ELECTRIC POWER
RESEARCH INSTITUTE

State-of-Knowledge: Non-Phosphorous and Low-Phosphorous Cooling Water Treatment

2014 TECHNICAL REPORT

State-of-Knowledge: Non-Phosphorous and Low-Phosphorous Cooling Water Treatment

3002001276

Final Report, December 2014

EPRI Project Manager
R. Breckenridge

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

REFERENCE HEREIN TO ANY SPECIFIC COMMERCIAL PRODUCT, PROCESS, OR SERVICE BY ITS TRADE NAME, TRADEMARK, MANUFACTURER, OR OTHERWISE, DOES NOT NECESSARILY CONSTITUTE OR IMPLY ITS ENDORSEMENT, RECOMMENDATION, OR FAVORING BY EPRI.

THE FOLLOWING ORGANIZATION, UNDER CONTRACT TO EPRI, PREPARED THIS REPORT:

Water Technology Consultants™, Inc.

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute, EPRI, and TOGETHER…SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2014 Electric Power Research Institute, Inc. All rights reserved.

ACKNOWLEDGMENTS

The following organization, under contract to the Electric Power Research Institute (EPRI), prepared this report:

Water Technology Consultants™, Inc.
27515 Mountain Park Road
Evergreen, Colorado 80439

Principal Investigator
K. Selby

This report describes research sponsored by EPRI. EPRI would like to acknowledge the support of the following organizations:

Applied Specialties, Inc.
Buckman
ChemTreat
GE Water and Process Technologies
Nalco, an Ecolab Company
Solenis

This publication is a corporate document that should be cited in the literature in the following manner:

State-of-Knowledge: Non-Phosphorous and Low-Phosphorous Cooling Water Treatment. EPRI, Palo Alto, CA: 2014. 3002001276.

PRODUCT DESCRIPTION

Background

In most, if not all, areas of the United States, the use of phosphorous-containing chemicals is being limited, in some cases significantly. Phosphorous has been eliminated from laundry detergents and most dishwashing detergents. There are increasing restrictions on phosphorous in cooling water corrosion and mineral scale inhibitors.

Cooling water treatment for power plants has undergone many changes over the years. Chromate-based treatment programs provided excellent carbon steel and copper alloy corrosion protection and also served as a biocide. Because of the pH range under which most chromate-based programs operated, mineral scale deposition was not a significant problem and scale-inhibiting chemicals were typically not necessary.

Chromate-based programs for open cooling water systems were eliminated for environmental reasons. In many cases, they were replaced by programs containing phosphorous. These included polyphosphates and orthophosphate for carbon steel corrosion control and organo-phosphorous compounds for mineral scale deposition control.

Phosphorus-based corrosion control chemical treatments have outlasted or nearly outlasted all others for environmental and/or personnel protection, including chromate and zinc inhibitors. Other corrosion control product components such as molybdenum/molybdate have proven only marginally successful and/or prohibitively expensive at functioning concentrations.

Phosphorous-based mineral scale control programs, particularly for calcium carbonate scale inhibition, have also been the norm for many years, particularly as pH levels have increased to improve carbon steel corrosion control.

This report provides guidance on power plant cooling water corrosion and deposition control chemical programs that either eliminate or significantly minimize the use of phosphorous-containing chemicals.

This report has been produced with the cooperation of several water treatment service companies (WTSCs). As such, specific proprietary treatment programs are named and described. This does not constitute an endorsement or recommendation of specific WTSCs or programs.

Objectives

The objective of this report is to provide information about the state of knowledge on low-phosphorous and non-phosphorous cooling water treatment.

Approach

Current knowledge of electric utility cooling water treatment was assembled. In addition, leading WTSCs were asked to provide information on their low-phosphorous and non-phosphorous cooling water treatment programs.

Results and Findings

The guideline provides a solid background into cooling water treatment and the approaches that can be used to reduce the level of phosphorous discharge to the environment.

Application, Value, and Use

Currently, the use of phosphorous compounds is being limited because of environmental discharge concerns. This report describes corrosion and mineral scale deposition regimens that use either chemicals with no phosphorous content or chemicals with a significantly reduced phosphorous content.

Wherever metal and materials selection cannot be used to satisfactorily control iron corrosion, low-phosphate or non-phosphate alternative treatments are vital. These corrosion control treatments are presented here in the context of all modern treatment selection criteria. Mineral scale control using non- and low-phosphorus formulations is also presented in the context of state-of-knowledge treatment regimes.

Keywords

Corrosion control
Low-phosphorous treatment
Mineral scale control
Non-phosphorous treatment
Suspended solids deposition control

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
INTRODUCTION

Background

A cooling water treatment program must be designed to control mineral scale accumulation, corrosion, microbiological growth, and suspended solids deposition. This document will deal with mineral scale and corrosion control but not specifically microbiological growth or suspended solids accumulation.

Mineral scale accumulation and corrosion are often related. As cooling water pH decreases, mineral scale is less likely to form but the corrosion rate most likely increases. As cooling water pH increases, the corrosion rate decreases but mineral scale formation is more likely.

Mineral scale most often accumulates on heat transfer surfaces. The mineral scale has a lower thermal conductivity than water and impedes heat transfer. Scale can also be a factor in under-deposit corrosion.

There are many references that provide a great deal of information on open cooling water systems. These include EPRI documents,[1] technical books,[2, 3] and water treatment chemical supplier handbooks.[4, 5, 6, 7]

Reasons/Drivers for Non- and Low-Phosphorous Programs

Phosphorous and nitrogen act as nutrients in surface waters. These nutrients are related to algae blooms in surface water that result in low dissolved oxygen and fish kills. USEPA publishes recommended water quality criteria to reduce problems associated with excess nutrients in water bodies in specific areas of the country.

This results in adopting regional-specific and locally appropriate water quality criteria for nutrients in lakes, reservoirs, rivers, streams, and wetlands in fourteen ecoregions. Figure 1-1shows the Draft Aggregations Level III Ecoregions for the National Nutrient Strategy.[8]

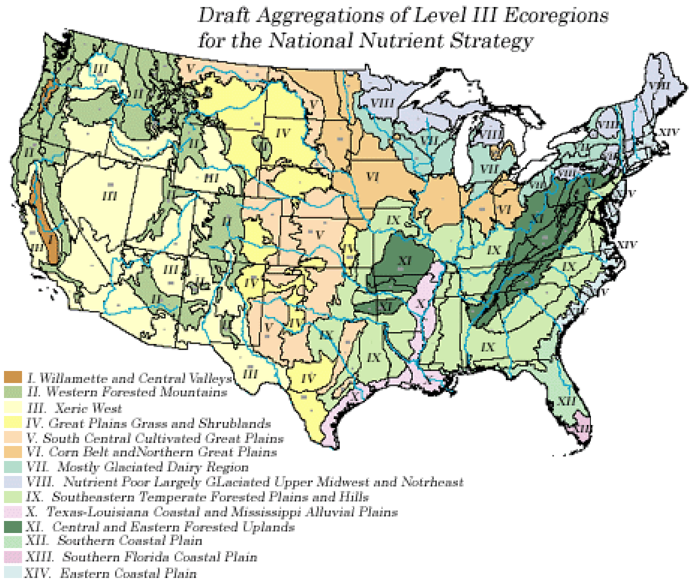


Figure 1-1
Level III Ecoregions for the National Nutrient Strategy

States are required to develop an impaired water list.[9] The number of phosphorous based impairments varies widely state-by-state. In 2010, there were 13 states (lower 48) with greater than 100 phosphorous impairments, 19 states with 10 to 99 phosphorous impairments, and 16 states with fewer than 10 phosphorous impairments.

Purpose

The purpose of this guideline is to provide information on current cooling water treatment regimes that either do not contain phosphorous or use significantly lower phosphorous levels than conventional treatment regimens.

