A Brief Review of Deposit Control Polymers in Industrial Water Treatment

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Introduction

The build-up of deposits in boilers and cooling towers is a persistent problem that can lead to decreased efficiency, overheating, unscheduled shutdown time, and costly maintenance. As steam is generated by a boiler or water evaporating from a cooling tower, dissolved minerals are left behind. More water is added to make up for the evaporation loss, resulting in more deposition of minerals (i.e. CaCO₃, CaSO₄, Ca₃(PO₄)₂, etc.), corrosion products (i.e. Fe₂O₃, etc.), particulate matter, and microbiological mass. These deposits accumulate in low circulation areas, becoming immobilized and building up on heat exchanger surfaces. Once a scale layer is formed, it will continue to get thicker unless treated, eventually blocking flow and decreasing productivity. Therefore, an effective water treatment program must control scale, corrosion, particulates, and biological growth.¹⁻³

Scale formation is prevented using compounds that adsorb onto crystal growth sites and inhibit crystal growth and/or alter the crystal morphology. Polyphosphates, phosphonates and deposit control polymers (DCPs) are commonly used components of industrial water treatment programs. Phosphonates, like those shown in Table 1, are used to sequester metal ions such as copper, manganese, iron, and zinc, and prevent crystal growth and exhibit some activity in dispersing suspended matter. DCPs function as scale inhibitors, crystal modifiers, and dispersants. Interaction with the DCPs modifies the precipitated solids and keeps them in suspension, inhibiting their ability to adhere to equipment surfaces.²⁻⁶

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Diethylenetriamine pentamethylene phosphonic acid</td>
<td>DETA</td>
</tr>
<tr>
<td>Aminotris(methylene phosphonic acid)</td>
<td>ATMP</td>
</tr>
<tr>
<td>1-Hydroxyethylidine 1,1-disphosphonic acid</td>
<td>HEDP</td>
</tr>
<tr>
<td>2-Phosphonobutane 1,2,4-tricarboxylic acid</td>
<td>PBTC</td>
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Water treatment formulations can incorporate one or multiple methods of scale inhibition, relying on synergistic components to effectively control corrosion, scaling, and microbiological fouling in the industrial water system. Several factors need to be considered when developing a treatment plan, including: component performance, cost, and stability, operating costs of using multiple methods, and field experience.

There are multiple types of experimental methods for investigating scale formation. Most of the results reviewed in this paper were acquired through static bottle testing (SBT). SBT keeps water at a consistent temperature, without agitation, for several hours. The initial and final soluble ion content is determined through various spectroscopic methods and percent inhibition determined by comparing samples with and without inhibitor.⁷ Two other experimental methods involve dynamic scale testing. Under dynamic conditions, the water is pumped through metal tubing to simulate the agitated conditions of a boiler or cooling tower. The dynamic scale testing rig (DSTR)
is designed to evaluate corrosion and scale control by controlling water temperature and pH as it flows through and around various metal alloys. Inhibitor performance is evaluated by spectroscopic methods, calculating corrosion rates, and visually inspecting for scale formation. The dynamic scale loop (DSL), pumps water through a temperature and pressure regulated metal capillary sample loop and monitors the difference in pressure before and after passing through the loop. As scale builds, pressure increases.

Why polymers?

Phosphorous based compounds, like those shown in Table 1, are broadly effective in water treatment programs to control mild steel corrosion and inhibit calcium carbonate (CaCO₃) scale. They are key components in all-organic industrial water treatment programs, but under high stress conditions (i.e. high pH, temperature, etc.) they can react stoichiometrically with Ca²⁺ creating a Ca-phosphonate salt that may precipitate out of solution. The tolerance of phosphonate to calcium ions is the minimum concentration of phosphonate at a given pH, temperature, and ion concentration necessary to cause precipitation of phosphonate. The calcium tolerance of three phosphonates from Table 1 per 250 mg/L calcium ion at 45°C are as follows:

**PBTC (73 mg/L) > ATMP (13.5 mg/L) > HEDP (7.5 mg/L)**

Ca-phosphonate salt formation alone can cause problems, but the problem is exacerbated as depletion of the phosphonate inhibitor allows CaCO₃ scale to form. Continuous and effective system performance requires a treatment program that keeps phosphonates in solution and available to prevent precipitation and deposition. The addition of DCPs can extend the calcium tolerance of phosphonates, control calcium phosphate and the formation of other types of scale (CaCO₃, SrSO₄, CaF₂, etc.), and disperse suspended solids in the recirculating water, minimizing potential deposition on system surfaces.

