16 min which is over 500% larger than the \(\beta\) value for HEDP (3 min). Similarly, TP2 gives higher induction time than TP1 suggesting that sulfonate groups in TP2 improve the
performance of PBTC. Second, both terpolymers work synergistically with PBTC and HEDP, but the TP2/PBTC (3:1) blend at 40 mg/L performs better than TP1/PBTC under similar experimental conditions. For example, relative inhibition values obtained for TP2/PBTC and TP1/PBTC blends are 88 and 72%, respectively. The higher performance exhibited by TP2 over TP1 is consistent with earlier investigations on the performance of these polymers as calcium phosphate and calcium phosphonates.  

**Effect of Phosphonates, Polymers, and Phosphonates/Polymer Blends on CaCO₃ Crystal Morphology**

The influence of polymeric and non-polymeric inhibitors on the formation of various CaCO₃ polymorphs has been the subject of numerous investigations. Sarig and Kahana₁⁷ reported the inhibition of crystal growth of calcite by poly(glumatic acid) due to structural matching of polymeric anions with cations in calcite crystals. According to Dallas, et al.₁⁸ sulfonated poly(styrene) and poly(styrene-di-vinyl benzene) polymers are suitable substrates for the growth of CaCO₃ monohydrate. Kitamoto₁⁹ reported that organic materials with which calcium is strongly chelated, favored the formation of Mg-rich calcite in the presence of Mg²⁺. Borman, et al.₂⁰ found a strong inhibition of CaCO₃ formation by Ca²⁺-binding polysaccharides.

As discussed above, we investigated a number of polymers, phosphonates, and phosphonate/polymer blends by a pH-stat method for their efficacy as CaCO₃ inhibitors. Several concentrations of each inhibitor were tested giving results ranging from induction time of <1 minute (in the absence of inhibitor) to >120 minutes. The uptake of NaOH as a function of time for various inhibitors are presented in Figures 2 and 3. The CaCO₃ crystals formed in the absence and presence of inhibitors were examined by x-ray diffractometry (XRD) and scanning electron microscopy for crystal morphology.

Table 4 summarizes the composition of CaCO₃ polymorphs formed in the presence and absence of inhibitors as determined by XRD data. It is evident from Table 4 that at the four CaCO₃ super-saturations investigated in the absence of inhibitors the crystals formed are a mixture of calcite, vaterite, and aragonite with calcite, the thermodynamically most stable polymorph, as a major component (~60%). It is interesting to note that at low super-saturation (i.e., 125x calcite saturation) the percent calcite formed increases to 81% compared with ~60% obtained at higher calcite super-saturations. However, the situation in the presence of phosphonate, polymer, and phosphonate/polymer blends is different in the sense that the predominant polymorph is calcite (>90%) with vaterite as a minor (<10%) component. This suggests that both aragonite and vaterite polymorphs are stabilized by inhibitors evaluated in the present study.

Figure 13 shows electron micrographs of CaCO₃ crystals formed in the absence of inhibitor. The modified CaCO₃ crystals formed in the presence of 5 mg/L PBTC are presented in Figure 14. The influence of TP2 at 7.5 and 15 mg/L are illustrated in Figures 15 and 16, respectively. It can be seen that not only does TP2 modify the crystal structure but it also increases the crystal size as TP2 concentration is increased from 7.5 to 15 mg/L.

CaCO₃ crystals in the absence (control) and presence (TP2/PBTC blend) of inhibitor are presented in Figures 17 and 18 respectively. The CaCO₃ crystals (calcite and aragonite) shown in Figure 17 (control or absence of inhibitor) are <10 microns and have regular shapes (mostly cubical). Whereas the CaCO₃ crystals structures in Figure 18 (inhibited system) are
fewer in number, most are >10 microns, and significantly distorted with spherical shapes. The inhibited (TP2/PTBC) system CaCO$_3$ crystals are more readily dispersed and less likely to adhere to heat exchanger surfaces.

