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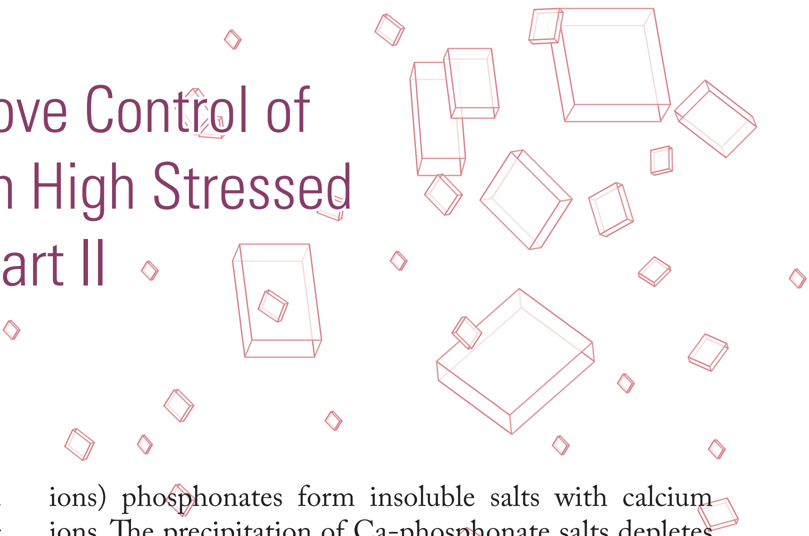

The Use of Polymers to Improve Control of Calcium Carbonate Scaling in High Stressed Cooling Water Systems*—Part II

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Introduction

Cooling water chemical treatment programs are designed to cost effectively maintain cooling system equipment (i.e., heat exchangers, pumps, pipes, etc.) and minimize water consumption for each industrial water system and its feedwater. Water technologists design cooling water treatment programs that incorporate a variety of components or additives to control corrosion, minimize scale formation, and prevent microbiological fouling. Preventing calcium carbonate deposition, particularly in high stress cooling water systems, is almost always a concern. The most frequently used means for minimizing the precipitation of calcium carbonate is by incorporating phosphonates that function as scale inhibitors at "sub-stoichiometric" dosages. The phosphonates adsorb onto crystal growth sites of sub-microscopic crystallites thereby interfering with crystal growth and altering the crystal morphology.

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

Chemical Name	Acronym	MW
Aminotris (methylenephosphonic acid)	AMP	299
1-Hydroxyethylidine 1,1-diphosphonic acid	HEDP	206
2-Phosphonobutane 1,2,4-tricarboxylic acid	PBTC	270

The use of deposit control polymers (DCPs) as dispersants in industrial applications is well known to the water technologist. It is generally agreed that polymers, when present at low concentrations, not only inhibit the precipitation of scale-forming salts (i.e., calcium carbonate, calcium sulfate, calcium phosphate, barium sulfate)[1-3], but are also effective dispersants for suspended matter. In a recent article[4], it was reported that under harsh conditions (i.e., high pH, high temperature, high hardness ions) phosphonates form insoluble salts with calcium ions. The precipitation of Ca-phosphonate salts depletes the solution concentration of phosphonates and thereby also increases the potential of calcium carbonate scale formation.

The present study addresses the role of phosphonates in preventing the precipitation of calcium carbonate, especially under stressed cooling water conditions. In addition, experiments were also carried out to investigate the performance of a variety of commercially available DCP and DCP/phosphonate blends as calcium carbonate ($CaCO_3$) inhibitors.

Experimental

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. The DCPs and the water chemistries used in the present investigation are summarized in Tables 2, and 3, respectively.

Table 2 - Polymers Evaluated

Polymer	Acronym	MW
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^{2+})	210 mg/L	250 mg/L
Magnesium (as Mg^{2+})	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 $CaCO_3$ precipitation experiments were performed 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 $CaCO_3$ supersaturation conditions used in this study were determined by using WaterCycle® (a proprietary computer software program supplied by French Creek Software) 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.

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 $CaCO_3$ 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 $CaCO_3$ solids collected on the membrane filters were analyzed by x-ray diffraction and scanning electron microscopy.

