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**The Use of Polymers to Improve Control
of Calcium Phosphonate and Calcium Carbonate
in High Stressed Cooling Water Systems**

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**Carbosperse™ K-700
Water Treatment Polymers****

Introduction

Phosphonates and polyphosphates are used in water treatment processes for a variety of reasons. Most importantly, phosphonates and polyphosphate inhibit the formation of scale forming salts and control steel corrosion. Scale inhibition is prevented in a “sub-stoichiometric” manner as phosphorus containing compounds adsorb onto crystal growth sites of sub-microscopic crystallites thereby interfering with crystal growth and altering the crystal morphology. Phosphonates are used to sequester metal ions such as copper, manganese, iron, and zinc. Additionally, these phosphorus containing compounds also exhibit some dispersancy activity for suspended matter such as clay, silt, and calcium carbonate. Although there are many phosphonates available, the three most commonly used phosphonates in industrial water treatment applications are shown in Table 1 below:

Table 1
Phosphonates Commonly Used in Industrial Water Treatment Applications

<u>Chemical Name</u>	<u>Acronym</u>	<u>Molecular Weight</u>
Aminotris(methylenephosphonic acid)	AMP	299
1-Hydroxyethylidene 1,1-diphosphonic acid	HEDP	206
2-Phosphonobutane 1,2,4-tricarboxylic acid	PBTC	270

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. Ashcraft¹ 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 calcium carbonate scaling due to the decrease in phosphonate concentrations.

Inhibition of calcium phosphonate precipitation by polymeric inhibitors has been the subject of intensive research. Smyk, et al.² in their investigation on the influence of various polymers on the precipitation of calcium phosphonate showed that acrylic acid based terpolymers perform better than homo-polymers of acrylic acid and maleic acid. Amjad³ in another study showed that various factors (i.e., solution hardness, pH, temperature) greatly influence the precipitation of calcium phosphonate salts. Furthermore, inhibition data also suggest that polymer performance strongly depends upon the composition, molecular weight, and ionic charge of the polymer.

Currently, many cooling systems are operated at high cycles of concentration due to water conservation and waste water discharge regulations. However, these practices increase scaling tendency in recirculating water and necessitate the use of high performance scale and deposit control additives to prevent the formation and deposition of unwanted materials on heat exchanger and other equipment surfaces.

In order to deal with these challenging problems, an effective cooling water treatment program must control scale, corrosion, particulate matter, and microbiological matter.

The use of polymers as scale inhibitors and dispersants in industrial applications is well known to the water technologists. It is generally agreed that polymers when present at low concentrations greatly inhibit the precipitation of scale forming salts (i.e., calcium carbonate, calcium sulfate, calcium phosphate, barium sulfate).^{4,6} The incorporation of polymers in water treatment formulations also enables the water technologist in stabilizing metal ions (i.e., Fe, Mn, Cu) in recirculating cooling water systems.⁷

In the present work, we have investigated the tolerance of phosphonates with calcium ions under different water chemistry (i.e., calcium ion concentration, pH, temperature). The ability of polymers to improve the calcium tolerance of phosphonates has also been studied. In addition, experiments were carried out to investigate the performance of deposit control polymers (DCPs), phosphonates, and phosphonate/DCP blends as calcium carbonate (CaCO₃) inhibitors under stressed conditions.

Experimental

Phosphonate Tolerance (Turbidity Test)

Phosphonates tolerance towards calcium ions was measured by turbidity monitoring. The test set-up used a constant temperature water bath, pH meter, and a Brinkmann PC 800 Colorimeter with 420 nm filter (for transmittance measurements).

A known volume of stock calcium chloride solution was added to glass bottles containing known volume of deionized/distilled water to obtain a final concentration of calcium ion (250, 500, or 750 mg/L as Ca). To these calcium solutions were added varying amounts of DCP stock solutions to yield required (1 to 100 mg/L) of DCP in solutions. The bottles were capped and equilibrated at the required temperature for 30 minutes. Subsequently, phosphonate stock solution (to yield 10 to 50 mg/L) was added. The total volume of final solution was kept constant (i.e., 100 mL). The pH levels of these solutions were adjusted to pH 9.0 with dilute NaOH and/or HCl solution. At a known time (typically 45 minutes) transmittance readings were taken using a fiber-optic probe.

When the concentration of phosphonate in the experimental solution exceeded the solubility limit, the solution became turbid and was detected by a steep decrease in light transmittance. Data acquisition was continued with experimental solutions containing varying concentrations of phosphonates to precisely determine the inflection point.

Calcium Carbonate Inhibition Test

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 DCPs used in this study were commercial materials and stock solutions of these inhibitors were prepared on an active solids

basis. Tables 1 (shown earlier) and 2 identify the phosphonates and deposit control polymers (DCPs), respectively evaluated in this work. As can be seen from Table 2, the DCPs 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.

Table 2 - Polymers Evaluated

Polymer	Acronym	Molecular Weight
Poly(acrylic acid)	PAA	<5,000
Poly(maleic acid)	PMA	<2,000
Poly(acrylic:maleic)	AMC	<3,000
Poly(acrylic:sulfonic)	ASC*	<15,000
Multifunctional polymer	MFP	<15,000
Poly(acrylic:sulfonic:sulfonated styrene)	AST*	<15,000

* ASC and AST are Good-Rite® K-700 co- and terpolymers, respectively supplied by Noveon, Inc.

Table 3 - Water Chemistries used in Calcium Carbonate Inhibition

Parameter	Condition A	Condition B
LSI	2.76	2.89
Calcite saturation	180	223
Calcium (as Ca)	210 mg/L	250 mg/L
Magnesium (as Mg)	63 mg/L	75 mg/L
Sodium (as Na)	228 mg/L	240 mg/L
Bicarbonate (as HCO ₃)	380 mg/L	450 mg/L
Carbonate (as CO ₃)	100 mg/L	100 mg/L
Chloride (as Cl)	558 mg/L	626 mg/L
pH	9.00	9.00
Temperature	50°C	50°C

The CaCO₃ precipitation experiments were done in a 250 mL double-walled Pyrex® glass cell thermostatted by water circulated from a constant temperature bath. The working solution was stirred with a Teflon® coated stirring bar. The solution pH was measured by a combination electrode. The CaCO₃ super-saturation conditions used in this study were determined by using WaterCycle® common ion computer modeling 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.

Note: WaterCycle® is a proprietary computer software program supplied by French Creek Software.

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.

DCP, phosphonate, and DCP/phosphonate blend efficacy as CaCO₃ inhibitor was calculated using the following equation:

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

Where:

[Ca]_{sample} = concentration of Ca in the filtrate in the presence of inhibitor at 1 hr
 [Ca]_{control} = concentration of Ca in the filtrate in the absence of inhibitor at 1 hr
 [Ca]_{initial} = concentration of Ca in the solution at t @ 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 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

Tolerance of Phosphonates with Calcium Ions

The tolerance of phosphonate with calcium ions is defined as the minimum concentration of phosphonate at given water chemistry (i.e., pH, temperature, hardness ion concentration) necessary to cause precipitation of phosphonate. It is recognized that precipitation of Ca-phosphonate salts can cause fouling of heat exchanger surfaces and that these deposits can be construed as Ca-phosphate fouling. In addition, the phosphonate concentration decreases in the system to the extent that severe CaCO₃ scaling can occur. It should be noted that Ca-phosphonate scales usually have the same inverse solubility features commonly observed with other mineral scales and they impede heat transfer.

Using the experimental procedure described above, a large number of experiments were conducted to determine the tolerance limits of various phosphonates. Figure 1 illustrates the typical “% transmittance” (%T) as a function of phosphonate concentration (i.e., PBTC) in the presence of 500 mg/L Ca as calcium, at pH 9.0, and 45°C. The inflection point in the transmittance-PBTC concentration was used to calculate the point of onset of turbidity (i.e., minimum concentration of PBTC needed to cause precipitation). The good reproducibility ($\pm 7\%$) of phosphonate tolerance is also illustrated in Figure 1. The tolerance limit of PBTC as calculated from the data in Figure 1 is 56 ± 3 mg/L.

The tolerance of PBTC, AMP, and HEDP was also investigated in the presence of 250 mg/L Ca and at 45°C. Results obtained for these phosphonates are shown in Figure 2. The phosphonates can be ranked according to their Ca tolerance in descending order (as mg/L soluble phosphonate per 250 mg/L Ca [as Ca ion]) as follows:

$$\text{PBTC (73 mg/L)} > \text{AMP (13.5 mg/L)} > \text{HEDP (7.5 mg/L)}$$

Effect of Hardness Ion Concentration

Cooling water systems are increasingly operated at higher cycles of concentrations causing greater driving forces for the precipitation of scale forming salts especially CaCO_3 . Figure 3 illustrates the effect of hardness ion in the range 250 to 750 mg/L Ca on the tolerance of AMP, HEDP, and PBTC at 45°C. It is evident that tolerance of these phosphonates decreases as the Ca ion concentration is increased. For example, in the presence of 250 mg/L Ca, the tolerance values obtained for AMP, HEDP, and PBTC are 13.5, 7.5, and 73 mg/L, respectively compared with 7.0, 4.8, and 50 mg/L obtained in the presence of 750 mg/L Ca. Thus, Ca ion tolerance decreases by a factor of 1.5 to 2.0 times for AMP, HEDP, and PBTC. It is evident from Figure 3 that PBTC is much more resistant to precipitation as Ca salt than either HEDP or AMP.