Scope of Guideline

The guideline is limited to the open cooling water systems used for condenser cooling or auxiliary system cooling in power plants. It does not include treatment regimens for closed cooling water systems as these systems do not normally discharge to the environment.

Microbiological growth and control are outside the scope of this guideline although it is recognized that microbiological growth can play a part in both scaling and corrosion mechanisms. Copper alloy corrosion inhibitors (e.g. azoles) are also outside the scope of the guideline but are often needed in addition to a steel corrosion inhibitor.

Much of the discussion is focused on systems with evaporative cooling towers. Once-through systems often also require treatment for scale and corrosion control. These will be addressed wherever possible.

This guideline discusses specific proprietary cooling water treatment programs from several water treatment service companies (WTSCs). **The fact that these companies and their products are mentioned by name is for informational purposes only and does not imply an endorsement of any of these programs or suppliers by EPRI.** It should also be noted that these companies do not constitute all of the WTSCs that are capable of providing water treatment products to power plants. There are organizations with a national scope that are not listed in this document as well as regional organizations. In addition, the organizations in this document are located in the USA although some of them have international operations.

Assumptions

For purposes of this document, non-phosphorous products are those that do not contain any phosphorous in the chemical molecules that make up the program or in the overall product. Background phosphorous may be present in the makeup water used in the cooling system and does not “count against” a non-phosphorous program.

For purposes of this document, low-phosphorous programs are defined as those that contribute less than 0.5mg/L total phosphorous to the cooling system discharge. Implementation of a low-phosphorous program involves the whole treatment program and may involve makeup treatment, concentration control (cycles of concentration), pH control, and use of low-phosphorous products.

2

CORROSION IN POWER PLANT COOLING SYSTEMS - BASICS

Corrosion can impact a system in more than one way. First of all, corrosion represents a loss of material and a reduction in equipment life. In addition, corrosion generates metal oxides which can act as a system foulant. Microbiologically Influenced Corrosion (MIC), a specialized form of corrosion, often results in significant localized equipment damage.

This report will present the basics of corrosion in cooling water systems. Much more detail can be found in other documents such as References 1 through 7.

Metallurgy

The most common materials in cooling water systems are carbon steel (e.g. mild steel), copper alloys, and 300 series stainless steel. In some cases plastics such as high-density polyethylene (HDPE) and fiber-reinforced plastic (FRP) are used.

There are numerous EPRI publications that discuss the degradation of materials in circulating water and service water systems. These documents include:

- Open Cooling Water Chemistry Guideline.[1]
- Service Water System Corrosion and Deposition Sourcebook.[10]
- Service Water Piping Guideline.[11]
- Life Cycle Management Sourcebook for Nuclear Plant Service Water Systems.[12]
- Sourcebook for Microbiologically Influenced Corrosion in Nuclear Power Plants.[13]

There are other industry documents that deal with degradation mechanisms. These include"

- Nalco Guide to Cooling Water Systems Failure Analysis.[14]
- Cooling Water Treatment Principles and Practice, Colin Frayne [15]

Corrosion Mechanisms

In nature, metals normally exist as oxides, which is their most stable state. When metals are purified or refined, they enter a metastable state. Corrosion is an electrochemical reaction which returns the refined material from the metastable metallic state to the more thermodynamically stable state as an oxide, carbonate, sulfate, or sulfide.

There is both an anode and a cathode in the corrosion reaction. The corrosion occurs at the anode as shown in Figure 2-1.

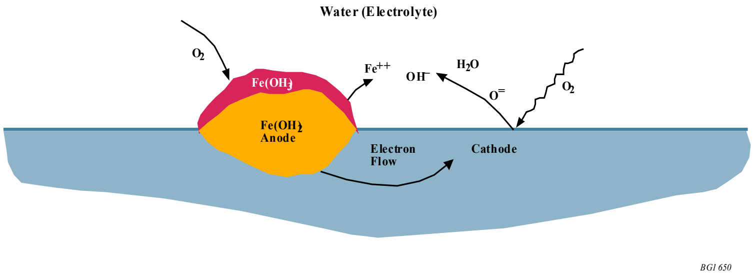


Figure 2-1
Corrosion Diagram
Source: ChemTreat

There are several different corrosion mechanisms.

General Corrosion

General corrosion refers to essentially uniform loss of metal from the surface of the metal exposed to the corrodent (in this case, circulating or service water). Anodic and cathodic sites are not fixed, so that any location may act as an anodic site at one moment and a cathodic site at the next. This shifting of anodic and cathodic sites results in loss of metal over the entire surface.

Localized Corrosion

Localized corrosion is where the corrosion occurs in a limited area of the metal surface. It is of particular concern because the localized rate of corrosion may be high and lead to through-wall failure. Types of localized corrosion include pitting corrosion, crevice corrosion, and galvanic corrosion.

Pitting is defined as localized corrosion on broadly exposed surfaces. It is of concern because the pits can penetrate the metal rapidly and result in through-wall failure.

Crevice corrosion is a form of localized corrosion that is caused by a geometric discontinuity that promotes the formation of local anodic areas. The crevice causes a stagnant condition that maintains a separation between anodic and cathodic areas.

Galvanic corrosion is caused when two dissimilar metals are connected and exposed to a water solution. The less noble metal becomes anodic and the more noble metal becomes cathodic. This creates a galvanic corrosion cell. The anode deteriorates rapidly while the cathode is given greater corrosion resistance than it normally would have as a result of the electron transfer

Environmentally Assisted Cracking

Several specific types of corrosion fall into the category of environmentally assisted cracking (EAC), including stress corrosion cracking (SCC), hydrogen damage (hydrogen embrittlement), and corrosion fatigue. EAC occurs due to the combination of loading and environmental conditions. EAC is especially insidious because the corrosion proceeds quite rapidly as compared to other forms of corrosion.

Stress corrosion cracking involves the metal being subject to a tensile stress and a corrosive environment. SCC can occur in carbon steel but is more associated with stainless steels exposed to a high-chloride environment and copper alloys exposed to ammonia.

Other environmentally assisted cracking mechanisms include corrosion fatigue and hydrogen damage. These are not typical in cooling water systems.

Dealloying or selective leaching can occur in some copper alloys, particularly brass alloys. One element in the alloy is selectively attacked which damages the integrity of the alloy.

Some alloys are susceptible to erosion or cavitation mechanisms. This can occur with softer metals such as many copper alloys when exposed to high water velocities. Cavitation is a special case, usually with respect to pump impellers, where localized negative pressure (vacuum) results in the formation of gas bubbles which attack the metal when they burst. Cavitation can also occur where there are rapid changes in velocity, such as downstream of flow orifices.

Microbiologically Influenced Corrosion

Microorganisms working in conjunction with traditional corrosion mechanisms can significantly alter the kinetics of the reaction - hence the name microbiologically influenced/induced (MIC) corrosion. The corrosion inducing aspect of the MIC name usually refers to the establishment of a deposit or crevice by microbiological growth thereby initiating corrosion which otherwise would not occur. Microorganisms influence corrosion in many ways, such as:

- Excretion of metabolic byproducts which accelerate corrosion.
- Concentration of halides which rapidly corrode ferrous materials.
- Interference with the cathodic half-reaction under oxygen-free conditions resulting in increased anodic dissolution.
- Oxidation of metallic cations to less soluble forms (e.g., Fe^{+2} to Fe^{+3} by iron oxidizing bacteria).
- Destruction of protective coatings.
- Destruction of corrosion inhibitors.

Both aerobic and anaerobic bacteria can be found in service water systems and both types can cause microbiologically influenced corrosion. They can live under a wide variety of temperatures and pressures. Some of the species which are likely to be found in service water systems are described below.