DCP, phosphonate, and DCP/phosphonate blend efficacy as $CaCO_3$ 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:

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

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

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

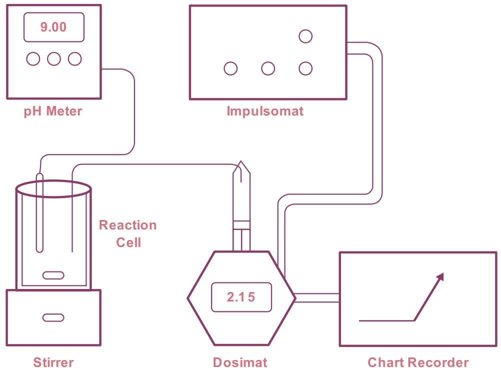
Because $CaCO_3$ precipitation reaction in the absence of inhibitor is essentially completed in less than 10 minutes, a 1-hr precipitation was chosen as the basis for comparing results. It should be noted that the use of a different precipitation period would lead to a change in absolute inhibition values. However, changing the precipitation time should not affect the findings and conclusions regarding the performance of phosphonates and phosphonate/polymer blends as $CaCO_3$ inhibitors.

Results and Discussion

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).[5] The conditions in this study were 180x and 223x calcium saturation (equivalent to LSI 2.76 and 2.89, respectively).

As discussed in a recent article[4], 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 polymers in preventing $CaCO_3$ precipitation under high stressed conditions by phosphonates, a series of precipitation experiments were carried out using the pH stat method as described in a previous paper.[6] Figure 1 shows the experimental set-up used to evaluate inhibitor performance.

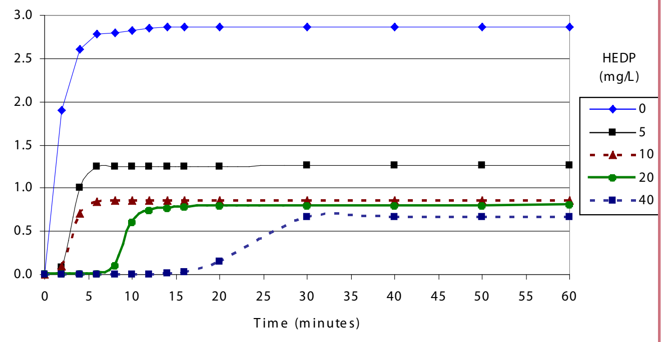
Figure 1. Experimental Set-Up for Calcium Carbonate



Phosphonate Performance

Figure 2 presents typical NaOH uptake vs. time profiles for experiments that were conducted in $CaCO_3$ supersaturated solutions (calcite saturation at 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 approximately 10 minutes. Figure 2 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 less than 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.

Figure 2. Effect of HEDP Dosage on $CaCO_3$ Precipitation - Amount of NaOH Required to Maintain pH 9.0 vs. Time



$CaCO_3$ 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 3 and 4. Results obtained for both water chemistries as shown in 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 reaches a plateau at greater than 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 cannot completely prevent the precipitation of $CaCO_3$.

Figure 3. $CaCO_3$ Inhibition by Phosphonates (180x calcite saturation)

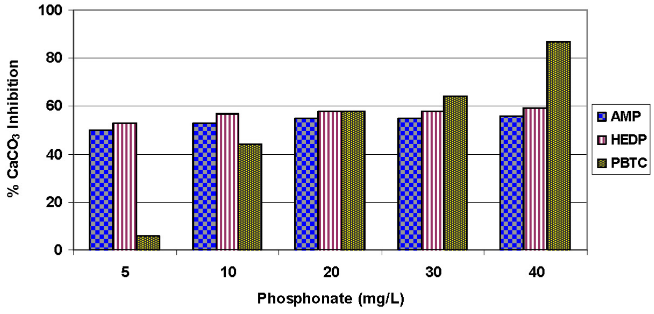
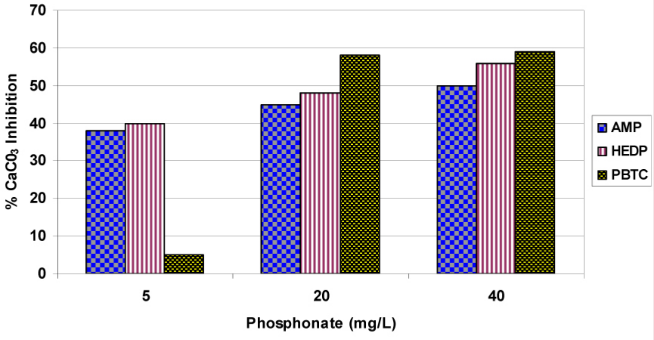


Figure 4. $CaCO_3$ Inhibition by Phosphonates (223x calcite saturation)



Based on the results collected under both water chemistries, $CaCO_3$ scale inhibition using 5 mg/L phosphonate has the following order of effectiveness:

HEDP ≥ AMP >> PBTC

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

At 180x calcite saturation: PBTC >> HEDP ≥ AMP

At 223x calcite saturation: PBTC > HEDP ≥ AMP

Thus, it is clear from data presented in Figures 3 and 4 that PBTC performs better than both AMP and HEDP in waters containing high calcite saturations.

