The studies and conclusions reported in this paper are the results of the author’s own work. CTI has not investigated, and CTI expressly disclaims any duty to investigate, any product, service process, procedure, design, or the like that may be described herein. The appearance of any technical data, editorial material, or advertisement in this publication does not constitute endorsement, warranty, or guarantee by CTI of any product, service process, procedure, design, or the like. CTI does not warranty that the information in this publication is free of errors, and CTI does not necessarily agree with any statement or opinion in this publication. The user assumes the entire risk of the use of any information in this publication. Copyright 2014. All rights reserved.

Presented at the 2014 Cooling Technology Institute Annual Conference
Houston, Texas - February 3-6, 2014
Development and Application of Phosphorus Free Cooling Water Technology

Raymond M. Post, ChemTreat
Richard Tribble, ChemTreat
Prasad Kalakodimi, ChemTreat

Abstract
Phosphate based corrosion and scale inhibitor programs emerged as the cooling water treatment technology of choice when the industry was strongly encouraged to eliminate chromates some 35 years ago. At that time, we were certainly aware of the many troublesome issues associated with phosphate based programs: the precise control required to prevent phosphate deposits on hot bundles, inadequate admiralty brass corrosion using only azoles, escalating dispersant demand due to phosphate precipitation with well water iron and aluminum carryover, and excessive algae growth on the towers and the associated chlorine demand. Although we were aware of impending phosphorus regulations we continued to perfect phosphate based cooling water programs because there simply was no reasonable alternative ….until now. This paper describes the development of a promising phosphorus free corrosion and deposit control program, including laboratory and field application performance data from several challenging applications.

Background
Cooling water treatment from the 1930s through the early 1980s relied primarily upon 5-500 ppm hexavalent chromium to inhibit corrosion of steel and copper alloys in conjunction with acid to maintain the pH of the system in the 6.0-7.0 range to control scale formation. In the last decades of the chromate era, zinc and polyphosphate supplements were added to support lower levels of chromate. Chromate proved to be an excellent steel and copper corrosion inhibitor, but its greatest attribute was its forgiving nature. 50 ppm provided excellent performance and 500 ppm performed even better across the broad pH 6.0-7.0 range. An overfeed did not lead to fouling, and more corrosive conditions, even brines, could always be overcome with higher treatment levels.

As chromate was phased out due to human health concerns and zinc has been mostly phased out due to aquatic toxicity, the cooling water treatment industry in the United States and Western Europe focused primarily on phosphate-based chemistries for both corrosion and scale control. Progressive advances have led to polymers that are more efficient in maintaining higher levels of orthophosphate in solution. Organic phosphate components provide both scale inhibition and cathodic corrosion inhibition for steel. Aromatic azole supplements are used to overcome phosphate’s deficiency in protecting copper alloys.

Today’s phosphate chemistries perform adequately in most circumstances, but demand precise control. The concentration of phosphate must be balanced carefully with calcium, polymeric dispersant, pH, and temperature. If all five factors are not perfectly balanced at all times and at all points in the system, either corrosion or fouling will occur. This is particularly problematic in the chemical industry due to the prevalence of high temperature, low flow bundles together with steel piping operating at much lower temperature.

Apart from unforgiving control requirements, phosphate has several additional weaknesses. Phosphate by itself is an effective inhibitor only for steel and a marginal inhibitor for galvanized surfaces. It has little or no beneficial effect on copper or aluminum corrosion. Phosphate programs often perform poorly in soft or low hardness waters, requiring much higher levels of phosphate to form an effective calcium phosphate film. Phosphate will also precipitate with well-water iron and aluminum clarifier carryover, forming deposits and causing excessive polymeric dispersant demand.
Emerging Phosphorus Regulations

Recently, US regulations have begun to restrict the industrial discharge of phosphorus as an undesirable aquatic nutrient for cyanobacteria and algae in the environment. Controlling algae growth by restricting phosphorus can be traced to Justus Von Liebig, a 19th century German chemist considered to be the “father of the fertilizer industry”. He is credited with popularizing Liebig’s “Law of the Minimum” which states that growth is controlled not by the total amount of resources available, but by the scarcest resource.