Effect of Solution Temperature

It is well documented that various factors (e.g., pH, temperature, and total dissolved solids) affect the solubility of scale-forming salts. It is also well known that solubility of scale-forming salts such as CaCO_3 , calcium phosphate, and calcium sulfate are inversely dependent on solution temperature.

Figures 4 to 6 present data for our investigations to determine the influence of solution temperature (25 to 60°C) in the presence of 250 to 750 mg/L Ca at pH 9.0 for AMP, HEDP, and PBTC. These data clearly indicate that solution temperature has a pronounced effect on the tolerance of phosphonates with Ca ion. Figures 4 to 6 show that increasing the solution temperature from 25 to 60°C results in corresponding 1.5x to 2x decreases in phosphonate tolerances.

Extending Phosphonate Tolerance of Ca Ion

For industrial water treatment, phosphonates have been shown to be broadly effective in controlling scale and mild steel corrosion. A loss of scale and corrosion control can occur if calcium phosphonate salts precipitate. Although phosphonates are generally considered tolerant to hardness ions, harsh conditions (i.e., high hardness, high pH, high temperature) such as discussed above can cause phosphonates to precipitate as calcium salts or co-precipitate with other salts and deposit on heat exchanger surfaces. Thus, for better scale and corrosion control it is important to prevent the precipitation of calcium phosphonates or extend the hardness tolerance limit of phosphonate by using an appropriate DCP.

DCPs have been used extensively to prevent the precipitation of various scale forming salts such as calcium phosphate, calcium phosphonate, CaCO_3 , calcium sulfate, calcium oxalate, and calcium fluoride. However, DCP efficacy is affected by cooling system operating conditions (i.e., pH, temperature, and relative supersaturation of scale forming salts). The ability of DCPs to extend the tolerance of phosphonates to Ca ions was investigated using the turbidity method.

Figure 7 illustrates the effect of acrylic co- and terpolymers (ASC and AST) to extend the limit of HEDP tolerance to calcium (Ca). As shown, a 10 mg/L addition of either AST or ASC provides a marked improvement in HEDP tolerance to Ca ion. For example, at 750 mg/L Ca, the HEDP tolerance values obtained in the presence of 10 mg/L of AST and ASC were 6.0 and 8.2 mg/L, respectively, compared to 4.2 obtained in the absence of polymer. Thus, an improvement of ~2x in HEDP tolerance is observed with AST. From a practical point of view, incorporating an appropriate DCP in a treatment program for a high stressed cooling water system would increase HEDP tolerance to Ca (i.e., would decrease the potential of Ca-HEDP precipitation in recirculating water containing high calcium ions) and thereby extend the operating range.

The influence of DCP composition in extending phosphonate tolerance was also investigated. Figure 8 presents performance data for several commercial DCPs that are used to prevent deposition in cooling water systems. The data in Figure 8 clearly show that DCP performance as a Ca-HEDP inhibitor strongly depends on polymer architecture. The data also demonstrate that polyacrylic acid (PAA), polymaleic acid (PMA), acrylic acid/maleic acid copolymer (AMC), and the multifunctional polymer (MFP) exhibit poor performance in preventing Ca-HEDP precipitation. For example, HEDP tolerance values obtained in the presence of 10 mg/L PAA, PMA, AMC, and MFP are 2, 4.0, 3.5, and 2.5, respectively, compared to 7.5 mg/L tolerance obtained in the absence of DCP. The observed decrease in HEDP tolerance may be attributed to poor polymer tolerance of calcium ion under similar experimental conditions. The poor polymer tolerance of PAA and PMA with Ca ions observed in the present investigation is consistent with our previously published report on polymer-Ca interactions.⁸ The excellent performance exhibited by AST in extending HEDP tolerance is also shown in Figure 8.

Calcium Carbonate Inhibition

The precipitation and deposition of calcium carbonate on heat exchanger surfaces poses serious operational problems especially under highly stressed conditions. Acid addition (typically sulfuric acid) is an effective mean to control calcium carbonate scale. However, the drawbacks of acid addition include (a) worker safety concerns, (b) potential corrosion problems, (c) the potential for calcium sulfate formation and scaling, and (d) failure of process control acid feed system.⁹ Furthermore, if the acid feed stops, an increase in cooling system pH can cause rapid CaCO_3 deposition. It is generally agreed that conventional phosphorus-based and polymeric CaCO_3 scale inhibitors are effective up to a maximum of 100x to 125x calcite saturation (equivalent to a LSI of +1.9 to 2.2).¹⁰ The conditions in this study were 180x and 223x calcium saturation (equivalent to LSI 2.76 and 2.89, respectively).

As discussed above phosphonate tolerance to calcium ions plays an important role in cooling water systems operating under stressed conditions. Good system performance demands that phosphonates remain in solution and be available to prevent precipitation and deposition. To understand the role of DCPs in preventing CaCO_3 precipitation under high stressed conditions by phosphonates, a series of precipitation experiments were carried out using the pH-stat method.⁴ Figure 9 shows the experimental set-up used to evaluate inhibitor performance.

Phosphonate Performance

Figure 10 presents typical NaOH uptake vs. time profiles for experiments that were conducted in CaCO_3 supersaturated solutions (calcite saturation @ 180x) containing 0, 5, 20, and 40 mg/L HEDP. As shown, in the absence of HEDP, precipitation starts immediately and the reaction is completed in ~10 minutes. Figure 10 also shows that the addition of HEDP to the CaCO_3 supersaturated solution causes two effects: (a) extension of the induction time and (b) reduction of the CaCO_3 precipitation rate. For example, induction times observed in the presence of 5, 10, 20, and 40 mg/L of HEDP are 1, 2, 8, and 18 minutes, respectively, compared with <1 minute obtained in the absence of HEDP. In addition, the initial rate of CaCO_3 precipitation decreases by a factor of five (5) as HEDP concentration is increased from 5 to 40 mg/L.

CaCO_3 inhibition data collected in the presence of varying concentrations of various phosphonates at two different water chemistries (i.e., 180x and 223x calcite saturation) are presented in Figures 11 and 12. Results obtained for both water chemistries (see Table 3) suggest that CaCO_3 inhibition increases as the phosphonate concentration is increased from 5 to 40 mg/L. The CaCO_3 inhibition increase is rapid up to 5 mg/L for both AMP and HEDP, then begins to level off, and finally reaching a plateau at ≥ 20 mg/L for both phosphonates. However, PBTC performance increases gradually as the concentration is increased from 5 to 40 mg/L of PBTC. It should be noted that 100% CaCO_3 inhibition was not obtained for either water chemistry A or B (see Table 3) even using up to 40 mg/L phosphonate concentrations. The data clearly indicate that the three phosphonates (i.e., AMP, HEDP, and PBTC) evaluated can not completely prevent the precipitation of CaCO_3 .

Based on the results collected under both water chemistries, CaCO₃ scale inhibition using 5 mg/L phosphonate has the following order of effectiveness:

$$\text{HEDP} \geq \text{AMP} \gg \text{PBTC}$$

Whereas, when increasing the phosphonate to 40 mg/L the performance ranking is as follows:

$$\begin{aligned} @ 180x \text{ calcite saturation: } & \text{PBTC} \gg \text{HEDP} \geq \text{AMP} \\ @ 223x \text{ calcite saturation: } & \text{PBTC} > \text{HEDP} \geq \text{AMP} \end{aligned}$$

Thus, it is clear from data presented in Figures 11 and 12 that PBTC performs better than both AMP and HEDP in waters containing high calcite saturations.