Sulfate Reducing Bacteria

The sulfate reducing bacteria (SRB) *Desulfovibrio* and *Desulfomaculum* are responsible for the largest economic impact of all the bacteria associated with MIC. These anaerobic bacteria convert sulfate to sulfide. The sulfide is very aggressive to cast iron, carbon and low alloy steels, stainless steels, high nickel alloys, and copper alloys. The pitting of copper alloys is significantly increased in the presence of as little as 0.2 mg/L sulfide.

SRB damage to stainless steel and carbon steel is indicated by the presence of black iron sulfide (FeS). Pitting in high nickel and copper based alloys can often be attributed to sulfide attack.

Iron and Manganese Bacteria

Pseudomonas bacteria are aerobic slime formers. They contribute to MIC by scavenging oxygen and forming biofilm deposits which can harbor SRB. *Pseudomonas* can also reduce Fe^{+3} to Fe^{+2} which can contribute to corrosion by exposing bare metal.

Gallionella bacteria are associated with the pitting of carbon and stainless steels. They are aerobic iron bacteria that excrete high levels of iron and manganese in their waste. The morphology of stainless steel pits caused by these microbes is characterized by a small opening leading to a cavernous corroded area. Corrosion deposits on carbon steel are hemispherical.

Crenothrix, *Leptothrix*, *Clonothrix*, and *Sphaerotilus* are aerobic, filamentous iron oxidizing bacteria. They oxidize soluble iron to the insoluble $Fe(OH)_3$. Hemispherical tubercles which are typically brown or reddish brown are formed by these bacteria.

Sulfur Oxidizing Bacteria

Thiobacillus and *Ferrobacillus* are aerobic bacteria which oxidize sulfide to sulfate and form sulfuric acid. They often coexist with the sulfate reducing bacteria. They appear to be much less damaging to metals than they are to concrete.

Thiothrix and *Beggiatoa* are aerobic bacteria that oxidize H_2S to elemental sulfur. The yellow sulfur reaction product is often visible when these bacteria are present. Their major contribution to MIC is the formation of slime in which SRB can live.

3

MINERAL SCALE IN POWER PLANT COOLING SYSTEMS - BASICS

Description of Scale Formation

Water contains many dissolved minerals which have a tendency to precipitate when exposed to the conditions within an open cooling water system. Precipitation in the form of crystalline growth occurs when the solubility of the chemical compound is exceeded. The term scale applies when the precipitate crystallizes on the surfaces of the equipment within the open cooling water system thereby forming a hard, tenacious layer. The most commonly found scales are compounds of calcium and include calcium carbonate, calcium sulfate and calcium phosphate. Of these, calcium carbonate is the most prevalent scale. Other scales which have been encountered are silica, manganese, magnesium silicate, iron oxide and magnesium oxide deposits. More than one mineral scale type can form in a given deposit.

The formation of scale creates a problem because the scale usually accumulates on a heat transfer surface. Scales have low thermal conductivity and act as an insulator. This impairs the heat transfer capability of the equipment. In addition, scale accumulation can interfere with eddy current testing.

Scaling Species

The most common scaling species are calcium carbonate, calcium sulfate, calcium phosphate, magnesium silicate, and silica. A more detailed discussion can be found in the EPRI Open Cooling Water Chemistry Guideline.[1]

Calcium Carbonate

Almost all natural waters contain dissolved calcium and bicarbonates which are the building blocks of calcium carbonate (CaCO3) scale. The most common forms of calcium carbonate are calcite (a hexagonal colorless crystal) and aragonite (a rhombic colorless crystal). Calcium carbonate displays an inverse solubility relationship with temperature; in other words, it becomes less soluble as the temperature increases, rather than more soluble which is the norm for crystalline substances. This inverse solubility is why calcium carbonate forms preferentially on the hotter surfaces of the service water system, which unfortunately, is usually the heat exchanger tubing. Calcium carbonate is a good insulator, and substantially interferes with heat transfer.

Calcium Sulfate

As stated previously, almost all natural waters contain calcium salts. This is also true of sulfate salts. However, it is common practice in many systems to add sulfate by injecting sulfuric acid to prevent calcium carbonate scale. This is effective because calcium sulfate scale is approximately 40 times more soluble than calcium carbonate. However, at high enough temperatures, calcium and sulfate concentrations, calcium sulfate scale can form. It is very rare, however, in systems which do not add sulfuric acid.

Gypsum ($CaSO_4 \bullet 2H_2O$) is the type of calcium sulfate most likely to form in open cooling water systems. It is a dense, off-white, hard scale that is very difficult to remove. It will normally be found in the hot end of heat exchanger tubes because it becomes less soluble as temperature increases above a temperature of approximately 100^oF. Unlike calcium carbonate, gypsum will not effervesce if contacted by acid. A positive identification of the deposit requires laboratory analysis. Calcium sulfate scale is not pH sensitive as is calcium carbonate scale.

Calcium Phosphate

Calcium phosphate scale is even less soluble than calcium carbonate and begins to form when 5-10 ppm of soluble orthophosphate (PO_4) is present along with about 100 ppm of calcium hardness (as $CaCO_3$). Orthophosphate may occur naturally, but it is more likely to be added as a corrosion inhibitor, or be generated in-situ by the reversion of polyphosphates or phosphonates (also added as part of a chemical treatment program). Tertiary treated sewage effluent contains a substantial amount of orthophosphate which is usually, but not always, removed before using the water in a service water system.

Tricalcium phosphate [$Ca_3(PO_4)_2$] is the form of calcium phosphate scale found in open cooling water systems. It is an amorphous white powder in its pure form but tends to be off-white to tan in color due to included substances within the deposit. Calcium phosphate formation becomes more prevalent as pH and temperature increases and may be the predominant scale in otherwise clean systems. As with all the calcium scales, calcium phosphate has an inverse solubility with temperature and is therefore likely to be found in the heat exchangers (especially the hotter end). It does not effervesce when brought into contact with acid. A laboratory test is required to positively identify the compound.

Silica

One of the most common elements on earth is silica and natural waters contain levels from less than 1 ppm to as much as 90 ppm (as SiO_2). Silica can also be added when silicate corrosion inhibitors are used in the open cooling water system. Under certain conditions, the solubility of silica can be exceeded.

In certain parts of the U.S., especially the Southwest and Northwest, the silica concentration in natural waters is sufficiently high such that the operation of a cooling tower at typical cycles of concentration will cause silica to exceed its solubility. Silica deposits are essentially “glass” and are very difficult to remove and require very aggressive chemical cleaning techniques.

Silica forms a hard white deposit which should be analyzed in a laboratory for positive identification. Silica exhibits a normal solubility/temperature relationship, that is, it becomes more soluble as temperature increases. It is therefore found in cooler areas of the system such as the cooling tower fill. The solubility of silica increases as pH increases.

The safe operating range (in the absence of any silica scale inhibitors) will vary depending upon the total water chemistry and operating conditions of the system. Some precipitating minerals such as calcium carbonate can affect the silica solubility level. At high pH (8.5-9.0) silica is more soluble but the presence of magnesium hydroxide may also cause magnesium and silica deposits. As a "rule-of-thumb", silica scale will not form in low pH cooling waters (<7.5) if the silica concentration is kept below 150 ppm as SiO_2. In the higher pH waters (>8.5) silica may be soluble up to 225 ppm and higher.

Magnesium Silicate

Under certain conditions, magnesium silicate scale can occur in an open cooling water system. Because of the silica content, magnesium silicate is difficult to remove once formed. The color of the pure deposit is white but can be off-white or tan due to other impurities included in the deposit.