The XRD data obtained for CaCO$_3$ crystals formed in the absence of magnesium are presented in Table 4. It is interesting to note that at low calcite saturation and in the absence of magnesium ion, the predominant (>90%) polymorph is vaterite with calcite as a minor component. This is in agreement with other studies in which it was reported that when spontaneous precipitation occurs vaterite is the initially forming polymorph. As shown in Table 4, both fulvic acid (or FA a natural polymer containing phenolic and carboxyl groups) and a synthetic polymer [i.e., poly(acrylic acid) or P-AA] used at low concentrations exhibit different effects on the crystal morphology. It is evident from the data presented in Table 4 that whereas in the presence of FA the predominant polymorph formed is calcite, in the presence of P-AA the predominant polymorph is vaterite. The change in crystal morphology observed in the presence of FA and P-AA suggest that functional groups present in the inhibitors not only influence the kinetics of precipitation but also affects the stabilization of different CaCO$_3$ polymorphs.

**SUMMARY**

The data presented in this paper suggest that both non-polymeric (i.e., phosphonates) and polymeric (homo-, co, and ter-polymers) inhibitors exhibit different influence on the precipitation of CaCO$_3$ from super-saturated solutions. It has been found that under high stressed water chemistries used in the present investigations neither phosphonates nor any type of polymeric inhibitors completely prevent the precipitation of CaCO$_3$. It has also been observed that blends of ter-polymers (i.e., AA:SA:SS, TP2) with PBTC exhibit synergistic influence on the precipitation of CaCO$_3$.

The XRD data on crystals formed during precipitation in the presence of inhibitors reveal that crystal morphology strongly depends upon solution super-saturation and the type and concentrations of inhibitors. It has been found that phosphonates, polymers, and phosphonate/polymer blends favor the formation of calcite, thermodynamically the most stable polymorph whereas in the absence of inhibitors a mixture of calcite, vaterite, and aragonite is formed. In addition, the crystals formed in the presence of inhibitors are highly modified and larger in size compared to crystals formed in the absence of inhibitors.

**ACKNOWLEDGEMENTS**

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

**REFERENCES**


4. J. C. Cowan and D. J. Weintritt (Eds), Water Formed Scale Deposits, Gulf Publishing, Houston, TX (1976).


### Table 1

<table>
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<tr>
<th>Chemical Name</th>
<th>Acronym</th>
<th>Molecular Weight</th>
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<tr>
<td>Aminotris(methyleneephosphonic acid)</td>
<td>AMP</td>
<td>299</td>
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<tr>
<td>1-Hydroxyethylidene 1,1-diphosphonic acid</td>
<td>HEDP</td>
<td>206</td>
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<tr>
<td>2-Phosphonobutane 1,2,4-tricarboxylic acid</td>
<td>PBTC</td>
<td>270</td>
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### Table 2 - Polymers Evaluated

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<th>Polymer</th>
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<tr>
<td>Poly(acrylic acid)</td>
<td>HP1</td>
<td>&lt;5,000</td>
</tr>
<tr>
<td>Poly(maleic acid)</td>
<td>HP2</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>Poly(acrylic:maleic)</td>
<td>CP1</td>
<td>&lt;3,000</td>
</tr>
<tr>
<td>Poly(acrylic:sulfonic)</td>
<td>CP2</td>
<td>&lt;15,000</td>
</tr>
<tr>
<td>Multifunctional polymer</td>
<td>TP1</td>
<td>&lt;15,000</td>
</tr>
<tr>
<td>Poly(acrylic:sulfonic:sulfonated styrene)</td>
<td>TP2</td>
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*CP2 and TP2 are Good-Rite® K-775 copolymer and K-798 terpolymers, respectively supplied by Noveon, Inc. The other polymers are supplied by other companies.
### Table 3 - Water Chemistries used in Calcium Carbonate Inhibition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition A</th>
<th>Condition B</th>
<th>Condition C</th>
<th>Condition D</th>
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<td>2.76</td>
<td>2.66</td>
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<td>223</td>
<td>180</td>
<td>150</td>
<td>125</td>
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<td>Calcium (mg/L as Ca)</td>
<td>250</td>
<td>210</td>
<td>180</td>
<td>154</td>
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<tr>
<td>Magnesium (mg/L as Mg)</td>
<td>75</td>
<td>63</td>
<td>54</td>
<td>46</td>
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<tr>
<td>Sodium (mg/L as Na)</td>
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<td>228</td>
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<td>Bicarbonate (mg/L as HCO(_3))</td>
<td>450</td>
<td>380</td>
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<td>100</td>
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<td>558</td>
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### Table 4. - XRD Data for Calcium Carbonate Polymorphs formed under Different Water Chemistries and in the Presence of Various Inhibitors