Phosphorus is generally the limiting nutrient for cyanobacteria and algae growth, not only in the environment but also in many cooling tower systems. Algae and cyanobacteria derive energy from abundant sunlight and carbon for cellular growth from abundant bicarbonate in the water. Cyanobacteria and many species of algae can “fix” atmospheric nitrogen into water. They colonize water bodies in thick mats and produce cyanotoxins that are hazardous to aquatic mammals, fish, shellfish, and even humans. In the environment, the periodic die-offs of algae and cyanobacteria cause dissolved oxygen “sags” that adversely affect aquatic life. According to USEPA, phosphorus and nitrogen nutrients are the cause of degradation in half of impaired water bodies and are associated with fish kills, sediment accumulation, unhealthful trihalomethanes (THMs) in chlorinated drinking water, and a 6,000 square mile low dissolved oxygen “dead zone” in the Mississippi River delta drainage area.

USEPA’s strategy for regulating nutrients under the Clean Water Act is based on the concept of a Total Maximum Daily Load (TMDL) for a particular nutrient or pollutant entering a watershed. If a watershed is deemed to be impaired, a Waste Load Allocation (WLA) must be developed for that pollutant which restricts the amount entering the watershed to an amount that is below its assimilative capacity. At this point in time, an inventory of all the impaired water bodies in the US has been compiled, along with the pollutants responsible for the impairment. If the watershed is impaired by phosphorus, a more stringent limit for phosphorus discharge is likely to be incorporated into the site’s NPDES permit at the time of renewal. Figure 1 illustrates this water quality based TMDL approach.

Figure 1. TMDL development & application

In cooling towers, algae and cyanobacteria convert inorganic bicarbonate into organic carbon which support the growth of bacteria. The dense algae mats that form on cooling tower decks and exposed areas support higher life forms such as protozoans and amoeba which can harbor and amplify Legionella bacteria. As shown in Figure 2, halogen demand is directly proportional to chlorophyll concentration. According to Liebig's Law of the Minimum, restricting phosphorus entering the cooling system is an effective means for reducing algae growth and chlorine demand.

Figure 2. Chlorine demand as a function of chlorophyll concentration
Objective
Considering emerging environmental restrictions on phosphorus discharge and the many shortcomings of phosphorus based cooling water treatment technologies, a multi-year research effort was undertaken to develop a versatile and totally phosphorus and zinc free cooling water treatment technology. The requirements for the program were to have no orthophosphate, polyphosphate, or organic phosphonates or phosphinates, yet be cost competitive with traditional phosphorus programs. The program also had to be non-toxic to aquatic life at 10x the nominal use concentration, with an overall Environmental Health and Safety (EH&S) profile similar to or better than current phosphorus-based programs.

Laboratory studies
Scale Inhibitor Development
Organic phosphates have been the primary calcium carbonate scale inhibitors used by the industry since the mid-1970’s. They also serve an additional role as cathodic corrosion inhibitors for steel. Our first goal was to identify and evaluate non-phosphorus chemistries for calcium carbonate scale inhibition. Initial screening studies were conducted in heated beakers, and the most promising candidates were evaluated more carefully in a matched pair of fully instrumented pilot cooling towers (Figures 3-5).

The pilot cooling towers each have a 15 gallon (56.7 L) sump and evaporate 45 gallons (170 L) daily, with a cold supply water temperature of 100 °F (37.8 °C) and a hot return temperature of 107.5 °F (41.9 °C). For the purpose of these experiments, heat exchanger skin temperatures were maintained in the range of 135-142 °F (57-61 °C) with a heat flux of 26,100 Btu/hr-ft² (82,319 W/m²). Superficial water velocity in the annular flow space was maintained at 4 fps (1.2 m/s). The test methodology was to add the scale inhibitor chemistry and cycle up the makeup water (Table 1) gradually over a three week period until a “crash point” was reached, as indicated by scale formation on the heat exchanger tubes (Figure 6). Figure 7 indicates that the best of the non-phosphorus scale inhibitors could achieve an LSI of 2.96, corresponding to 5.5 cycles of concentration on the test water.
Table 1. Makeup water used for non-P moderate alkalinity pilot cooling tower study