The monomer structure(s) and molecular weight of each DCP provide insight on its performance against scale and corrosion. Homopolymers are comprised of a single repeating unit, copolymers – 2 repeating units, terpolymers – 3 repeating units, etc.

Table 2. Common deposit control polymers used in industrial water treatment.

<table>
<thead>
<tr>
<th>Polymer Types</th>
<th>Examples</th>
<th>Structure</th>
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<tbody>
<tr>
<td>Natural</td>
<td>Starches, alginates, lignins, tannins, &amp; cellulose derivatives</td>
<td></td>
</tr>
<tr>
<td>Homopolymers</td>
<td>polyacrylic acid (PAA)</td>
<td><img src="image" alt="PAA" /></td>
</tr>
<tr>
<td></td>
<td>polymethylacrylic acid (PMAA)</td>
<td><img src="image" alt="PMAA" /></td>
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<tr>
<td></td>
<td>polymaleic acid (PMA)</td>
<td><img src="image" alt="PMA" /></td>
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Specific types of scale will respond better to specific functional groups. For example, acrylic acid based terpolymers inhibit calcium phosphonate better than acrylic or maleic acid homopolymers. Polysulfonic acid homopolymers are more tolerant to calcium than both PAA and PMA homopolymers, but combining sulfonic and acrylic acid into a copolymer extends calcium tolerance compared to the three homopolymers.\textsuperscript{10} PAA, PMAA, and other DCPs dominated by carboxyl groups exhibit excellent CaCO\textsubscript{3}, calcium sulfate, and calcium fluoride inhibition, while DCPs with larger, hydrophobic, and strong acid groups perform better as calcium phosphate scale inhibitors and suspended solids dispersants.\textsuperscript{12} Among PAA homopolymers, as MW decreases, calcium tolerance and CaCO\textsubscript{3} inhibition increases. The opposite phenomenon is seen in strontium sulfate scale; as MW increases, scale inhibition decreases (Figure 1). PAA inhibition of calcium phosphate and calcium sulfate is also MW dependent, but reaches threshold inhibition at \textasciitilde2k; increasing the MW above 2k does not improve performance.

**Figure 1.** Representation of PAA performance vs. MW for Ca ion tolerance, and CaCO\textsubscript{3} and SrSO\textsubscript{4} scale inhibition.
MW differences for similar composition polymers can contribute to performance differences as lower MW polymers generally adsorb faster than the high MW polymers due to steric hinderance.\textsuperscript{6,11,13} Investigations into the relationship between MW and inhibition have revealed that optimum MW is dependent of the polymer composition and targeted scale.

In general, solvent-polymerized PAAs provide somewhat better performance than water-polymerized PAAs. This is attributed to distinctive end groups and branching not seen in water-polymerized PAA or other polymers. This relationship between MW and synthesis conditions of homopolymers is depicted in Table 3.

Further investigation has shown that sulfonated terpolymers perform better as overall scale inhibitors at lower doses compared to homo- or copolymers. Blends of the PAAs and poly(AA/SA/SS) inhibit scale characteristic of each polymer individually, providing a synergistic effect on scale inhibition and material dispersion.\textsuperscript{3,6,11}

**Table 3.** Ranking of homopolymer performance against CaCO\textsubscript{3} scale.\textsuperscript{4}

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Polymer Type</th>
<th>MW</th>
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<tbody>
<tr>
<td>1</td>
<td>solvent-polymerized PAA</td>
<td>2 k</td>
</tr>
<tr>
<td>2</td>
<td>water-polymerized PAA</td>
<td>2.3 k</td>
</tr>
<tr>
<td>3</td>
<td>solvent-polymerized PAA</td>
<td>6 k</td>
</tr>
<tr>
<td>4</td>
<td>water-polymerized PAA</td>
<td>7.3 k</td>
</tr>
<tr>
<td>5</td>
<td>PMMAA</td>
<td>5 k</td>
</tr>
</tbody>
</table>