DCP Performance

Figure 5 presents $CaCO_3$ inhibition data for several commonly used polymers as shown in Table 2 as components of cooling water treatment formulations. Figure 5 shows that PMA, AMC, and MFP exhibit poor performance as $CaCO_3$ inhibitors. The data in Figure 5 also indicate that ASC performs better than both AST and PAA. However, the Ca-HEDP inhibition data reported in our recent article[4] indicate that both AST and ASC perform better than PAA; this may be due to the relatively lower calcium ion tolerance of PAA.[7]

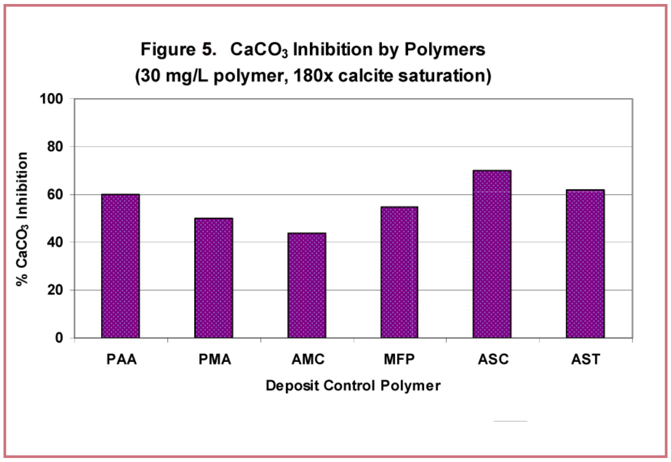


Figure 5. $CaCO_3$ Inhibition by Polymers (30 mg/L polymer, 180x calcite saturation)

DCP/Phosphonate Blend Performance

It is evident from the data presented in Figures 3 and 5 that neither phosphonates nor polymers alone provide greater than 80% $CaCO_3$ inhibition even at the lower stressed (i.e., 180x calcite saturation) conditions evaluated. Therefore, several polymer/phosphonate (3:1) blends were evaluated in experiments using water chemistry A (180x calcite saturation, see Figure 3). The results are discussed below:

DCP/HEDP Blends

Figure 6 shows the $CaCO_3$ inhibition for several DCP/HEDP (3:1) blends at 30 mg/L dosages and 180x calcite saturation and indicates the following order of effectiveness:

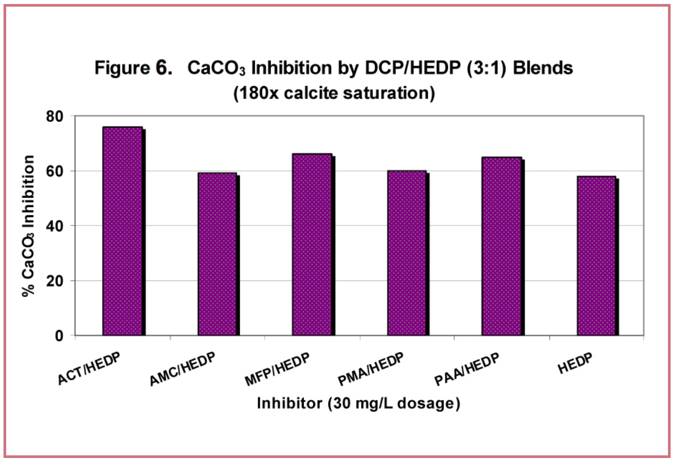


Figure 6. $CaCO_3$ Inhibition by DCP/HEDP (3:1) Blends (180x calcite saturation)

AST/HEDP > MFP/HEDP > PAA/HEDP > PMA/HEDP > AMC/HEDP

All of the DCP/HEDP blends provide better $CaCO_3$ 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 our earlier article^4, 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 $CaCO_3$ inhibitors. Furthermore, a DCP/HEDP/AMP (3:0.5:0.5) blend did not show any synergistic $CaCO_3$ inhibition compared to the polymer/HEDP (3:1) blend

B. DCP/PBTC

Figure 7 presents $CaCO_3$ inhibition data for three (3) DCP/PBTC (3:1) blends (incorporating high performance polymers [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.