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>Conductivity, µmhos</td>
<td>480</td>
</tr>
<tr>
<td>P-Alk, as CaCO$_3$, mg/L</td>
<td>8</td>
</tr>
<tr>
<td>M-Alk, as CaCO$_3$, mg/L</td>
<td>105</td>
</tr>
<tr>
<td>Ca, as CaCO$_3$, mg/L</td>
<td>104</td>
</tr>
<tr>
<td>Mg, as CaCO$_3$, mg/L</td>
<td>25</td>
</tr>
<tr>
<td>Total P, mg/L</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Na, mg/L</td>
<td>90</td>
</tr>
<tr>
<td>Cl, mg/L</td>
<td>66</td>
</tr>
<tr>
<td>SO$_4$, mg/L</td>
<td>54</td>
</tr>
<tr>
<td>SiO$_2$, mg/L</td>
<td>25</td>
</tr>
</tbody>
</table>

Corrosion Inhibitor Development

Initial screening for non-phosphorus corrosion inhibitors took place using spinner baths and electrochemical tests. The spinner bath units were operated so as to achieve a superficial velocity of 1 ft/sec at a controlled temperature. The solutions were aerated to maintain oxygen saturation. Most spinner bath tests were conducted at a bulk water temperature of 50 °C (122 °F). Corrosion inhibitor performance was also determined through Linear Polarization Resistance (LPR) measurements in cells containing rotating as well as static corrosion coupons. Most of the testing was conducted using the water chemistries shown in Table 2. Additional testing was conducted to evaluate more severe conditions by addition of supplemental chlorides and sulfates, as well as under conditions simulating field evaluation sites.

Table 2. Water composition used for development of soft water program

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.33</td>
</tr>
<tr>
<td>Conductivity, µmhos</td>
<td>197</td>
</tr>
<tr>
<td>&quot;M&quot;-Alk, as CaCO$_3$, mg/L</td>
<td>30</td>
</tr>
<tr>
<td>Ca, as CaCO$_3$, mg/L</td>
<td>28</td>
</tr>
<tr>
<td>Mg, as CaCO$_3$, mg/L</td>
<td>10</td>
</tr>
<tr>
<td>Iron, as Fe, mg/L</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Copper, as Cu, mg/L</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Zinc, as Zn, mg/L</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Sodium, as Na, mg/L</td>
<td>45</td>
</tr>
<tr>
<td>Potassium, as K, mg/L</td>
<td>3.9</td>
</tr>
<tr>
<td>Chloride, as Cl, mg/L</td>
<td>38</td>
</tr>
<tr>
<td>Sulfate, as SO$_4$, mg/L</td>
<td>15</td>
</tr>
<tr>
<td>Nitrate, as NO$_3$, mg/L</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Silica, as SiO$_2$, mg/L</td>
<td>5</td>
</tr>
<tr>
<td>LSI</td>
<td>-0.16</td>
</tr>
<tr>
<td>Larson Skold index</td>
<td>1.62</td>
</tr>
</tbody>
</table>

The testing focused on mild steel corrosion control. Several hundred non-phosphorus candidates were screened over a four-year period. Although many chemistries demonstrated efficacy in reducing corrosion, only a few were considered adequate phosphate replacements when dosage, commercial availability, and usage cost were considered.

Figures 8 and 9 show the corrosion coupons exposed for 3 days to the untreated baseline water compared to the best performing
non-phosphate program. The baseline corrosion rate for this corrosive, ultra-soft water was found to be 60 mpy at 50 °C for mild steel. The best-performing non-P program achieved <1 mpy on mild steel and <0.1 mpy on copper.

Figure 8. Baseline mild steel and copper coupon set - corrosive water test

![Figure 8](image1)

Figure 9. Best performing Non-P steel and copper corrosion coupon set from corrosive water test

![Figure 9](image2)

One major drawback to conventional phosphate and zinc programs is that they can be very unforgiving in terms of deposition and more flexible for corrosion control. In general, the only negative consequence of an overfeed of a non-P inhibitor is an increase in treatment cost. More corrosive conditions can be handled by simply increasing dosage.