Maintaining the correct dosage of scale inhibitor(s) can also play a key role in preventing deposit formation. Small doses of DCPs can be very effective in controlling scale as only 3-5% of a carbonate scale crystal needs to be covered by polymer for complete inhibition. This is compared to 16% coverage required with phosphonate inhibitors.\textsuperscript{2} In general, increasing the dosage increases the inhibition however, at some point the dosage reaches critical value and the inhibition rate plateaus. One study found that 5 ppm of copolymer was sufficient to inhibit >90% CaSO\textsubscript{4} scale, any increase in dosage resulted in a decrease in inhibition. However, 7.5 ppm was needed to reach threshold inhibition of CaCO\textsubscript{3} and as much as 40 ppm was needed to inhibit >70% of strontium and barium sulfate scale.\textsuperscript{3,8,13,14} Polymer dosage is critical to inhibition performance, and the best way to determine optimal dosage is through experimentation with the water being treated.

**High Stress Conditions**

As previously mentioned, phosphonates are effective scale inhibitors, but as Ca\textsuperscript{2+} concentration increases, the risk of Ca-phosphonate and calcium phosphate formation also increases. Investigations into CaCO\textsubscript{3} inhibitors have found that phosphonate and polymer scale used individually, inhibit < 80% CaCO\textsubscript{3} scale when dosed at 30 ppm in 180x calcite saturation. The phosphonate efficacy in high Ca\textsuperscript{2+} water is predicated on the polymer inhibitor. In studies that combined polymer with PBTC or HEDP, greater than 90% inhibition of CaCO\textsubscript{3} was seen under similar conditions at 40 ppm.\textsuperscript{1} The polymer works with the phosphonate or phosphate inhibitor by controlling the thickness of the film on metal surfaces in addition to controlling calcium phosphate
and phosphonate precipitation. At the same time, since the DCP is working to control both CaCO$_3$ and phosphorous-based scale, higher doses are often required for overall scale inhibition. Sulfonic acid terpolymers have the excellent Ca$^{2+}$ tolerance and can be blended with carboxylic acid based phosphonates, or low MW PAAs for synergistic water treatment.$^{3,8,10}$

**Thermal Degradation**

High stress often equates to high temperatures, which is when degradation of the scale inhibitor(s) becomes a key concern. In general, degradation rates increase with increasing temperature, but rates are also affected by pH, inhibitor dose, and exposure time. All polymers when subjected to stress conditions (up to 250°C for 20 hr at pH 10.5) undergo some degradation or compositional changes. The extent of the degradation is dependent on polymer composition. Homopolymers experience less degradation and structural changes at elevated temperatures than co- or terpolymers, with acrylic acid outperforming maleic acid homopolymers. Analytical characterization of polyacrylic acid (PAA), polymethylacrylic acid (PMAA), and polymaleic acid (PMA) polymers commonly used in boiler applications show that while all three homopolymers underwent some molecular weight loss indicative of degradation, PAA and PMAA had minimal performance changes in preventing CaCO$_3$ scale (Figure 2). PMA, however, suffered a substantial loss in performance as it inhibited twice as much scale before thermal stress than it did after.$^{4,5,15}$

![CaCO$_3$ Inhibition by Homopolymers vs. Thermal Stress](image)

**Figure 2.** A graph representation of the effect of thermal stress on CaCO$_3$ inhibition by homopolymers.$^{15}$ Solvent-polymerized PAAs (PAA-S) outperform water-polymerized PAAs (PAA-W) of the same MW. PAAs with a lower MW of 2k are better CaCO$_3$ inhibitors than their 5k counterparts, regardless of the thermal stress conditions. PMA performance is most affected by thermal stress; a sharp decrease in percent inhibition as the temperature was increased from 23 to 250°C.