Polymer Performance

Figure 13 presents CaCO₃ inhibition data for several DCPs (of varying compositions, see Table 2) commonly used as components of cooling water treatment formulations. Figure 13 shows that PMA, AMC, and MFP exhibit poor performance as CaCO₃ inhibitors. The data in Figure 13 also indicate that ASC performs better than both AST and PAA. However, the Ca-HEDP inhibition data in Figure 8 indicate that both AST and ASC perform better than PAA; this may be due to the relatively lower calcium ion tolerance of PAA.⁸

DCP/Phosphonate Blends

It is evident from the data presented in Figures 11 to 13 that neither phosphonates nor DCP alone provide >80% CaCO₃ inhibition even at the lower stressed (i.e., 180x calcite saturation) conditions evaluated. Therefore, several DCP/phosphonate (3:1) blends were evaluated in experiments using water chemistry B (180x calcite saturation, see Table 3). The results are discussed below:

Figure 14 show the CaCO₃ inhibition for several DCP/HEDP (3:1) blends at 30 mg/L dosages and 180x calcite saturation and indicate the following order of effectiveness:

$$\text{AST/HEDP} > \text{MFP/HEDP} > \text{PAA/HEDP} > \text{PMA/HEDP} > \text{AMC/HEDP}$$

All of the DCP/HEDP blends provide better CaCO₃ inhibition than HEDP alone. AST/HEDP blend provides the best performance. The performances exhibited by PAA, PMA, AMC, and MFP are consistent with results presented in Figure 8 indicating that these DCPs provide poor Ca-HEDP inhibitory activity compared to AST. Although the data are not presented herein, a similar ranking was also observed for DCP/AMP blends (3:1) as CaCO₃ inhibitors. Furthermore, a DCP/HEDP/AMP (3:0.5:0.5) blend did not show any synergistic CaCO₃ inhibition compared to the DCP/HEDP (3:1) blend.

Figure 15 presents CaCO_3 inhibition data for three (3) DCP/PBTC (3:1) blends (incorporating high performance DCPs [i.e., MFP, AMC and AST] as components) at various dosages (10 to 40 mg/L) and 180x calcite saturation. The data clearly show that DCPs impact CaCO_3 scale inhibition performance in different ways. The AST/PBTC blend is the most effective.

CaCO_3 Crystal Morphology Characterization

Crystals formed during the CaCO_3 precipitation experiments were filtered using 0.22-micron filter paper and the samples were dried. Scanning electron microscopy (SEM) was used to study the crystal structures. CaCO_3 crystals in the absence (control) and presence (AST/PBTC blend) of inhibitor are presented in Figures 16 and 17, respectively. The CaCO_3 crystals (calcite and aragonite) shown in Figure 16 (control or absence of inhibitor) are <10 microns and have regular shapes (mostly cubical). Whereas the CaCO_3 crystals structures in Figure 17 (inhibited system) are fewer in number, most are >10 microns, and significantly distorted with spherical shapes. The inhibited (AST/PBTC) system CaCO_3 crystals are more readily dispersed and less likely to adhere to heat exchanger surfaces.

The CaCO_3 crystals discussed above were also examined by x-ray diffractometer (XRD). Figures 18 and 19 present the XRD profiles of CaCO_3 crystals grown in the absence (control) and in the presence (AST/PBTC blend) of inhibitor. As shown, the un-inhibited crystals (Figure 18) are a mixture of primarily calcite and some aragonite whereas the inhibited CaCO_3 crystals (Figure 19) are all calcite.

Summary

The purpose of this work was to identify water chemistries where the potential exists for calcium-phosphonate salts precipitation and determine the feasibility of using deposit control polymers to prevent the deposition of unwanted salts on heat exchangers. In this study, a sulfonic acid containing terpolymer (AST) was identified as an effective inhibitor for calcium phosphonates and CaCO_3 especially when blended with PBTC for highly scaling waters (LSI 2.76 to 2.89). Finally, the ability of phosphonate, DCP, and phosphonate/polymer in changing crystal morphology of CaCO_3 was also explored.

The conclusions drawn from this work are as follows:

1. Phosphonates (e.g., AMP, HEDP, and PBTC) are effective components in cooling water treatment programs. However, these phosphonates form insoluble salts with calcium ions under typical cooling water conditions. PBTC–Ca salt is more soluble than Ca-HEDP and Ca-AMP salts.

2. The potential for precipitation of Ca-phosphonate salt increases with increasing pH, temperature, and calcium ion concentrations.
3. The tolerance of phosphonate with calcium ion can be extended by incorporating an effective dispersant or DCP (i.e., AST or sulfonated terpolymer) as a component of high performance water treatment programs.
4. AMP and HEDP do not perform effectively in preventing CaCO₃ scaling under the water chemistries evaluated (LSI 2.76 to 2.89 and 180x to 223x calcite saturation, respectively). PBTC exhibits better inhibitory activity than AMP and HEDP especially in moderately stressed conditions (i.e., 180x calcite saturation).
5. The performance of phosphonates as CaCO₃ inhibitors can be improved by the incorporation of high performance DCPs into the cooling water treatment programs.
6. DCP architecture plays an important role in preventing CaCO₃ scaling. The results presented in this study indicate that a sulfonated terpolymer (AST) compare to homo- and co-polymers offers an excellent tool for preventing the precipitation and deposition of both calcium phosphonates and CaCO₃ scales on heat exchanger surfaces.
7. An AST/PBTC blend provides excellent CaCO₃ inhibition under high stressed cooling water conditions. Compared to the control, the AST/PTBC inhibited system CaCO₃ crystals are fewer in number, larger (approximately twice as large), and significantly distorted with spherical shapes. The inhibited system crystals are by more readily dispersed and less likely to adhere to heat exchanger surfaces. The un-inhibited crystals are a mixture of primarily calcite and some aragonite whereas the inhibited CaCO₃ crystals are all calcite