Copper alloy corrosion inhibition

One weakness of phosphate is its inability to protect non-ferrous alloys. Aromatic azoles, typically TTA and BZT, must be added to the phosphate programs to protect copper alloys. This chemistry does not offer the same degree of protection for copper alloys as the heritage chromate programs under stressed conditions. Cooling programs operating in the pH 7.0-7.8 “stabilized phosphate” chemistry range frequently experience difficulties obtaining adequate copper corrosion protection especially during periods of heavy chlorination. The preferred non-P program was evaluated against the baseline stabilized phosphate-azole program in the laboratory using linear polarization resistance measurements. The test water was simulated 8-cycle Sabine River water containing 0.5 ppm free available halogen developed from sodium hypochlorite and sodium bromide. The pH of the water was maintained at 8.0-8.2 with 160 ppm alkalinity and 200 ppm calcium (as CaCO₃). As shown in Figure 10, the conventional 3 ppm azole program (red line) performed adequately at <0.1 mpy. However, the non-P program with no azole (blue line) outperformed azole alone. The combination of non-P program in conjunction with 2 ppm azole (green line) demonstrated synergistic behavior in providing the best performance at <0.01 mpy.

Figure 10. Copper corrosion inhibition comparing azole, the non-P inhibitor, and combination azole with non-P inhibitor

![Figure 10](image3)
The electrochemical tests were confirmed in the laboratory using 3-day “spinner bath” studies (Table 3). The studies indicate that the non-P program can produce results equivalent to the baseline phosphate-azole program on both steel and copper at the same 100 ppm product dosage. However, the non-P program is more flexible. The dosage can be dialed up by 30% to produce better corrosion and deposit control protection or reduced by 35% to reduce costs with a slight sacrifice in performance.

Table 3. Results of baseline phosphate vs. non-P programs in a 3-day spinner study

<table>
<thead>
<tr>
<th>Treatment Program</th>
<th>Coupons Copper / Steel</th>
<th>Corrosion (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline PO₄ 100 ppm Products</td>
<td>Admiralty 0.32 Steel: 2.1</td>
<td></td>
</tr>
<tr>
<td>Non-P 65 ppm Product</td>
<td>Admiralty 0.35 Steel: 4.05</td>
<td></td>
</tr>
<tr>
<td>Non-P 100 ppm Product</td>
<td>Admiralty 0.13 Steel: 1.21</td>
<td></td>
</tr>
<tr>
<td>Non-P 130 ppm Product</td>
<td>Admiralty 0.07 Steel: 0.86</td>
<td></td>
</tr>
</tbody>
</table>

Aluminum Corrosion Inhibition
Aluminum corrosion has been of increasing concern due to the more widespread use of aluminum alloys, particularly in closed cooling systems. Unlike steel, which becomes immune to corrosion at high pH, aluminum is an amphoteric metal that corrodes rapidly under alkaline conditions. A 3-day spinner bath study was conducted in aerated 50 °C (122 °F) tap water to which additional 300 ppm chloride and 100 ppm additional alkalinity were added to provide more challenging conditions. The pH of the water was allowed to fluctuate in the 8.0-8.7 range. Corrosion coupon appearance and aluminum concentration in the test solution were used as an indication of corrosion, since aluminum coupons actually gain weight as they corrode due to precipitation. The non-P formulated product was evaluated at 100, 200, and 300 ppm product. Results are shown in Table 4. Corrosion on aluminum occurs when the protective aluminum oxide layer is damaged either mechanically or chemically. Pits on the baseline coupons were surrounded by white precipitate, suggesting that anodic sites developed in the absence of effective treatment. The non-P treatment program completely eliminated anodic pitting at the 300 ppm product concentration.

Table 4. Effectiveness of non-P chemistry on aluminum corrosion

<table>
<thead>
<tr>
<th>Treatment Program</th>
<th>Coupons Al / Al</th>
<th>Aluminum ion in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline 100 ppm Product</td>
<td>2 ppm</td>
<td></td>
</tr>
<tr>
<td>Non-P 100 ppm Product</td>
<td>0.31 ppm</td>
<td></td>
</tr>
<tr>
<td>Non-P 200 ppm Product</td>
<td>0.07 ppm</td>
<td></td>
</tr>
<tr>
<td>Non-P 300 ppm Product</td>
<td>&lt;0.05 ppm</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Initial water analysis for 3-day aluminum spinner bath study