The pathway of DCP degradation during thermal stress is still being investigated. Figure 3 illustrates possible degradation routes in a poly(AA/SA) copolymer.
Figure 3. Pathways for thermal degradation of an acrylic and sulfonic acid copolymer. (A) Scission of backbone (B) Decarboxylation (C) Hydrolysis of pendent and/or end groups.

Relatively small MW losses are evident in lower MW PAAs, suggesting minimal scission of the polymer backbone. Homopolymers suffer less damage due to thermal degradation, losing < 8 % MW at 250°C, compared to > 10% loss in co- or terpolymers at ≥ 200°C. When comparing homopolymers, it is important to recognize differences between the synthesis and composition. PMA is made under different polymerization conditions, is structurally dissimilar with two carboxyl groups on adjacent carbon atoms compared to only one carboxyl group present in the PAAs, and its MW is much lower than other homopolymers. PMA is not as thermally stable as either the PAAs or PMAAs and may follow a different route or multiple routes of degradation.

**Calcium Carbonate**

Calcium carbonate is one of the most frequently encountered scale in industrial water treatment and has been the focus of many DCP performance studies. Most minerals are less soluble as the temperature decreases; calcium carbonate is an exception, and its formation is exacerbated by low pressure and high pH. Low pH, controlled by acid feed treatment, is an effective means to control calcium carbonate scale, but there are safety and corrosion drawbacks of acid addition.

As previously mentioned, MW and composition are key factors in predicting DCP performance. Studies have shown that higher carboxyl content and lower MW polymers perform well as CaCO₃ scale inhibition. This relationship is illustrated in Figure 4 below. Poly(AA/SA/SS) terpolymers inhibit less CaCO₃ compared to PAA homopolymers. This is due to the greater amount and accessibility of the carboxylate groups on PAA compared to the P(AA/SA/SS).

The same phenomenon is seen with phosphonates, as PBTC, which has a carboxylate group, outperforms both ATMP and HEDP in inhibiting CaCO₃. Under thermal stress, sulfonic acid polymer performance improves, most likely due to the hydrolysis of the sulfonic acid, which in turn increases the carboxyl content of the polymer. PMA, which loses carboxyl content during thermal stress is a poor inhibitor of CaCO₃ scale compared to PAAs at temperatures above 150°C.
Figure 4. CaCO$_3$ inhibition by various DCPs as a function of dose. Results were obtained from SBT at 66°C for 24hrs. P(AA/SA/SS) terpolymer (TP) performance, represented by the triangles, is not an effective CaCO$_3$ inhibitor when compared to the PAA homopolymers. The performance of PAA + TP (circles) lags, but loosely parallels, PAA-only performance.

With the addition of phosphonates to industrial water systems, the induction time of CaCO$_3$ formation is delayed, and the rate of CaCO$_3$ precipitation decreases by a factor of $\geq 5$ when the phosphonate concentration increases from 5 to 40 mg/L. While terpolymer performance is inferior to that of the PAAs in inhibiting CaCO$_3$ scale, a 3:1 blend of PBTC and sulfonic acid terpolymer outperformed other combinations of polymer and phosphonate in high stress conditions, due to the inhibition abilities of the combined functional groups.$^{4,6,16}$

**Calcium Phosphate**

Calcium phosphate deposits can occur on heat exchanger and reverse osmosis membrane surfaces, and an increase in the phosphate concentrations in lakes and rivers compounds the necessity for effective scale inhibition. Like CaCO$_3$, calcium phosphate forms more readily under stressed conditions when phosphorous-based scale inhibitors are more likely to react with calcium and precipitate out of solution. The addition of DCPs to a water treatment program can improve calcium phosphate inhibition.