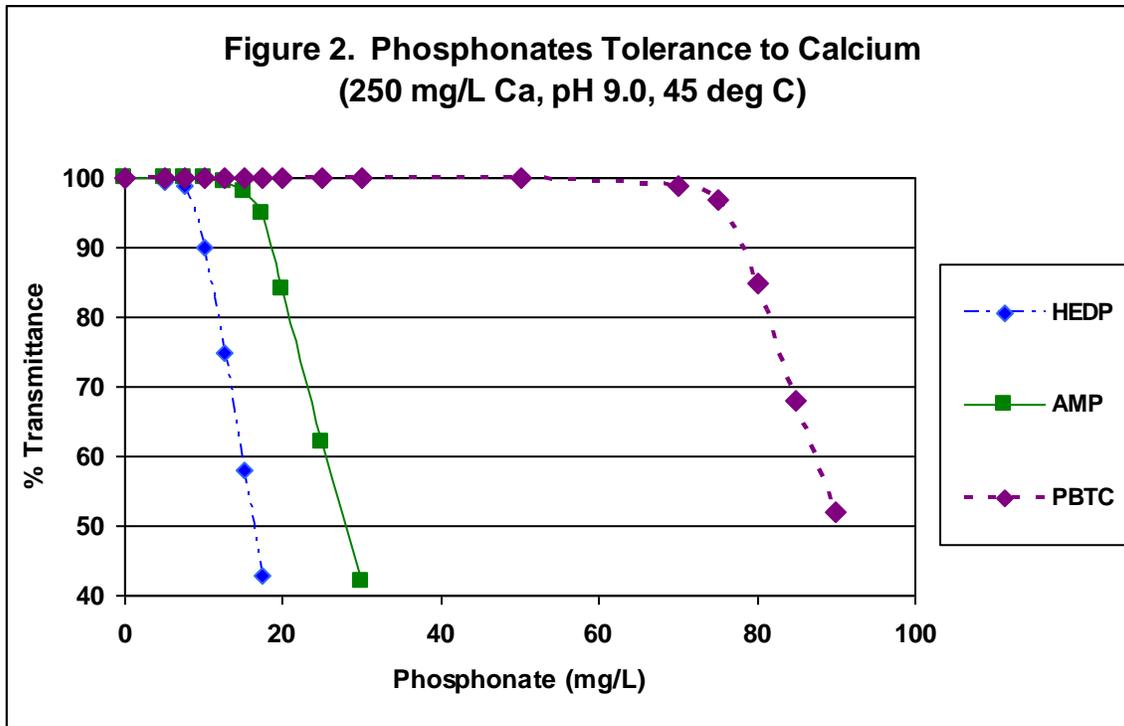
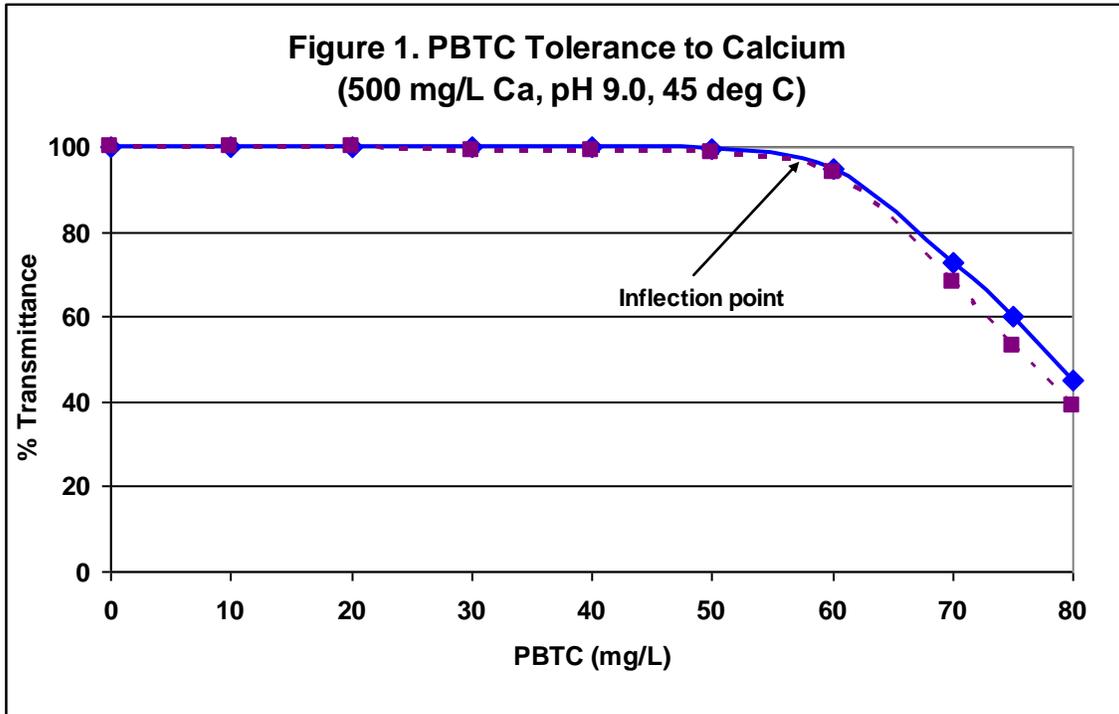
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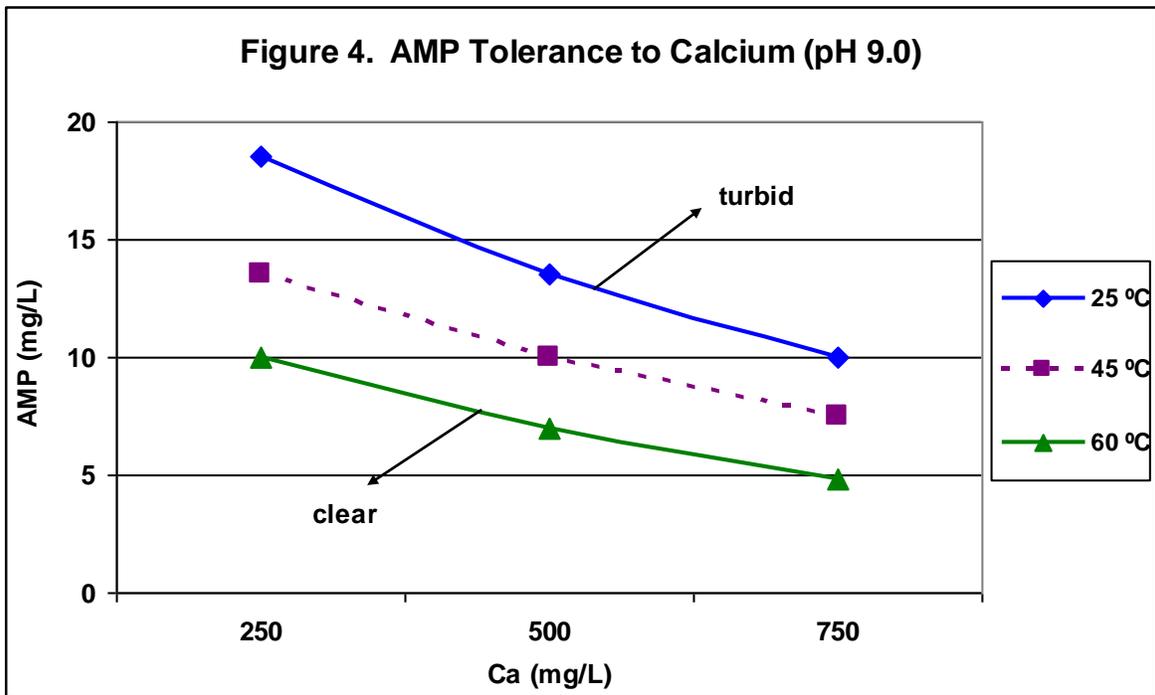
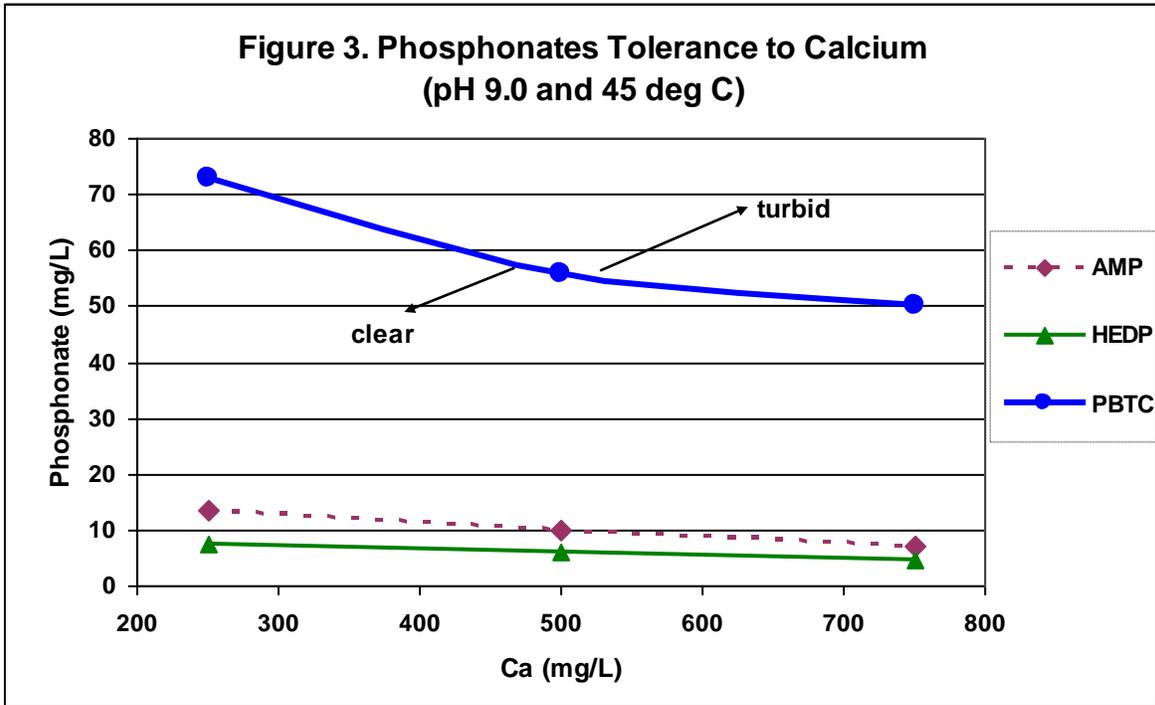


Figure 5. HEDP Tolerance to Calcium (pH 9.0)