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.97</td>
</tr>
<tr>
<td>Conductivity, µmho</td>
<td>1573</td>
</tr>
<tr>
<td>&quot;M&quot;-Alk, as CaCO₃, mg/L</td>
<td>145</td>
</tr>
<tr>
<td>Ca, as CaCO₃, mg/L</td>
<td>191</td>
</tr>
<tr>
<td>Mg, as CaCO₃, mg/L</td>
<td>20</td>
</tr>
<tr>
<td>Sodium, as Na, mg/L</td>
<td>272</td>
</tr>
<tr>
<td>Chloride, as Cl, mg/L</td>
<td>379</td>
</tr>
<tr>
<td>Sulfate, as SO₄, mg/L</td>
<td>74</td>
</tr>
<tr>
<td>Silica, as SiO₂, mg/L</td>
<td>7.9</td>
</tr>
<tr>
<td>Aluminum, mg/L</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Total P, as PO₄, mg/L</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Corrosion Control Mechanism
Electrochemistry studies were used to elucidate the corrosion inhibition mechanism of the new treatment chemistry on steel. As
shown in Figure 11, the corrosion inhibitor package inhibits both the anodic and cathodic corrosion processes, showing the tendency to form a particularly strong passive film on the anodic region.

**Figure 11. Electrochemical study of non-P inhibitor on steel**

Field applications of non-P Programs

1. **Low hardness, Low alkalinity Corrosive Water Application**

The best performing non-P program in the laboratory was formulated as a commercial product and taken to a field evaluation in a corrosive water application where phosphate discharge was becoming a concern. The small 2-cell Evapco cooling tower servicing a HVAC system was using a conventional phosphate-based program and obtaining marginal results of 3.4 - 4.6 mpy on mild steel. Process conditions made it difficult to obtain the consistent chemistry required by phosphate-based programs, and the small size of the system made it difficult to justify automating the chemical dosing systems. The non-P program improved performance to 1.4 mpy on mild steel and <0.01 mpy on copper. Thermal performance of critical heat exchangers has shown no decline in performance since transitioning to the non-P treatment program. Figures 12 and 13 show the copper and steel coupons after a 64-day exposure.

**Figure 12. Field trial coupons before cleaning**

2. **High Hardness, High Sulfate Corrosive Water Application**

A Midwest cogeneration plant faced stringent phosphate discharge regulations. The unclarified makeup water was high in calcium and alkalinity, requiring sulfuric acid for pH control. The resulting cooling water was relatively corrosive due to high sulfates from the use of acid. The circulating water is shown in Table 6.

Steel corrosion rates on the baseline low-phosphorus program were averaging about 10 mpy (Figure 14). Upon changing to the non-P chemistry, corrosion rates have been reduced to a 2 mpy average on steel (Figure 15) and 0.1 - 0.2 mpy on copper.

**Figure 13. Field trial coupons after cleaning**

**Table 6. High hardness and sulfate water**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.64</td>
</tr>
<tr>
<td>Conductivity (µmhos)</td>
<td>2.552</td>
</tr>
<tr>
<td>&quot;M&quot;-Alk, as CaCO₃, mg/L</td>
<td>267</td>
</tr>
<tr>
<td>Ca, as CaCO₃, mg/L</td>
<td>469</td>
</tr>
<tr>
<td>Mg, as CaCO₃, mg/L</td>
<td>672</td>
</tr>
<tr>
<td>Sodium, as Na, mg/L</td>
<td>189</td>
</tr>
<tr>
<td>Chloride, as Cl, mg/L</td>
<td>324</td>
</tr>
<tr>
<td>Sulfate, as SO₄, mg/L</td>
<td>807</td>
</tr>
<tr>
<td>Silica, as SiO₂, mg/L</td>
<td>9.3</td>
</tr>
<tr>
<td>LSI @ 120 °F</td>
<td>2.2</td>
</tr>
<tr>
<td>Larson Skold</td>
<td>4.9</td>
</tr>
</tbody>
</table>
3. **Gulf Coast Chemical Plant**

The formulated product was evaluated at a Gulf Coast chemical plant cooling tower operating at 9 cycles on clarified Sabine River water. The water is relatively corrosive and several heat exchangers with high temperatures have been prone to deposition over the years. Although the corrosion results have been excellent in the past, the plant wanted to use a more forgiving, non-fouling program. Corrosion coupon results have been excellent, with steel coupons showing rates of 1.07 mpy for the first 35 days, 0.89 mpy for the second 32 days, 0.80 mpy for the third 32 days, and 0.32 mpy for the first 99-days. Critical heat exchanger approach temperatures have remained flat. Figure 16 shows the appearance of the initial steel coupon after 35 days before and after cleaning.