Magnesium exhibits retrograde solubility, similar to calcium, so as the temperature and pH increases, the solubility decreases. Silica, on the other hand, demonstrates normal solubility and is more soluble as temperature and pH increase. However, as the pH increases above 8.0, the silica ion converts to the silicate ion with a negative charge, which seeks positively charged cations such as soluble metals or divalent ions such as magnesium.

The mechanism of magnesium silicate scale formation is not well understood. One source[16] states that the formation of magnesium silicate only occurs as a co-precipitation reaction which is initiated by the formation of magnesium hydroxide. Colloidal silica is then adsorbed onto the magnesium hydroxide to form $2MgO \bullet 2SiO_2 \bullet 2H_2O$. Other sources[17,18] take the more traditional approach that magnesium silicate has a solubility limit which depends on the concentrations of both magnesium and silicate ions. However, these sources disagree on the type of magnesium silicate which is formed.

4

CHEMICAL BUILDING BLOCKS OF WATER TREATMENT PROGRAMS

Introduction

While corrosion, mineral scale deposition, microbiological growth, and suspended solids accumulation in cooling water systems are considered separate issues, they are interrelated. These relationships must be kept in mind as a comprehensive water treatment program is developed. As noted in Section 1, this document deals mainly with chemicals used for mineral scale, corrosion, and suspended solids control. The document does not address microbiological control.

Also as noted in Section 1, mineral scale accumulation and corrosion are often related. As cooling water pH decreases, mineral scale formation becomes less likely but carbon steel corrosion rate increases. As cooling water pH increases, the corrosion rate decreases but mineral scale formation becomes more likely.

In many cases, increasing cooling tower cycles of concentration (COC) increases alkalinity and pH and reduces carbon steel corrosion risk but increases mineral scale deposition risk. This only applies up to the point where sulfuric acid is applied for pH control. Sulfuric acid replaces protective bicarbonate and carbonate alkalinity with corrosive sulfate. As COC increase with acid and chlorine addition, both sulfates and chlorides increase, often rendering the water very corrosive. Details on the impact of pH and COC will be discussed in Section 6.

The polymers and other compounds described in this section are manufactured by several companies in the U.S., Europe and Asia. These companies supply their products to the water treatment service companies who develop and apply end-use products using these basic materials. Although there are a few exceptions, for the most part the water treatment service companies do not manufacture the basic materials and polymers that are formulated into water treatment blends.

The intent of this section is to describe some of the basic “building blocks” of mineral scale and corrosion control that will be discussed in more detail in later sections on phosphorous-based, low-phosphorous, and non-phosphorous inhibition programs.

As chromate was phased out of open-recirculating cooling water treatment programs starting in the 1970’s, cooling systems began a trend towards operating at higher pH and alkalinity. Chromate is an excellent corrosion inhibitor for steel and copper alloys, and its removal dictated a need to operate under less corrosive, higher pH and alkalinity conditions where phosphate, zinc, and azole based corrosion inhibitor programs could be effective. More recent restrictions on zinc discharge have continued the push towards less corrosive, higher pH and alkalinity conditions. The beneficial effect of higher alkalinity in reducing steel corrosion has long been established. The Larson-Skold index, developed in 1958, relates the corrosiveness of water to the ratio of aggressive chloride and sulfate ions to alkalinity.[19] Singley developed a more encompassing corrosiveness model that incorporated those factors and included a measure of calcium carbonate solubility along with some additional factors. [20]

Although elevated pH and alkalinity reduce the corrosiveness of water, they also increase the scaling tendency for calcium carbonate and many other minerals as depicted in Figure 4-1.

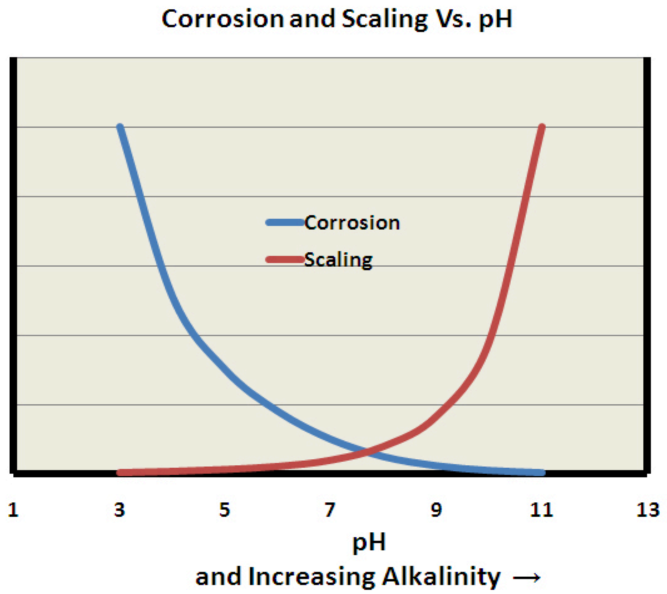


Figure 4-1
Corrosion and Scaling Tendencies vs. pH and Alkalinity
Source: ChemTreat

In contrast to the earlier chromate era where cooling systems were typically operated in the corrosive pH 6.5 range, cooling towers are now typically operated in a scaling regime that requires the presence of highly effective antiscalants. Restrictions on the use of phosphate and zinc will favor still higher pH and alkalinity conditions that stretch the limits of scale control technology. One problem with operating under highly scaling conditions is that the most common and effective calcium carbonate scale inhibitors in use today are organic phosphorus compounds. Most cooling water programs today incorporate one or more organic phosphorus compounds such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), or phosphinosuccinic oligomer (PSO) to inhibit scale formation. Therefore, the first challenge in developing a non-phosphorus corrosion control program is to develop superior non-phosphorus scale inhibitors that will allow operation under high pH and high alkalinity conditions.

Inorganic Chemicals for Corrosion and Scale Inhibition

There are several inorganic chemicals that can play a part in corrosion control. These include orthophosphates, polyphosphates, molybdate, zinc, and polysilicates.

Phosphorous-Based Chemistry

Phosphorous-based chemistry has been a staple of both mineral scale (especially calcium carbonate) and corrosion control. Polyphosphates are used for both corrosion and mineral scale control. Orthophosphate, in the form of stabilized phosphate programs is a mainstay of carbon steel corrosion control.

Polyphosphates

Polyphosphates are produced by dehydration and condensation of orthophosphate. Common polyphosphates are sodium hexametaphosphate, tetrapotassium pyrophosphate, and sodium tripolyphosphate. They are cathodic inhibitors since they react with hydroxyl ion at the cathodic surface. Reversion of the polyphosphates produces orthophosphates which act as anodic inhibitors. However, this reversion product is a potential scale-former with calcium and a foulant with iron, particularly if there is a loss of pH control or dispersant feed.

Polyphosphates are also known for their ability to sequester iron and calcium to help with deposition control

When used alone, polyphosphate dosage is usually in the range of 5 to 10 ppm as PO_4. However, in some cases dosages as low as 1 ppm have been effective. There has been some use of polyphosphates in once-through systems at threshold concentrations less than 1 ppm.

Since polyphosphates are cathodic inhibitors, underfeed leads to increased general corrosion but not pitting corrosion. They are nutrients for algal growth in cooling towers. When discharged into the waste system, they can cause algal blooms in lagoons and can contribute to eutrophication. They can, however, be removed by treatment before discharge.

Common polyphosphates are:

- Sodium hexametaphosphate (SHMP)
- Tetrapotassium pyrophosphate (TKPP)
- Sodium tripolyphosphate (STPP)

Polyphosphates do not protect copper and aluminum. They may be aggressive toward these alloys, especially if overfed. In many locations, environmental limitations on phosphate discharges may limit the use of polyphosphates as corrosion or scale inhibitors.

Stabilized Phosphate

After the chromate era, orthophosphate became the mainstay for carbon steel corrosion control in cooling water systems.