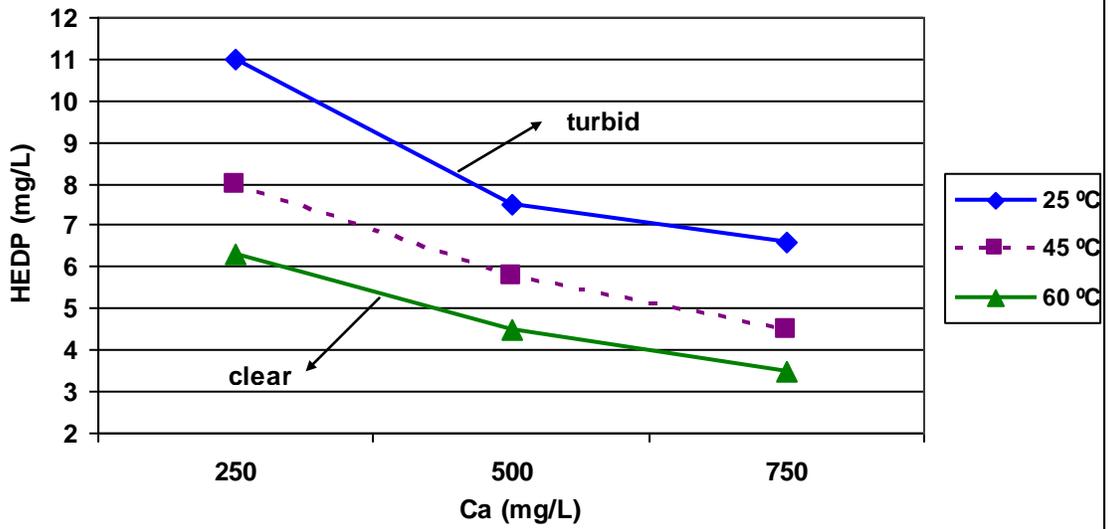
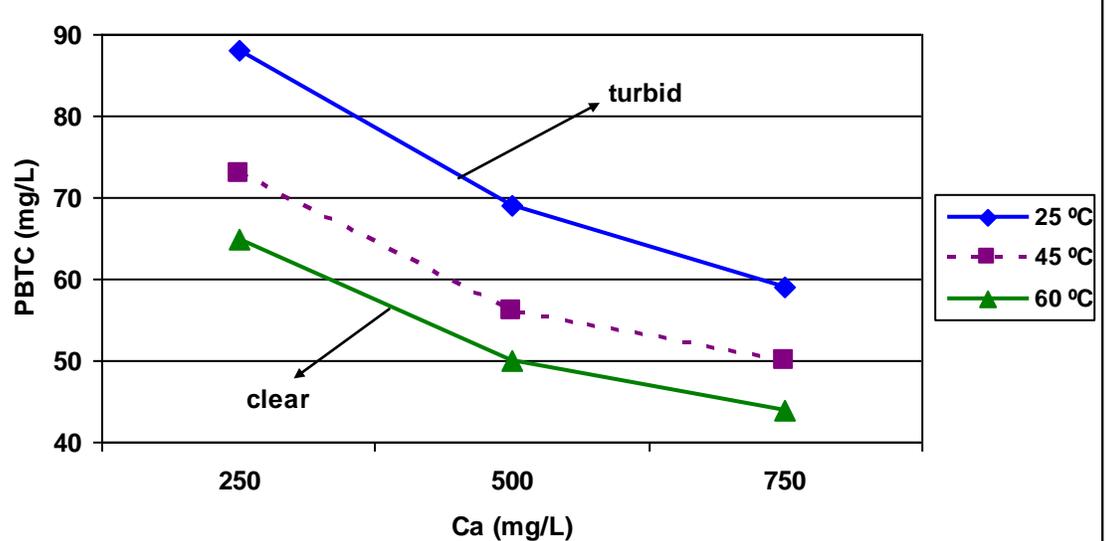
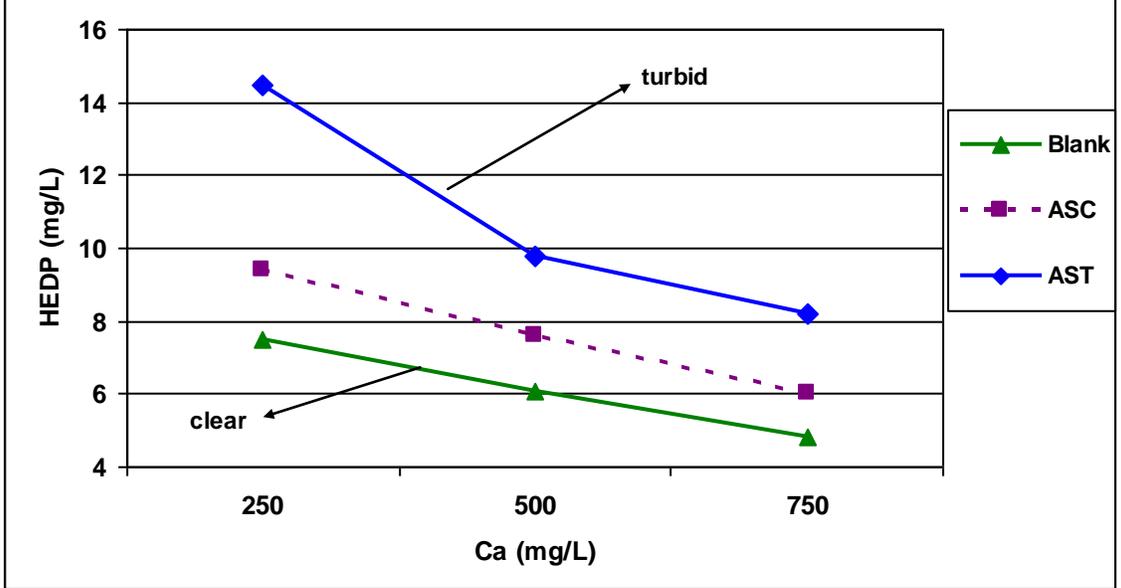


Figure 6. PBTC Tolerance to Calcium (pH 9.0)