**Figure 16. Initial steel coupon, 35 days, before and after cleaning, 1.07 mpy**

<table>
<thead>
<tr>
<th>Table 7. Average cooling water chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analyte</strong></td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Conductivity (µmhos)</td>
</tr>
<tr>
<td>&quot;M&quot;-Alk, as CaCO$_3$, mg/L</td>
</tr>
<tr>
<td>Ca, as CaCO$_3$, mg/L</td>
</tr>
<tr>
<td>Mg, as CaCO$_3$, mg/L</td>
</tr>
<tr>
<td>Sodium, as Na, mg/L</td>
</tr>
<tr>
<td>Chloride, as Cl, mg/L</td>
</tr>
<tr>
<td>Sulfate, as SO$_4$, mg/L</td>
</tr>
<tr>
<td>Silica, as SiO$_2$, mg/L</td>
</tr>
</tbody>
</table>

4. **High iron in well water application**

Well water iron poses a special challenge for phosphate-based treatment programs. The reactive iron precipitates the phosphate corrosion inhibitor, rendering the phosphate ineffective and creating a sticky iron phosphate precipitate that creates additional polymer demand and tends to precipitate on heat transfer surfaces. Non-phosphorus treatment programs are particularly suited to such applications because the corrosion inhibitor does not react with the iron and the dispersant is only required to disperse the iron itself rather than precipitated iron phosphate. A Gulf Coast air separation plant with 2-5 ppm iron in its well water was experiencing heat exchanger fouling problems on a phosphate based treatment program. The problems were severe enough to require shutdowns to clean the exchangers. Figure 17 shows the last set of coupons removed from the phosphate program with heavy deposition and obvious corrosion.

**Figure 17. Phosphate program, steel, admiralty, and copper coupons with high well-water iron**

The treatment program was converted to the non-phosphorus program with the addition of a non-P supplemental dispersant for iron. Results on both corrosion and fouling have improved substantially. Figure 18 shows the first coupon set removed after 35 days.

**Figure 18. Non-P program first coupon set removed at 35 days. Steel 1.06 mpy, admiralty 0.68 mpy, and copper 0.31 mpy**
The automation system had not been installed yet, and there were several periods of high chlorine residual that adversely affected copper alloy corrosion. The second set of coupons exposed for 73 days fared better with corrosion rates of 0.11 mpy on 90-10 copper-nickel (Figure 19) and 1.55 mpy on mild steel.

![Figure 19](image1.png)

**Figure 19.** Non-P program 90-10 Cu: Ni coupons, 73-day exposure in high iron water before and after cleaning

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0-8.4</td>
</tr>
<tr>
<td>Conductivity (µmhos)</td>
<td>2,000-2,500</td>
</tr>
<tr>
<td>Ca, as CaCO₃, mg/L</td>
<td>450-550</td>
</tr>
<tr>
<td>&quot;M&quot;-Alk, as CaCO₃, mg/L</td>
<td>150-250</td>
</tr>
<tr>
<td>Chloride, as Cl, mg/L</td>
<td>150</td>
</tr>
<tr>
<td>Sulfate, as SO₄, mg/L</td>
<td>1,000</td>
</tr>
<tr>
<td>Iron, as Fe, mg/L</td>
<td>3-10</td>
</tr>
</tbody>
</table>

Table 8. Cooling water chemistry

Approach temperatures have improved during the first four months on the non-phosphorus program (Figure 20) along with an increase in tower water turbidity, indicating that softer deposits are slowly being removed.