It is generally known that homopolymers are not good inhibitors for calcium phosphate scale. Studies have shown that PAAs offer $< 20\%$ inhibition when dosing at greater than 15 ppm. It has also been established in the previous section that the same PAAs that poorly inhibit calcium phosphate, excel at inhibiting calcium carbonate. The benefit to introducing sulfonic acid functional groups is a significant increase in the performance of DCPs at low doses. Remarkably, co- and terpolymers containing a blend of functional groups of different ionic charge are more effective calcium phosphate and calcium phosphonate inhibitors (Figure 5).$^{17}$ The use of poly(SA/AA) copolymers increases the calcium phosphate inhibition to 50$\%$ at 15 ppm. Terpolymers containing a blend of acrylic acid, sulfonic acid, and sulfonated styrene improve inhibition to $> 90\%$ at the same dose.$^{3,6,10}$
Figure 5. Calcium phosphate inhibition by DCPs as a function of dose. Results were obtained from SBT at 70°C for 24 hrs. Poly(AA/SA/SS) outperforms the P(AA/SA) copolymers followed closely by a terpolymer with a non-ionic functional group. Lowering the MW of the P(AA/SA) copolymer lowers its inhibition performance, possibly due to the decreased amount of available SA groups.¹⁸

Iron Oxide Dispersion

The mechanism for DCPs in industrial water treatment applications include preventing deposition of suspended matter such as iron oxide by adsorbing onto the surface of the particles and dispersing the particulates throughout the solution, preventing them from settling on metal surfaces. The most commonly encountered iron oxides in industrial water applications, hematite and magnetite, are often the result of equipment corrosion or precipitation of soluble iron. DCPs of varying functional groups and MWs have been the subject of multiple experiments to stabilize iron oxide in solution.

Table 4. Ranking of common DCPs as iron oxide dispersants

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Polymer Type</th>
<th>MW</th>
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<tbody>
<tr>
<td>1</td>
<td>poly(AA/SA/SS)</td>
<td>&lt; 15 k</td>
</tr>
<tr>
<td>2</td>
<td>poly(AA/SA/SS)</td>
<td>&lt; 10 k</td>
</tr>
<tr>
<td>3</td>
<td>poly(AA/SA)</td>
<td>&lt; 15 k</td>
</tr>
<tr>
<td>4</td>
<td>solvent-polymerized PAA</td>
<td>6 k</td>
</tr>
<tr>
<td>5</td>
<td>water-polymerized PAA</td>
<td>6 k</td>
</tr>
</tbody>
</table>

Under mild conditions, Poly(AA/SA/SS) significantly outperforms other homo- and copolymers, offering > 70% iron oxide dispersion at a relatively small dose of 1 ppm (Figure 6).⁶ The excellent performance of the terpolymer is likely due to the electrostatic interactions of the sulfonated groups with the negative charge of iron oxide. There is also evidence that the sulfonated co- and terpolymers have a stronger influence on the iron oxide particle size in solution.¹⁹ As with most scale inhibition studies, lowering the DCP dose lowers performance. Less than 50% iron oxide is
dispersed at 0.25 ppm poly(AA/SA/SS). In general, the addition of suspended matter to recirculating water antagonizes DCP performance. Higher doses are necessary to achieve scale inhibition and dispersion.\textsuperscript{8,19}

![Graph representation of iron oxide dispersion by various DCPs at 1 ppm as a function of time. P(AA/SA/SS) terpolymer clearly outperforms both solvent and water-polymerized PAAs, reaching a threshold dispersion of \textasciitilde80% after 3 hours.\textsuperscript{6}]

\textbf{Conclusion}

Based on the performance data reviewed within, deposit control polymers could be a critical addition to any industrial water treatment program, whether added independently or paired with a polyphosphate or phosphonate inhibitor. A wide range of homopolymers, copolymers, and terpolymers are available for mineral scale inhibition (i.e. CaCO\textsubscript{3}, Ca-phosphate, etc.), crystal modification, and particle dispersion (i.e. iron oxide). In brief, low MW solvent-polymerized PAAs outperform other DCPs at inhibiting CaCO\textsubscript{3} scale, while P(AA/SA/SS) terpolymers are industry mainstays, inhibiting several types of scale and dispersing suspended matter. Selecting the ideal DCP or combination of DCPs depends on the functional groups, MW, water content, and treatment conditions.
References