**Figure 7. Effect of Polymers on HEDP Tolerance to Ca
(10 mg/L polymer, pH 9.0, 45 deg C)**



**Figure 8. Ca-HEDP Inhibition by Polymers
(250 mg/L Ca, 100 mg/L polymer, pH 9.0, 45 deg C)**

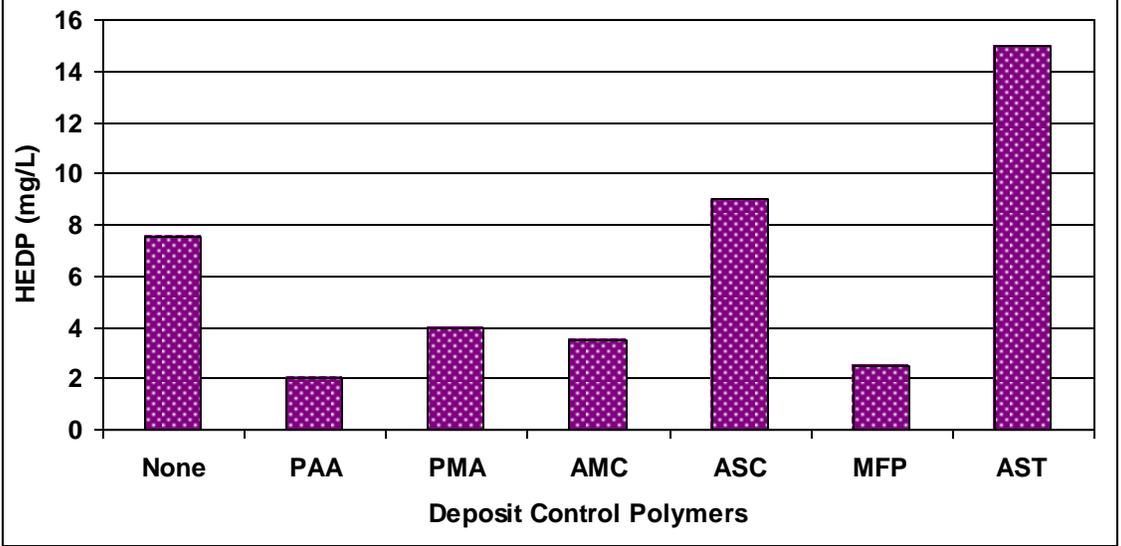
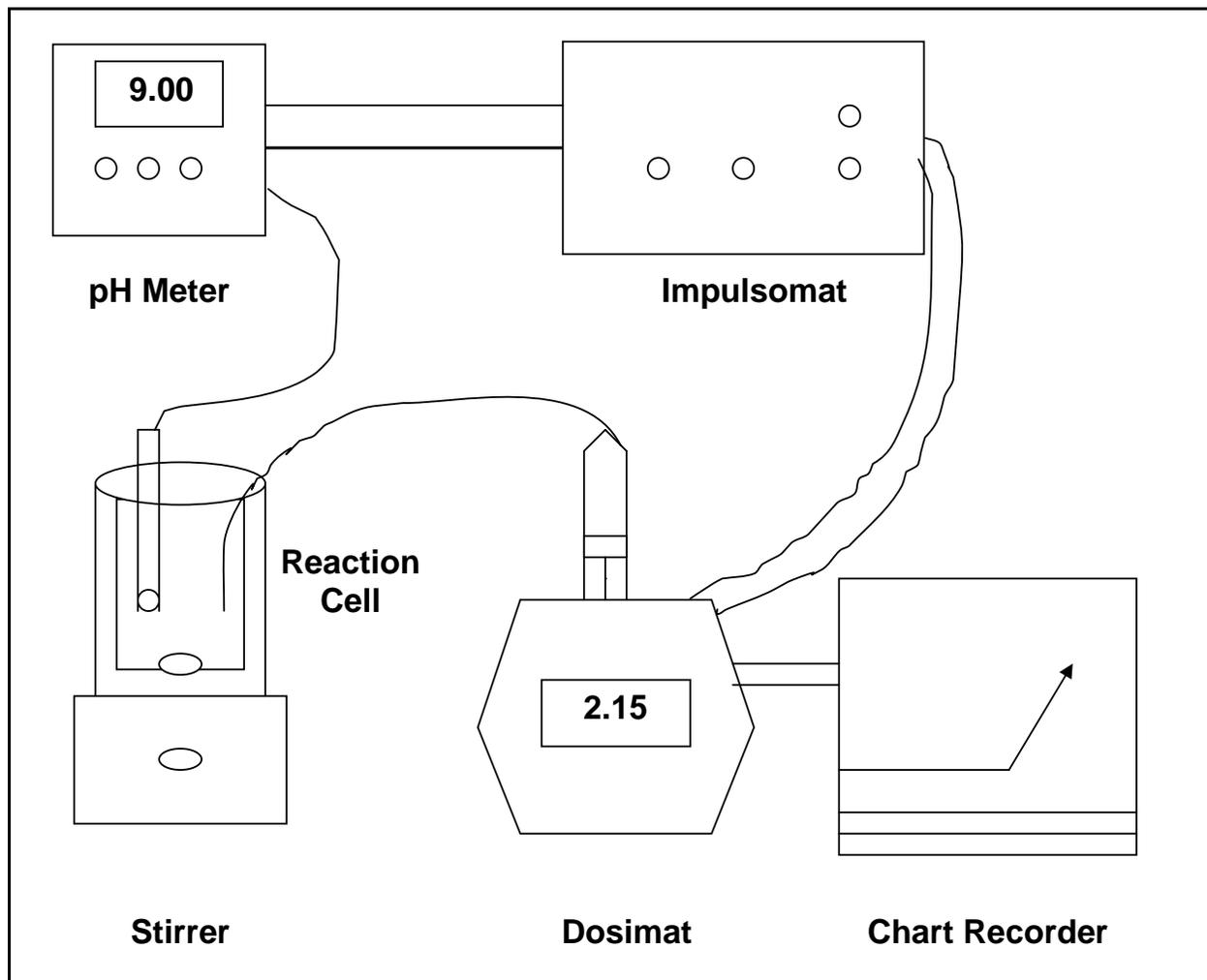
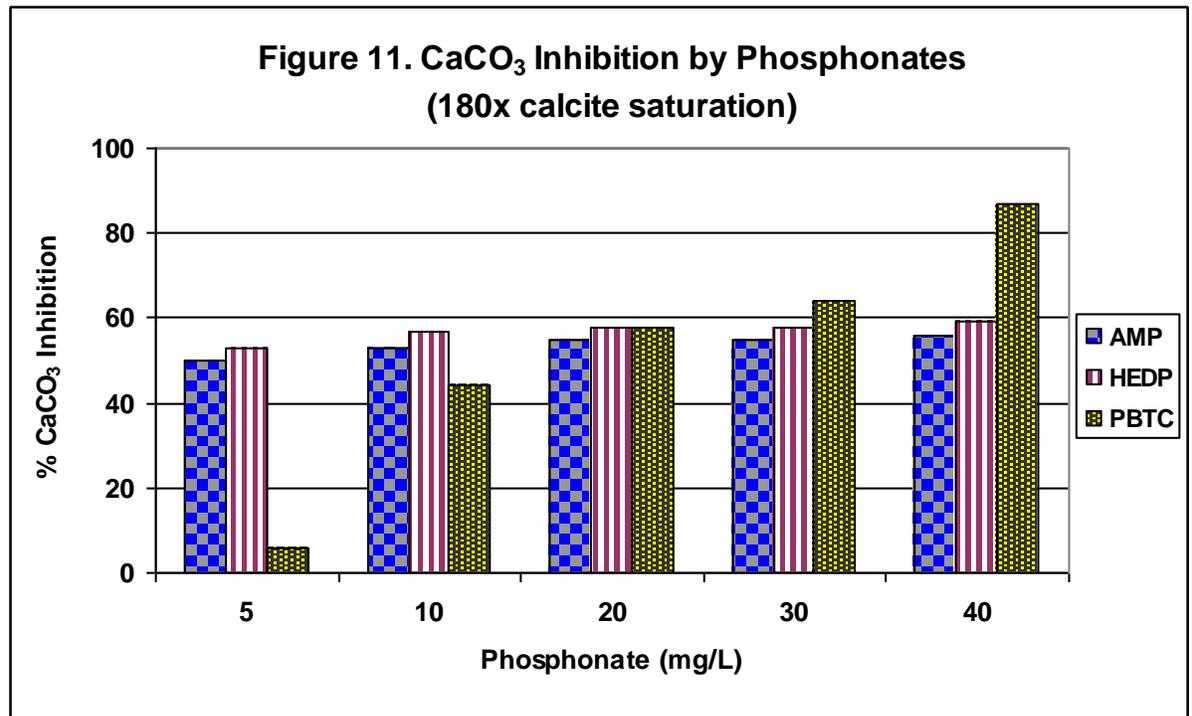
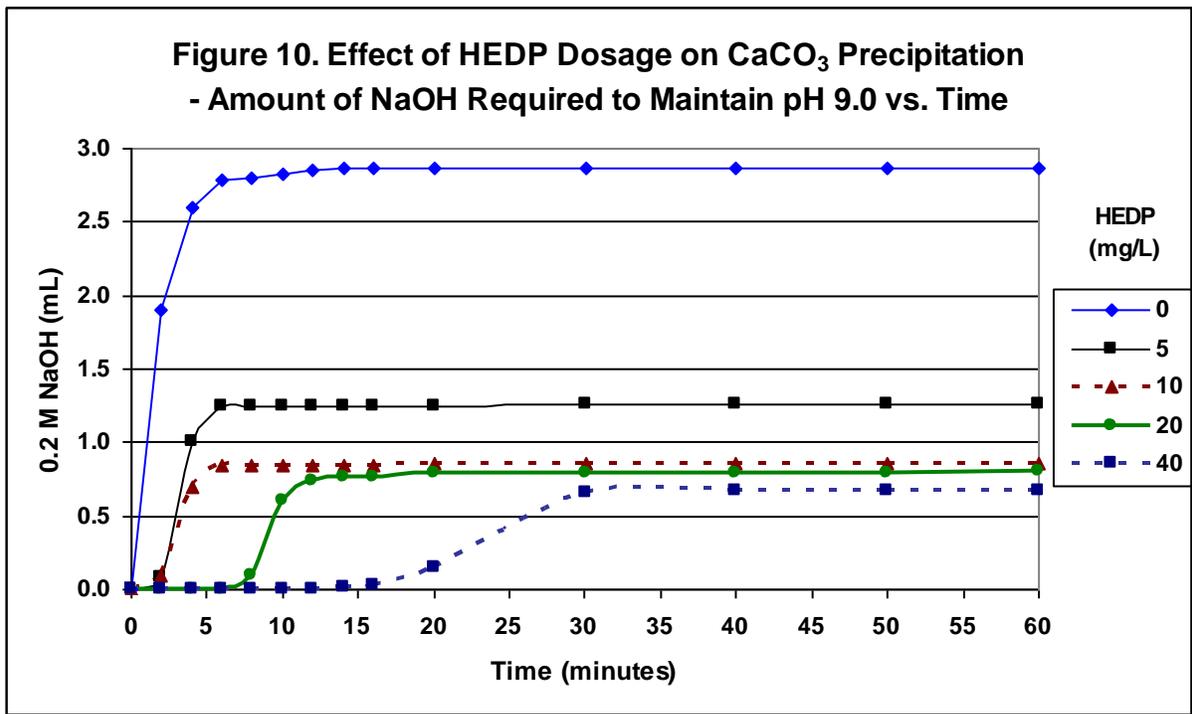
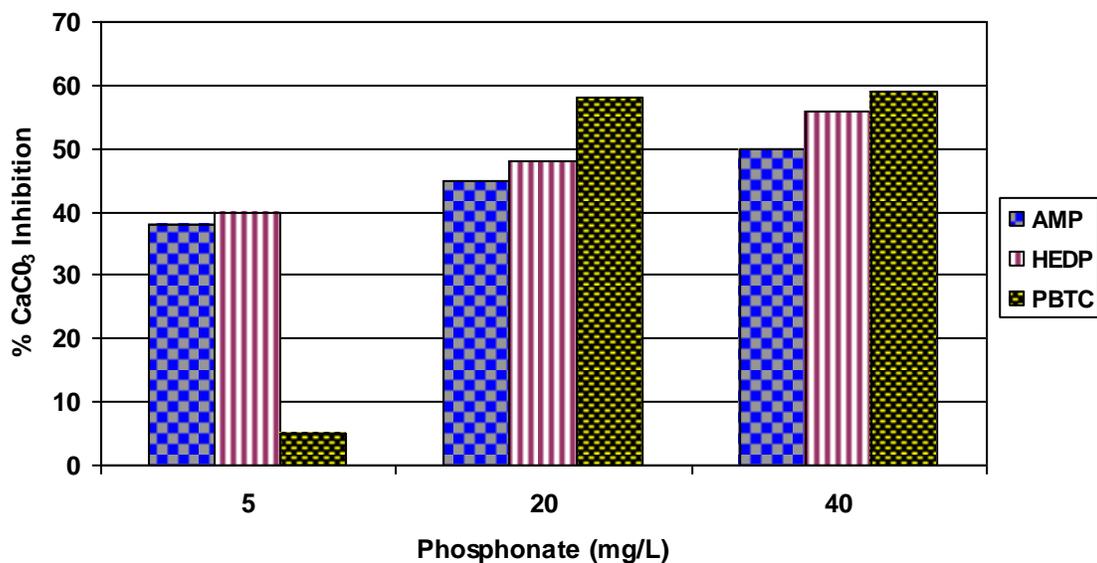