Under neutral pH conditions orthophosphate greater than 10 ppm acts primarily as an anodic corrosion inhibitor. The orthophosphate ion reacts with oxygen and the steel's surface to form a thin, protective gamma-iron oxide film. A polymeric dispersant is required to inhibit calcium orthophosphate from forming at high o-PO_4 concentrations. As the system pH increases, lower orthophosphate residuals are maintained (less than 10 ppm) and orthophosphate acts as a cathodic inhibitor and will tend to precipitate at the high pH formed at the cathode. Some orthophosphate can react with calcium in the water and deposit a thin layer of tricalcium phosphate at cathodic sites.

A minimum level of calcium, usually greater than 50 ppm, is required for steel inhibition with orthophosphate. Polymeric dispersants are used to maintain calcium orthophosphate solubility with increased concentrations and higher pH and alkalinity. These are considered “stabilized phosphate” programs. The chemicals used as phosphate stabilizers are discussed in the section on “Non-Phosphorous Polymers” below.

Dosages of orthophosphate are typically in the range of 5 to 20 ppm as PO_4. In some cases, dosages as low as 1 ppm have been effective. Threshold treatment dosages for once-through systems below 1 ppm have been shown to be effective in reducing corrosion.

Because orthophosphate is an anodic inhibitor, underfeed can lead to pitting. This is because underfeed of an anodic corrosion inhibitor can leave some areas of the metal surface unprotected. The corrosion driving force is then concentrated in the unprotected areas.

Overfeed of orthophosphates, loss of pH control, or over cycling the cooling water can lead to the formation of tricalcium phosphate [$Ca_3(PO_4)_2$] and iron phosphate foulants.

In many locations, there are environmental limitations on phosphate discharges. This may limit the use of orthophosphates as corrosion inhibitors. This is a primary driver for low-phosphorous and non-phosphorous corrosion control programs.

Biological organisms require carbon, phosphorus, and nitrogen for their metabolism. Orthophosphate provides one of the nutrients that can promote algae and other biological growth.

Molybdate

Molybdate is an anodic inhibitor for steel corrosion control. It is not considered a copper alloy corrosion inhibitor. It is in the same chemical group as chromate. Molybdate is usually combined with another corrosion inhibitor such as zinc or phosphate. Molybdate is not widely used as a stand-alone corrosion inhibitor in open cooling systems due to cost considerations.

The typical dosage range for molybdate when used alone is 10 to 20 ppm as MoO_4 (6 to 12 ppm as Mo). In some cases lower dosages have been successful.

The corrosion control abilities of molybdate are not well documented and the cost is typically high.

While molybdate is not considered highly toxic, discharges are often regulated. Many public treatment works regulate the discharge of molybdate to sewer systems to limit its concentration in sludge intended for land application. Molybdate is also heavily regulated in Western Europe.

Zinc

Zinc is a cathodic inhibitor. It reacts with hydroxyl ion at the locally high pH cathodic surface. Since zinc is a cathodic inhibitor, underfeed leads to increased general corrosion but not pitting corrosion. Zinc is typically used with other inhibitors such as orthophosphate and polyphosphate.

Zinc is typically used in the range of 0.2 to 3 ppm as soluble zinc. Since it is used in combination with other inhibitors, usually phosphate, the effective dosage may be as low as 0.2 ppm. Dosage requirements are site-specific and depend on system operating conditions and water quality considerations.

Unless adequately stabilized using polymeric dispersants, zinc can contribute to zinc hydroxide fouling at elevated pH levels. Zinc is typically “base fed” based on flow without attempting to recover all the zinc, as much will be insoluble and precipitate onto surfaces.

Zinc-adversely affects aquatic life at low levels and discharge is often restricted. In the United States, power plants are restricted to discharging no more than 1 ppm total zinc. In many cases, the allowable discharge may be <0.1 ppm, essentially eliminating zinc as a candidate for corrosion control.

Polysilicates

Glassy amorphous polymeric silicates (polysilicates) can provide corrosion protection. Polysilicates are considered adsorption inhibitors.[21] With continuous feeding of the silicates, the protection extends to the cathodic areas.[22] The most common sodium silicate for this use is the 3:22 SiO_2:Na_2O weight ratio. For lower pH waters, a more alkaline silicate can be used.[23] Silicates can be used to protect copper, aluminum, and cast iron as well as carbon steel.

An initial dosage of approximately 25 ppm above background (or greater) is used for the first one to two months. After the initial dosage period, a maintenance dosage of approximately 8 to 10 ppm is used. Maintenance dosages as low as 4 to 5 ppm have been used. The high level has an impact on economics. Also, the film formed by silica is fragile and can be easily penetrated by corrosive chlorides and sulfates.

Silicates may displace iron oxide deposits in existing systems and cause “red water” problems. The protective film is fragile and is lost if not replenished continuously. Polysilicates work best under flowing conditions. They are much less effective under static (stagnant) conditions. Silicates should not be used if total silica in the cooling water will approach 150 ppm due to potential silica scale issues.

Polysilicates have no effect on biological waste systems nor are they affected by reducing conditions. There are few environmental restrictions on silicates but permitting would be required in many cases.

Phosphorous-Containing Organic Chemicals

There are several organo-phosphorous that are very effective for control of calcium carbonate deposition. They can be particularly useful in “low-P” programs because they provide some cathodic inhibition while at the same time allowing the cooling system to operate at a less corrosive alkaline pH without calcium carbonate deposition.

Organo-Phosphorous Compounds (Phosphonates)

Phosphonates can be grouped into two general categories, amino-phosphonates and non-nitrogen phosphonates. Amino-phosphonates suffer from poor chlorine stability and see limited use in cooling systems today. Amino-phosphonates are generally excellent inhibitors for sulfate salts and are widely used in reverse osmosis (RO) scale inhibitors. Non-nitrogen phosphonates, HEDP and PBTC, are primarily used in industrial cooling systems today.

Phosphonates inhibit calcium carbonate deposition primarily by threshold stabilization that interferes with the nucleation and aggregation of calcium carbonate crystals.

Organic phosphates are produced from "thermal phosphorus" (P_4). In most cases, P_4 is reacted with chlorine gas to produce PCl_3, a more stable intermediate. PCl_3 is hydrolyzed to phosphorous acid. The United States has no thermal phosphorus capacity.

The most common organo-phosphorous compounds are discussed below.

HEDP (1-hydroxyethylidene-1,1-diphosphonic acid)

The structure of HEDP is shown in Figure 4-2. The molecule contains approximately 30% phosphorous by weight (92% as PO_4). HEDP provides excellent calcium carbonate scale inhibition even at low dosages, <1 ppm. It is typically applied in cooling towers at dosages of 0.5-6 ppm, with the higher dosages used to provide carbon steel corrosion protection as well as calcium carbonate scale control in the alkaline range (>pH 8.0). HEDP provides good chlorine stability, but degrades over time in the presence of bromine. HEDP performance is negatively affected by iron. At high pH and at high HEDP concentrations HEDP can precipitate with calcium. HEDP can be aggressive to galvanizing at high concentrations.