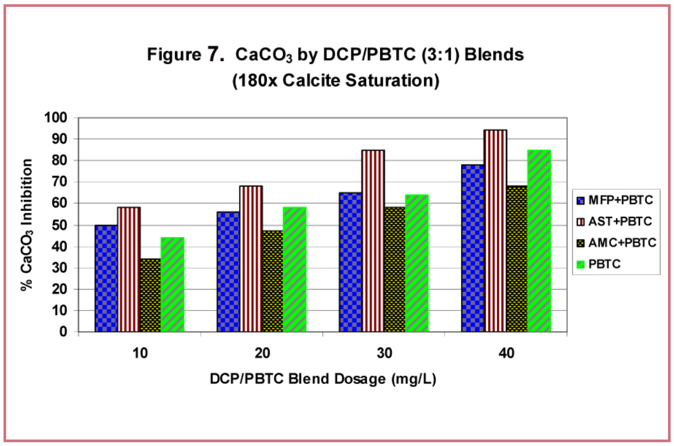


Figure 7. $CaCO_3$ by DCP/PBTC (3:1) Blends (180x Calcite Saturation)

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 8 and 9, respectively. The $CaCO_3$ crystals (calcite and aragonite) shown in Figure 8 (control or absence of inhibitor) are less than 10 microns and have regular shapes (mostly cubical). Whereas the $CaCO_3$ crystals structures in Figure 9 (inhibited system) are fewer in number, most are greater than 10 microns, and significantly distorted with spherical shapes. The inhibited (AST/PTBC) system $CaCO_3$ crystals are more readily dispersed and less likely to adhere to heat exchanger surfaces.

Figure 8. SEM Picture of $CaCO_3$ Crystals Grown in the Absence of Inhibitor

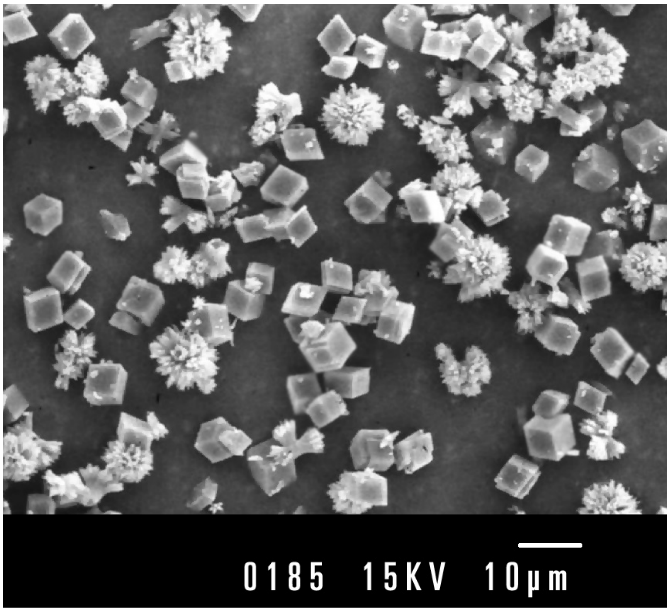
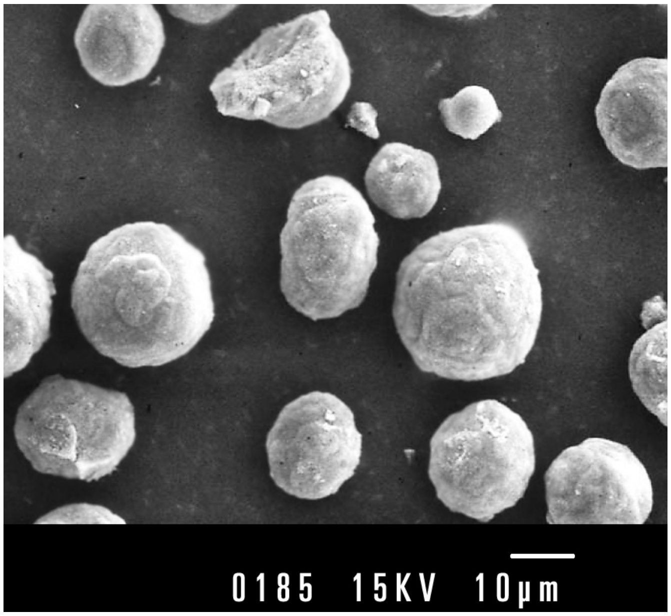


Figure 9. SEM Picture of $CaCO_3$ Crystals Grown in the Presence of the AST/PBTC Blend



The $CaCO_3$ crystals discussed above were also examined by x-ray diffractometer (XRD). Figures 10 and 11 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 shown in Figure 10 are a mixture of primarily calcite and some aragonite whereas the inhibited $CaCO_3$ crystals shown in Figure 11 are all calcite.