Figure 9
Experimental Set-Up for Calcium Carbonate

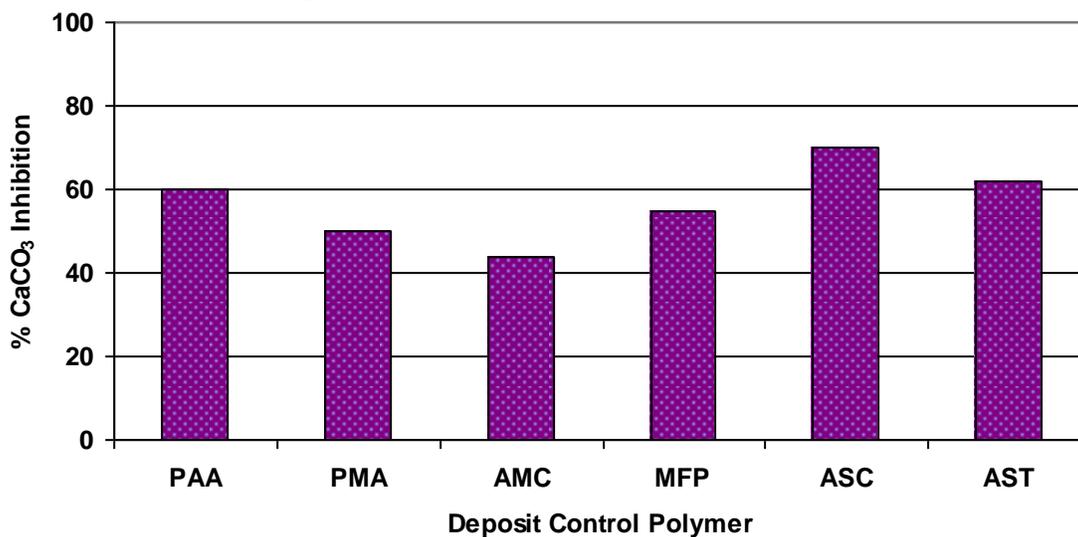




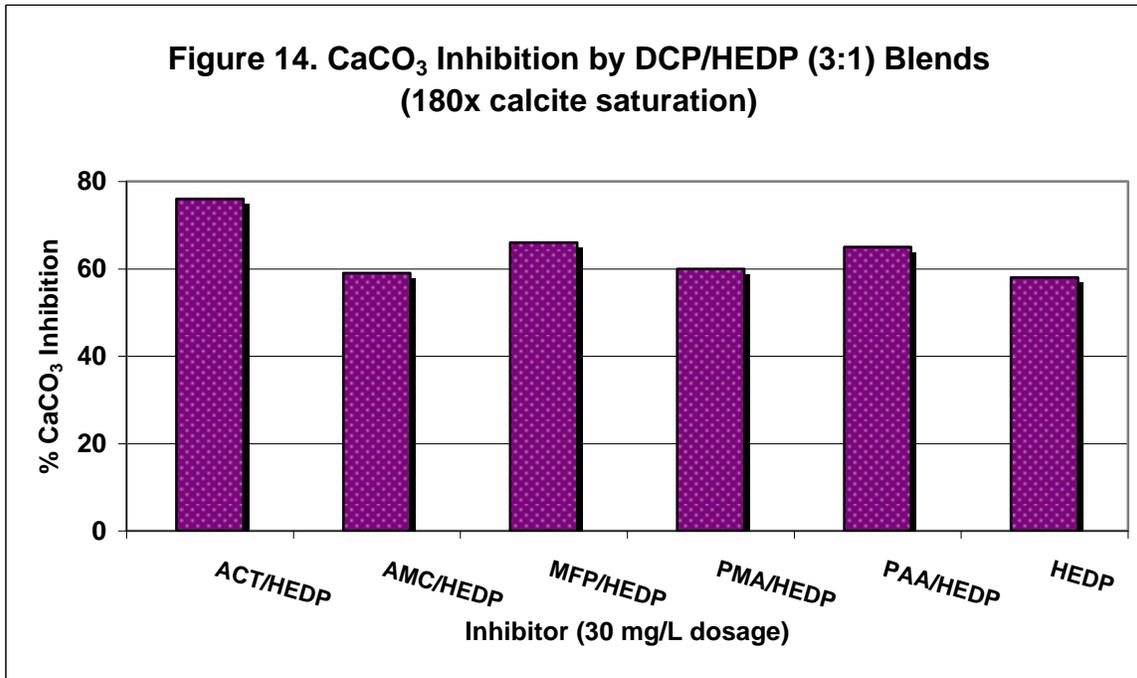
**Figure 12. CaCO₃ Inhibition by Phosphonates
(223x calcite saturation)**



**Figure 13. CaCO₃ Inhibition by Polymers
(30 mg/L polymer, 180x calcite saturation)**



**Figure 14. CaCO₃ Inhibition by DCP/HEDP (3:1) Blends
(180x calcite saturation)**



**Figure 15. CaCO₃ by DCP/PBTC (3:1) Blends
(180x Calcite Saturation)**

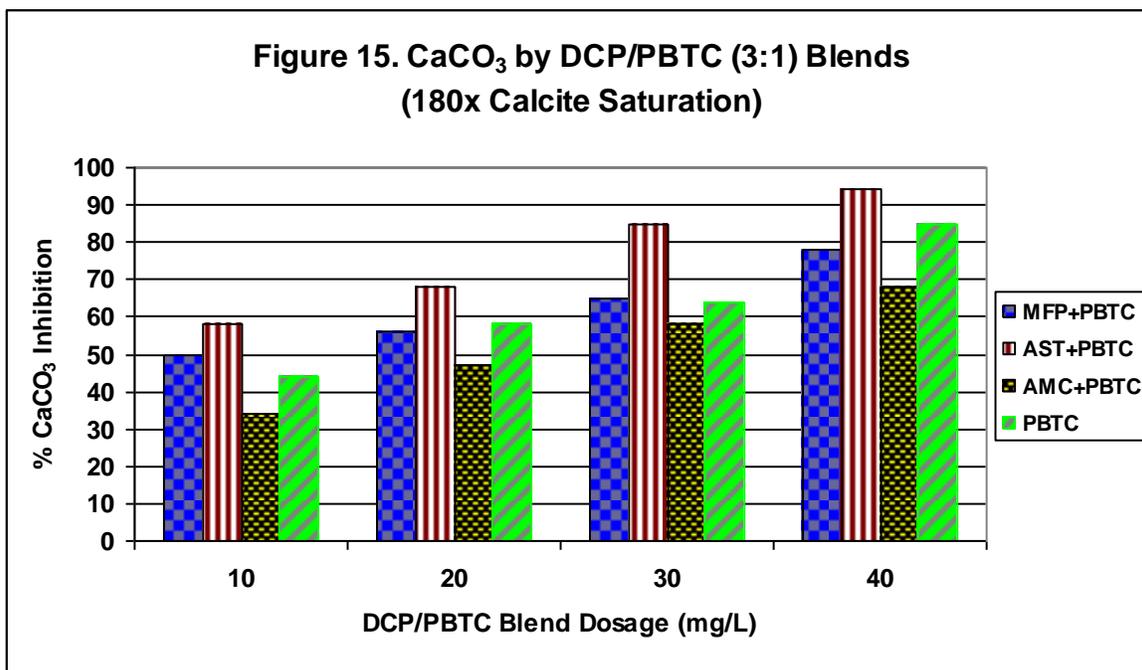


Figure 16. SEM Picture of CaCO₃ Crystals Grown in the Absence of Inhibitor

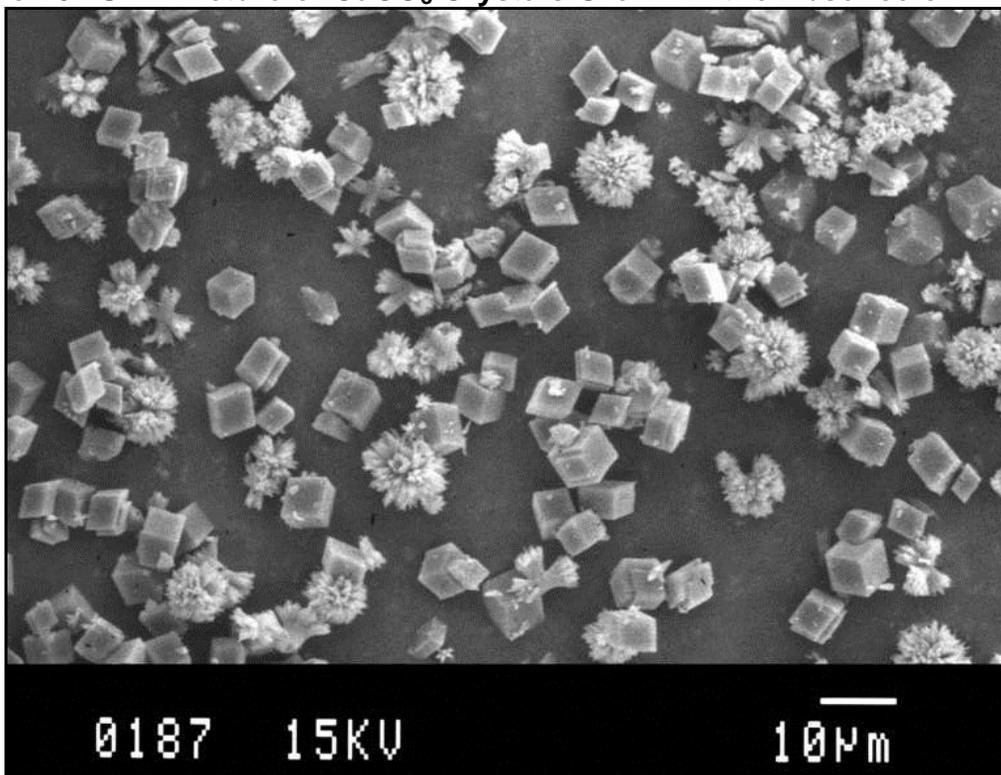


Figure 17. SEM Picture of CaCO₃ Crystals Grown in the Presence of the AST/PBTC Blend