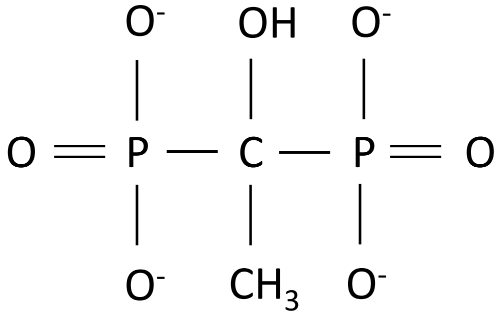


Figure 4-2
HEDP Structure

PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid)

PBTC contains about 12% phosphorous by weight (35% as PO_4). It is considered effective for calcium carbonate scale control under highly stressed conditions such as higher calcium hardness, high calcite supersaturation (high LSI), or temperature conditions. While most phosphonates were originally developed and introduced by the historic Monsanto Company, PBTC was developed somewhat later by the German Bayer chemical company under the Bayhibit trade name and remained on patent several years later than HEDP. PBTC has excellent stability with respect to both chlorine and bromine. It is much more tolerant of iron than HEDP and does not precipitate with calcium in high pH and high calcium environments. As with other organic phosphates, PBTC is an effective cathodic inhibitor for steel at higher dosages. PBTC has both phosphonic and carboxylic functionality. This may provide some corrosion control functionality. PBTC is usually more expensive than HEDP and requires 50-100% higher dosage than HEDP, but its more robust nature makes it preferable in many circumstances. PBTC also contributes less phosphate, 35% PO_4 vs. 92% PO_4 for HEDP. Blends of PBTC and HEDP are commonly used to provide combined corrosion and scale control in alkaline (>pH 8.0) cooling water treatment programs. The structure is shown in Figure 4-3.

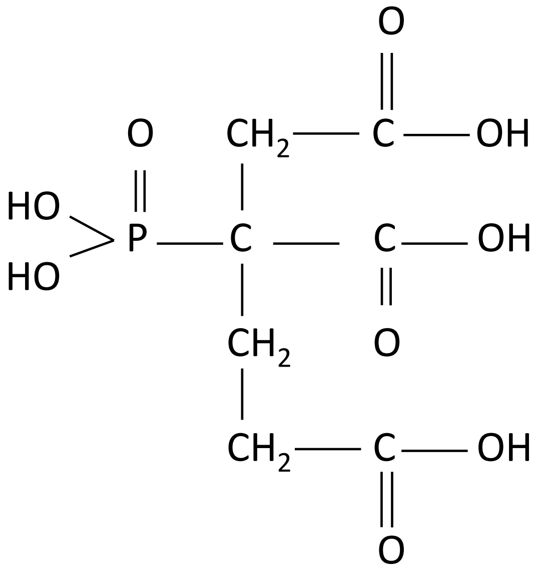


Figure 4-3
PBTC Structure

AMP (or ATMP, or NTP) [Amino tri(methylene phosphonic)] acid

AMP is one of the early phosphonates used in cooling water treatment. As a calcium carbonate inhibitor, it is somewhat less effective than HEDP and the amine linkage is very susceptible to degradation by chlorine. AMP is somewhat lower cost than HEDP and still finds occasional use in cooling water treatment. In the 1980’s AMP-zinc programs were widely used in the hard waters of Western Europe for corrosion and scale protection. The metal ligand renders the AMP more resistant to chlorine degradation. AMP is an excellent chelant, being the phosphonic acid equivalent of NTA. As with other amino phosphonates, AMP is also an excellent calcium sulfate inhibitor.

The structure of AMP is shown in Figure 4-4. The AMP molecule contains approximately 31% phosphorous by weight (95% as PO4).

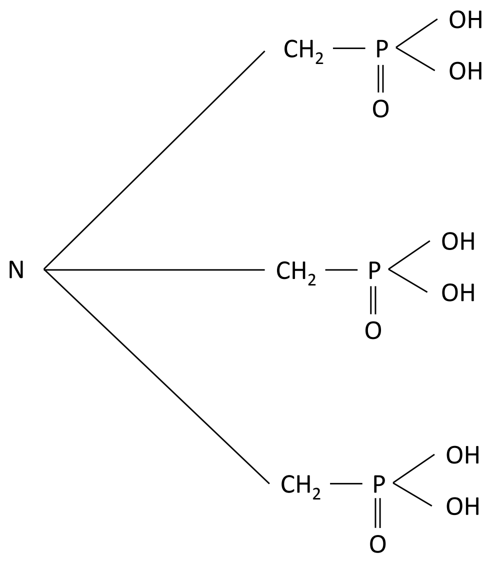


Figure 4-4
AMP Structure

Phosphono/Phosphino Compounds

PSO (Phosphino Succinic Oligomer)

PSO is a proprietary phosphonate developed primarily for use as replacement for polyphosphate as a cathodic corrosion inhibitor. Like other organic phosphates it also has some calcium carbonate scale inhibiting properties at higher dosages. PSO is chlorine tolerant like other non-amine organic phosphates. PSO is produced as a reaction product of maleic acid or fumaric acid with excess hypophosphite, resulting in several short chain polymers ("oligomers"), chiefly the one shown in Figure 4-5.

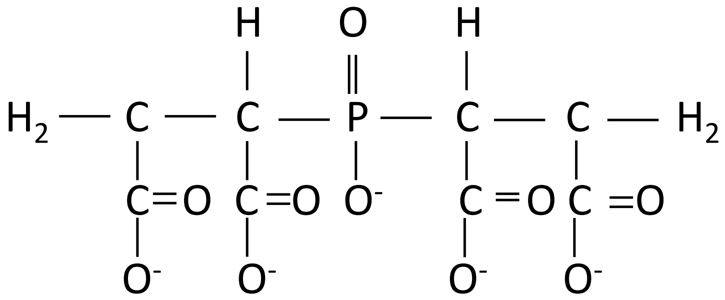
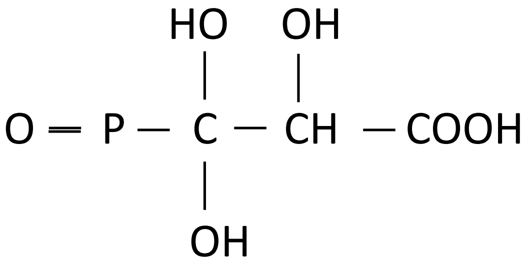


Figure 4-5
PSO Structure

HPA (Hydroxyphosphonoacetic Acid)

HPA is also called Hydroxyphosphonocarboxyllic acid (HPA) and Phosphono hydroxyacetic acid (PHA). The structure is shown in Figure 4-6. HPA degrades to orthophosphate very rapidly in the presence of chlorine. Its poor chlorine stability generally limits it to use as a corrosion inhibitor in closed cooling systems and in formulations containing more halogen stable scale inhibitors and calcium phosphate dispersants.



$$O = P - \overset{\displaystyle HO}{\underset{\displaystyle OH}{C}} - \overset{\displaystyle OH}{CH} - COOH$$

Figure 4-6
HPA Structure

PAPEMP (Polyamino Polyether Methylene Phosphonate)

PAPEMP serves both as a calcium carbonate scale inhibitor and a carbon steel corrosion inhibitor. As with other amino phosphonates, it has poor chlorine stability. It is occasionally used in cooling systems conjunction with bromine chemistry where high calcium tolerance and high pH are required. The structure is shown in Figure 4-7