Figure 10. XRD Profile of $CaCO_3$ Crystals Grown in the Absence of Inhibitor

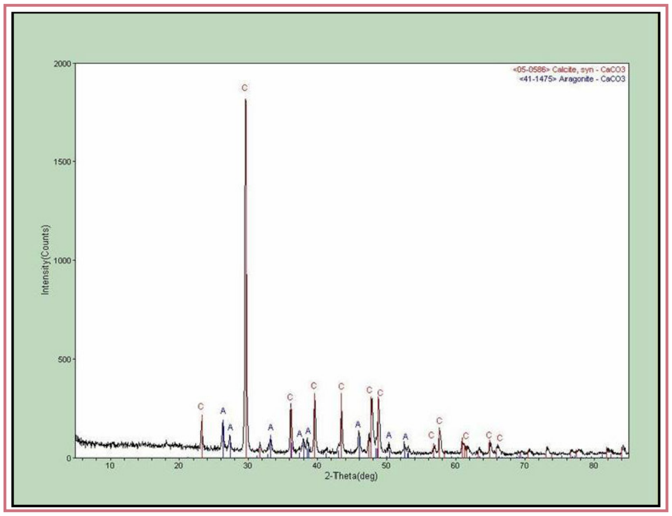
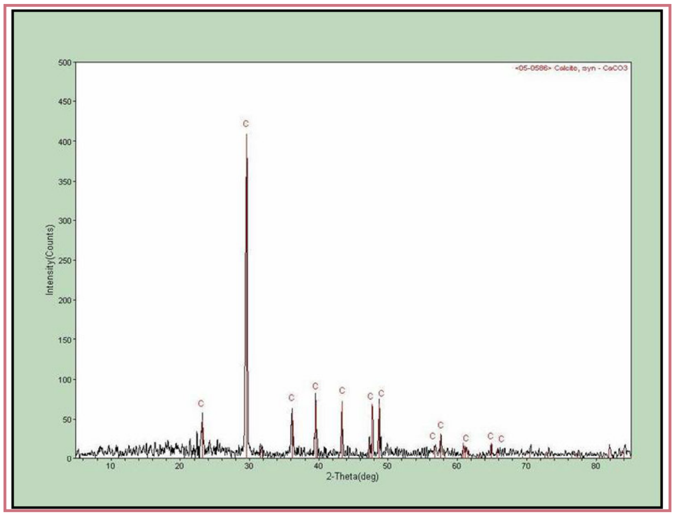


Figure 11. XRD Profile of $CaCO_3$ Crystals Grown in the Presence of the AST/PBTC Blend



Summary

This study showed that a terpolymer (AST) containing two sulfonated monomers is as an effective inhibitor for $CaCO_3$ especially when blended with PBTC for highly scaling waters (LSI 2.76 to 2.89). This work also explored the ability of phosphonate, DCP, and phosphonate/polymer to change the crystal morphology of $CaCO_3$.

The conclusions drawn from this work are as follows:

1. AMP and HEDP do not perform effectively in preventing $CaCO_3$ scaling under the water chemistries evaluated (LSI 2.76 to 2.89 and 180x to 223x calcite saturation, respectively). PBTC exhibits better inhibi-

tory activity than AMP and HEDP especially in moderately stressed conditions (i.e., 180x calcite saturation).

2. The performance of phosphonates as $CaCO_3$ inhibitors can be improved by the incorporation of high performance polymers into the cooling water treatment programs.
3. Polymers architecture plays an important role in preventing $CaCO_3$ scaling. It has been found 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 $CaCO_3$ scales on heat exchanger surfaces.
4. An AST/PBTC blend provides excellent $CaCO_3$ inhibition under high stressed cooling water conditions. Compared to the control, the AST/PTBC inhibited system $CaCO_3$ crystals are fewer in number, larger (approximately twice as large), and significantly distorted with spherical shapes. The inhibited system crystals are 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 $CaCO_3$ crystals are all calcite. 💧

** This article is based on the technical paper entitled "The Use of Polymers to Improve Control of Calcium Phosphonate and Calcium Carbonate in High Stressed Cooling Water Systems," that was presented at the Association of Water Technologies, Inc., 2004 Annual Convention in Nashville, TN.*

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