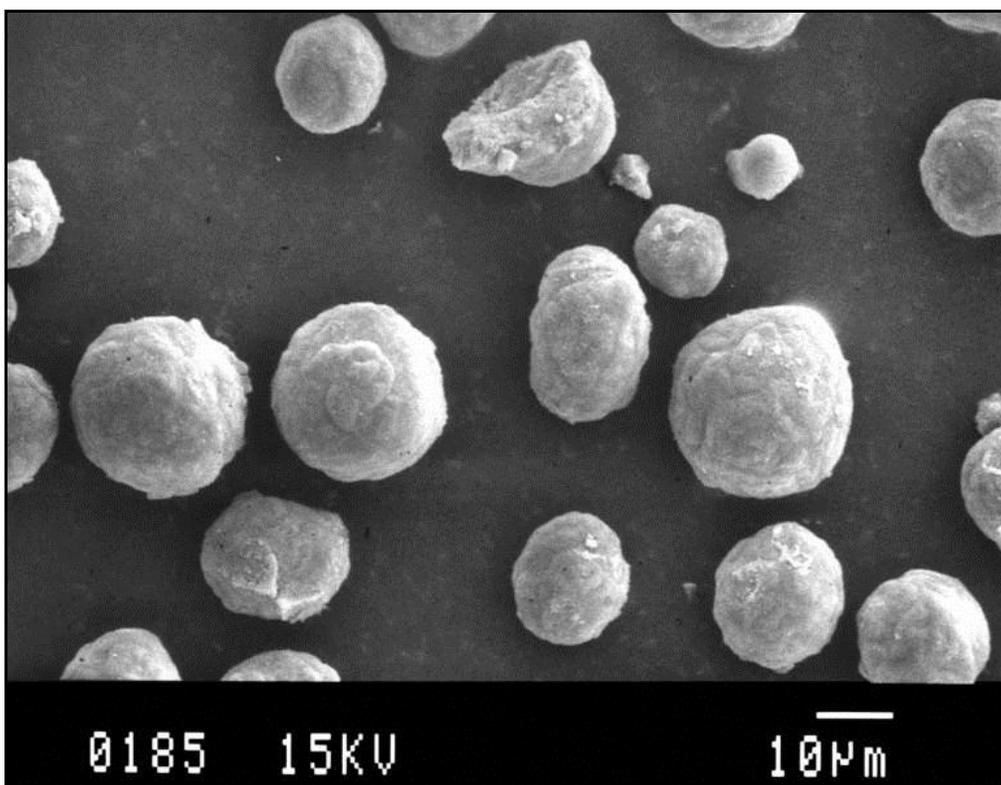


Figure 18. XRD Profile of CaCO₃ Crystals Grown in the Absence of Inhibitor

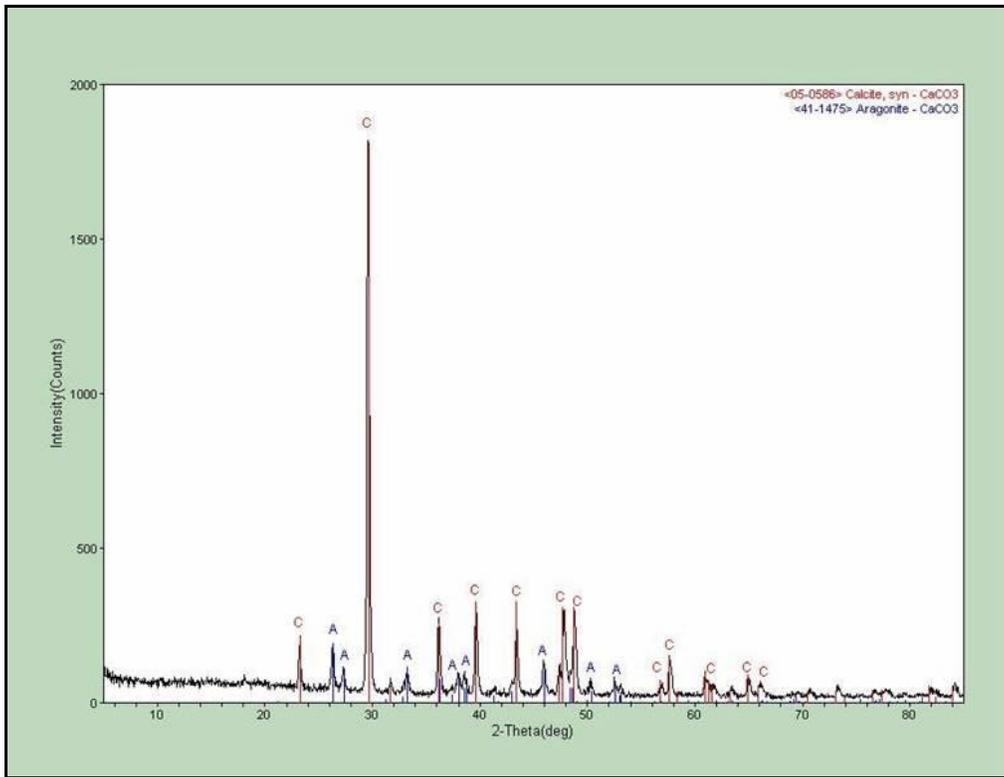
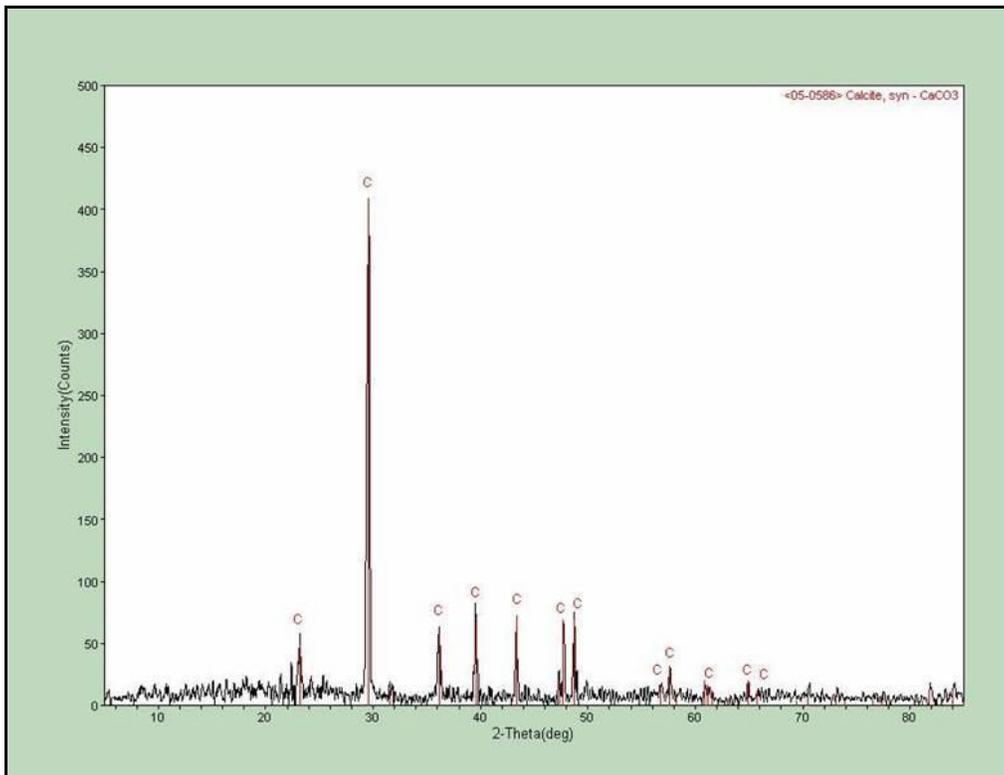


Figure 19. XRD Profile of CaCO₃ Crystals Grown in the Presence of the AST/PBTC Blend



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