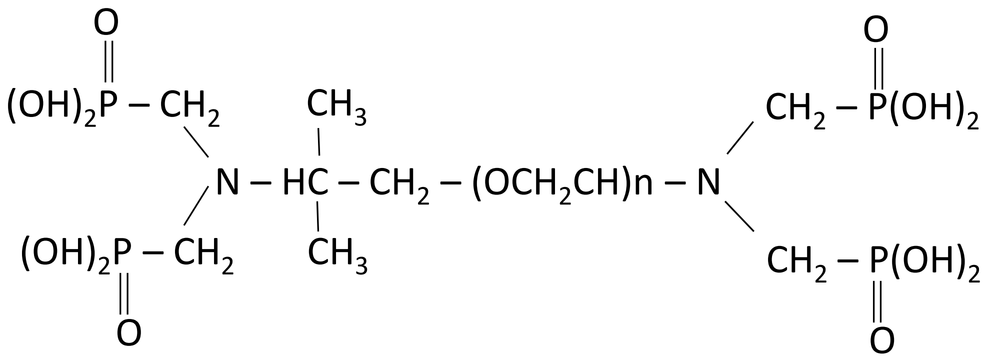


Figure 4-7
PAPEMP Structure

Non-Phosphorous Polymers

There is a wide range of non-phosphorous polymers that are used in water treatment. While most contribute mainly to scale control, many also have some corrosion control capability. These polymers consist of homopolymers, copolymers, and terpolymers. All water treatment polymers are produced using the free radical polymerization process. Free radicals are molecules containing a highly reactive unpaired electron, which has a strong affinity to strip electrons from another molecule. Carbon-carbon double bonds are particularly susceptible, since the second pair of electrons is less tightly held. In free radical polymerization, a monomer containing typically a single carbon-carbon double bond is charged to a reaction vessel along with a free radical initiator, typically a persulfate salt or hypophosphite salt. The initiator dissociates into free radicals, which "attack" the double bond on the monomer. The free radical splits the pair of electrons that comprise the second bond, covalently binding to the monomer and leaving one carbon with another highly reactive unpaired electron, which in turn attacks and adds onto another monomer. The polymerization process continues until the growing polymer chain encounters another free radical either from another initiator molecule, or from another growing polymer chain.

Homopolymers are polymeric compounds produced from a single monomer. Copolymers are constructed of two monomers with different functional groups. These may be carboxylate and sulfonate groups, hydroxyl groups, carboxylate and amid groups, etc. Terpolymers are constructed of three different monomers. Quad polymers are constructed with four monomers, and so on. Average molecular weight, molecular weight distribution, monomer ratio, branching, the length of side chains, the nature of the polymerization (random, block, or alternating e.g. AAABBB or ABABAB), and end groups are all characteristics that can be controlled by the polymer chemist. The polymerization process can be conducted entirely in the aqueous phase, or begun in a solvent phase and quenched in an aqueous phase. A recent trend is the incorporation of monomers that are relatively hydrophobic, or less charged, which often improves adsorption and performance.

As a general rule of thumb, carboxylic acid functionality (PAA, PMA) tends to perform best on calcium carbonate and calcium sulfate, making these the most useful as non-P substitutes for phosphonates under alkaline conditions. Sulfonated functionality tends to be best for calcium phosphate, iron, manganese, zinc hydroxide and zinc phosphonate. Lower molecular weight is often better for scale control. Somewhat higher molecular weight is better for silt. Still higher molecular weight is better in controlling silica.

Polymers, especially polymaleics, function primarily by crystal distortion and are often combined with crystal inhibiting phosphonates to provide the most effective scale control under very high calcite supersaturation levels.

Polyacrylates

Polyacrylates (polyacrylic acid and sodium polyacrylate) are the most widely used homopolymers in water treatment.

Description

Polyacrylates are widely used in water treatment applications. Polyacrylates can be produced with molecular weights ranging from about 1,000 to greater than 200,000. Molecular weights of less than 10,000 are used in water treatment applications. Different production techniques can result in a range of molecular weight distributions. Polyacrylates are often supplied as the sodium salt (sodium polyacrylate).

Applications

Polymers based on polyacrylic acid (PAA) can be effective for calcium carbonate and calcium sulfate scale control. They are not highly effective as calcium phosphate scale control agents, nor are they very effective as iron and manganese dispersants or stabilizing zinc hydroxide and phosphate. Polyacrylates are also effective as suspended solids dispersants, particularly on swelling clays (bentonite). As with all polymers, the molecular weight and molecular weight distribution are important factors in their effectiveness as scale inhibitors and dispersants. Molecular weights in the 2,000 range are typically most effective as scale inhibitors and higher molecular weights (5,000-10,000) are typically effective as suspended solids dispersants.

Structure

The structure of polyacrylic acid is shown in Figure 4-8.

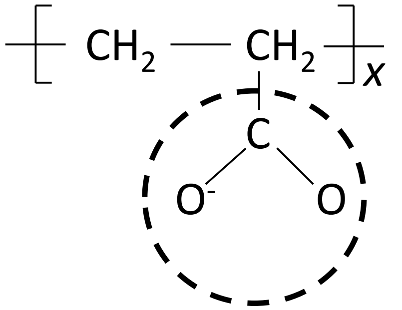

(charged carboxylic acid group)

Figure 4-8
Polyacrylic Acid Monomer

Polymethacrylates

Polymethacrylates are not commonly used in water treatment formulations but do find some application in boiler water applications.

Description

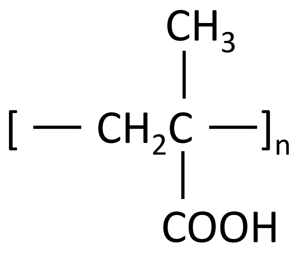
Polymethacrylates have a methyl group substituted for the hydrogen atom in polyacrylates.

Applications

Polymethacrylic acid polymers are used for the same scale deposition and suspended solids control as polyacrylates, primarily in boiler applications. In addition, polymethacrylates have better iron oxide dispersion properties.

Structure

The structure of polymethacrylic acid is shown in Figure 4-9.



$$\left[- CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}} - \right]_n$$

Figure 4-9
Polymethacrylic Acid Structure

Polymaleic Acid (PMA)

Description

PMA is a non-phosphorous homopolymers, produced by polymerization of maleic anhydride. The structure of maleic anhydride is shown in Figure 4-10.

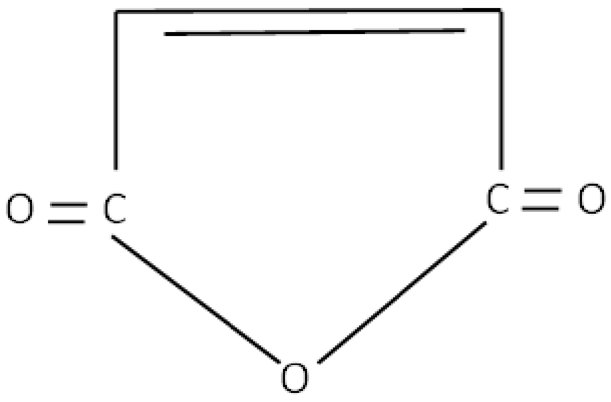


Figure 4-10
Maleic Anhydride

During aqueous phase polymerization, the ring opens, resulting in a polymer structure that is essentially polyacrylic acid, except with each carbon along the backbone having a charged carboxylic acid group as shown in Figure 4-11

Structure

The structure of polymaleic acid is shown in Figure 4-11.

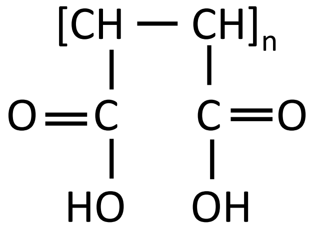


Figure 4-11
Polymaleic Acid Structure

When the polymerization occurs in the solvent phase, not all of the maleic anhydride hydrolyzes and the resulting maleic homopolymer is sometimes depicted as a copolymer as shown in Figure 4-12.

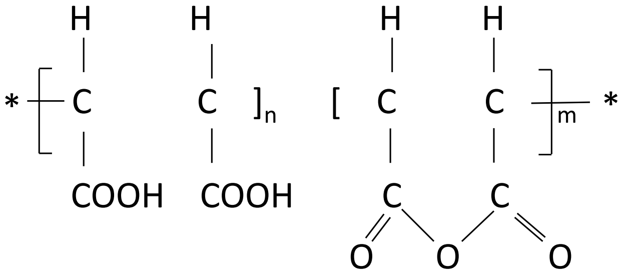


Figure 4-12
Maleic Copolymer

Applications

PMA is used in water treatment formulations primarily as a calcium carbonate scale inhibitor. As a calcium carbonate scale inhibitor, PMA is used under stressed conditions involving high calcium levels, alkalinity, and temperature. It also finds some use as a silica scale inhibitor.