![Figure 20](image2.png)

**Figure 20.** Approach temperature trend on the non-P program

5. **Steam Jacketed Vessel Application**

One particularly challenging application for phosphate based cooling water programs is the treatment of jacketed reactor vessels that are alternately exposed to steam for heating followed by cooling tower water for the process cooling cycle. The jacket is alternately exposed to high temperature steam followed by oxygenated cooling water. The protective film applied during the cooling cycle must somehow persist through the high temperature, low hardness steam heating cycle. This was readily achievable during the chromate and zinc era, but not generally possible with phosphate based programs. The non-P chemistry produces a much more persistent film than phosphate programs, making it an excellent application for steam jacketed vessels.

A Gulf Coast chemical plant was experiencing elevated steel corrosion rates in their jacket water cooling system, typical for a phosphate program. The corrosion rate was 6.8 mpy on steel coupons, resulting in nearly 4 ppm iron in the cooling tower water. The phosphate based program was overlaid with the non-P corrosion inhibitor program. Iron levels in the tower dropped to 0.5 ppm as shown in Figure 21, and the corrosion rate on the first 28-day coupon was reduced to 1.34 mpy.

![Figure 21](image3.png)

**Figure 21.** Cooling tower iron level for jacketed vessel cooling system transitioning to non-P program overlay
Table 9. Cooling Tower Chemistry for Jacketed Vessel

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0</td>
</tr>
<tr>
<td>Conductivity (µmhos)</td>
<td>1500</td>
</tr>
<tr>
<td>Ca, as CaCO₃, mg/L</td>
<td>150</td>
</tr>
<tr>
<td>&quot;M&quot;-Alk, as CaCO₃, mg/L</td>
<td>175</td>
</tr>
<tr>
<td>Sodium, as Na, mg/L</td>
<td>225</td>
</tr>
<tr>
<td>Chloride, as Cl, mg/L</td>
<td>270</td>
</tr>
<tr>
<td>Sulfate, as SO₄, mg/L</td>
<td>150</td>
</tr>
<tr>
<td>Total P, as PO₄, mg/L</td>
<td>3</td>
</tr>
</tbody>
</table>

Aquatic Effects and EH&S

Since the initial goal of the program was to develop an environmentally sound alternative to phosphate treatment programs, one of the major criteria was to have minimal aquatic effects, including mortality to EPA marker organisms, minimal human exposure hazards, no zinc, and no phosphorous in any form. A range of formulated products have been developed around the basic non-P corrosion inhibitor technology. Most are formulated at a mildly acidic pH. This is considerably less hazardous than most of the products it replaces, which must be formulated under strongly caustic or strongly acid pH. The cautionary wording is considerably less onerous, and the HMIS rating is typically 1-0-0-X. The basic formulated product is applied at a nominal dosage of 100 ppm. The LD₅₀ acute effect concentration is approximately 3,000 mg/L for both Ceriodaphnia and fathead minnow, and the 7-day chronic no-effect level for fathead minnow is 3,500 mg/L. Another version of the formulated product is also totally nitrogen free, including no azole and no acrylamide or AMPS containing polymers. The LD₅₀’s of that non-N and non-P product are 3,700 mg/L for Ceriodaphnia and 6,300 mg/L for fathead minnow. The significant safety margin between application dosage and aquatic effect concentration, the total absence of phosphorus and even nitrogen, and the mildly acid formulation should enable the products to be applied safely under current US regulations.

Conclusions

Practical non-phosphorus cooling water treatment programs have been developed to comply with emerging regulatory restrictions. Non-phosphorus chemistry offers several key benefits in addition to environmental compliance. Most importantly, these non-P programs:

- Are non-fouling with a broad control band
- Do not contribute to algae growth either in the environment or in the cooling tower, thus resulting in lower chlorine demand
- Are effective in zero hardness or high hardness waters
- Effective on steel, copper, and aluminum
- Are not affected by well-water iron or aluminum carryover
- Form a more persistent film, treating the surfaces rather than the bulk water
- Have minimal aquatic effects and a favorable EH&S profile

References

v Federal Register, 40C.F.R. Ch. 1 (7-01-08 Edition), §130.7(b)(4), p. 392.
vi USEPA. Overview of Impaired Waters and Total Maximum Daily Loads Program http://www.epa.gov/owow/tmdl/intro.html
vii Richardson, J; Cerra, H, and Tribble, R. Nutrient control – the key to a low environmental impact cooling water program. IWC 11-25. International Water Conference, 2011.