<table>
<thead>
<tr>
<th>Ca (mg/L)</th>
<th>Inhibitor</th>
<th>% Calcite</th>
<th>% Aragonite</th>
<th>% Vaterite</th>
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<tr>
<td>250</td>
<td>None</td>
<td>65</td>
<td>22</td>
<td>13</td>
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<td>180</td>
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<td>6</td>
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<td>85</td>
<td>8</td>
<td>7</td>
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<tr>
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<td>HP1</td>
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<td>0</td>
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<td>AMP @ 5 mg/L</td>
<td>95</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>210</td>
<td>HEDP @ 5 mg/L</td>
<td>96</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>210</td>
<td>PBTC @ 5 mg/L</td>
<td>96</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>210</td>
<td>TP2/PBTC (3:1) blend @ 30 mg/L</td>
<td>92</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>220*</td>
<td>Control</td>
<td>5</td>
<td>0</td>
<td>95</td>
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<tr>
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<td>Fulvic Acid @ 5 mg/L</td>
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<td>220*</td>
<td>Poly(acrylic acid) @ 0.5 mg/L</td>
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*220 mg/L Ca; 2,426 mg/L Na; 336 mg/L HCO\(_3\); 3,940 mg/L Cl; pH 8.5; and 35 °C
Figure 1. pH-Stat Apparatus Used

Figure 2. NaOH Added vs. Time to Maintain Constant pH in Calcite Saturated Solutions
Figure 3. Effect of HEDP Dosage on CaCO₃ Precipitation (223x Calcite Saturation)

Figure 4. Induction Time vs. Phosphonate Dosage (223x Calcite Saturation)
Figure 5. CaCO₃ Inhibition by Phosphonates
(223x Calcite Saturation)

Figure 6. CaCO₃ Inhibition by Phosphonates
(180x Calcite Saturation)
Figure 7. Induction Time vs. Calcite Saturation
(10 mg/L PBTC)

Figure 8. CaCO₃ Inhibition by Polymers
(180x Calcite Saturation, 30 mg/L Polymer Dosage)
Figure 9. CaCO₃ Inhibition by Polymer/HEDP (3:1) Blends (180x Calcite Saturation, 30 mg/L Inhibitor Dosage)

Figure 10. CaCO₃ Inhibition by Polymer/PBTC (3:1) Blends (180x Calcite Saturation)
Figure 11. Relative Inhibition vs. Phosphonate Dosage

Phosphonate Dosage (mg/L)

% Relative Inhibition

AMP
HEDP
PBTC

Figure 12. Effect of Inhibitor Systems on Relative Inhibition and Induction Time (223x Calcite Saturation, 40 mg/L Inhibitor)

Relative Inhibition (%) and Induction Time (min)

Inhibitor Systems

TP1
TP1/PBTC
TP2
TP2/PBTC
TP2/PBTC/HEDP
HEDP
PBTC

Relative Inhibition
Induction Time
Figure 13 – SEM Picture of Calcium Carbonate Formed in the Presence of Inhibitor (180x Calcite Saturation).

Figure 14 – SEM Picture of Calcium Carbonate Formed in the Presence of 7.5 mg/L PBTC (180x Calcite Saturation).
Figure 15 - Scanning Electron Micrograph of CaCO₃ Formed in the Presence of 7.5 mg/L TP2 (180x Calcite Saturation).

Figure 16 – SEM Picture of CaCO₃ Formed in the Presence of 15 mg/L TP2 (180x Calcite Saturation).
Figure 17. - SEM Picture of CaCO$_3$ Crystals Grown in the Absence of Inhibitor.

Figure 18 - SEM Picture of CaCO$_3$ Crystals Grown in the Presence of TP2/PBTC Blend.