Alkyl Epoxy Carboxylate (AEC)

AEC is a non-phosphorous polymer for calcium carbonate scale control.

The structure of AEC is shown in Figure 4-13.

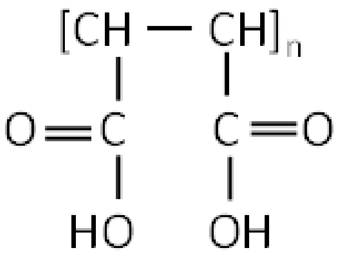


Figure 4-13
AEC Structure

Polyaspartic Acid (PASA)

Description

PASA is a non-phosphorous scale inhibitor. Although less effective as a scale inhibitor than PAA or PMA, polyaspartic acid has the advantage of being more readily biodegradable, an important factor in some Western European applications.

Applications

PASA is claimed to control calcium carbonate, calcium sulfate, barium sulfate, and calcium phosphate deposition.

Structure

The structure of polyaspartic acid is shown in Figure 4-14.

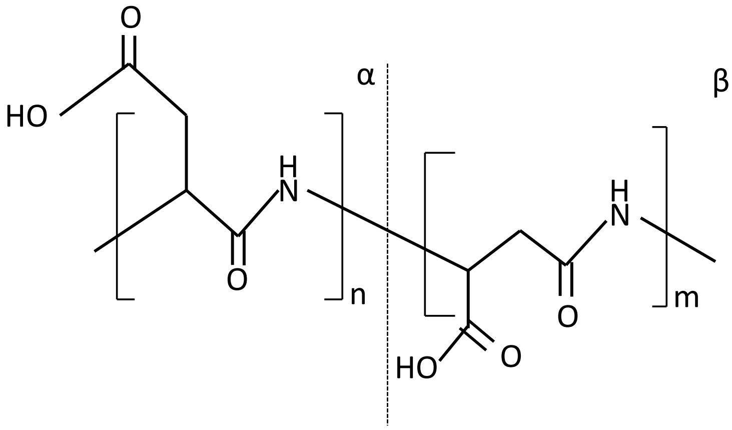


Figure 4-14
Polyaspartic Acid Structure

Sulfonated Polymers

Many of the water treatment copolymers contain one or more of the sulfonated polymers. Although calcium phosphate inhibition is the main reason for selecting sulfonated polymers, phosphate is often present in makeup waters. Natural waters frequently contain 0.2-0.5 ppm ortho phosphate. Many cities add 0.5-2 ppm phosphate to comply with lead and copper regulations. Phosphate is also present at high levels in many grey waters.

Sulfonated Styrene (SS)

Description

Sulfonated styrene is used in several copolymer blends such as sulfonated styrene – maleic anhydride (SS-MA) and AA/AMPS/SSMA.

Applications

Copolymers made with sulfonated styrene have good temperature resistance and iron and phosphate dispersion capabilities. Sulfonic acid remains charged at low pH which can provide improved formulatability at low pH and effectiveness in very low pH applications. The high cost of the sulfonated styrene monomer limits its commercial application.

Structure

The structure of sulfonated polystyrene is shown in Figure 4-15.

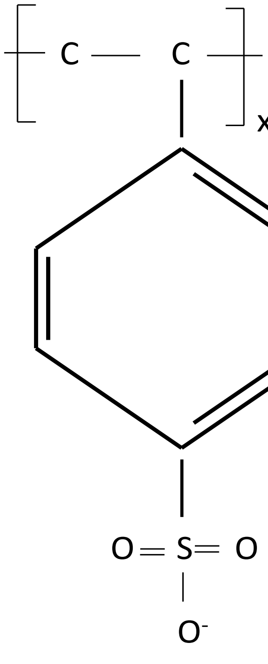


Figure 4-15
Sodium Styrene Sulfonate Structure

2-Acrylamido-2-methylpropane Sulfonic Acid (AMPS®)

Description

AMPS is a sulfonated monomer.

Applications

AMPS is used in copolymers and terpolymers. It provides excellent calcium phosphate dispersion characteristics.

Structure

The structure of the AMPS polymer is shown in Figure 4-16.

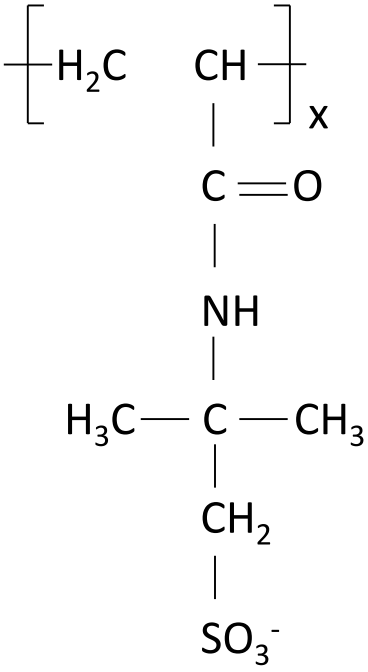


Figure 4-16
AMPS Polymer Structure

Tertbutyl Acrylamide (TBA)

Description

TBA is similar to AMPS without the sulfonic group.

Applications

TBA is an excellent calcium phosphate inhibitor.

Structure

The TBA structure is shown in Figure 4-17.

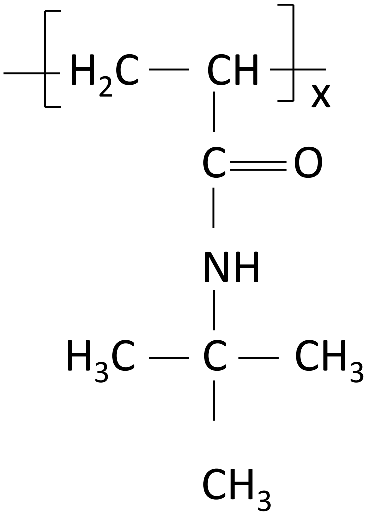


Figure 4-17
Tertbutyl Acrylamide

Copolymers

There are many copolymers available from water treatment service companies. Some of the most common are:

- AA/AMPS (acrylic acid/2-acrylamido-2-methylpropane sulfonic acid)
- SS/MA (sulfonated styrene/maleic anhydride)
- AA/MA (acrylic acid/maleic anhydride)

Terpolymers

There are also numerous terpolymers available in the water treatment market. These include:

- AA/AMPS/SS (acrylic acid/2-acrylamido-2-methylpropane sulfonic acid /sodium styrene sulfonate
- AA/AMPS/TBA acrylic acid/2-acrylamido-2-methylpropane sulfonic acid/tert butyl acrylamide

5

CONVENTIONAL PROGRAMS FOR CORROSION & SCALE CONTROL WITH SIGNIFICANT PHOSPHOROUS

Introduction

After chromate chemistry was phased out as the basis of corrosion control programs for open cooling water systems in the 1970-1980 timeframe, phosphorous became a main component. Orthophosphates along with polyphosphates are often used as carbon steel corrosion inhibitors.

Metallurgy Considerations

Orthophosphates and polyphosphates are carbon steel corrosion inhibitors. They do not protect copper alloys.

Relationship of Corrosion and Scale Control

Corrosion control and scale control go hand-in-hand in many ways. Conditions that tend to reduce carbon steel corrosion rates such as increasing cycles of concentration or pH may also tend to increase scaling tendency. Likewise, conditions that tend to reduce scaling tendency such as decreasing cycles of concentration or lowering pH may also tend to increase corrosion rates.

Corrosion vs. pH

Carbon steel corrosion rates are significantly influenced by pH. Figure 4-1 showed the relationship between pH and the relative corrosion rate of low carbon (mild) steel. It also shows the relationship between pH and scaling tendency.

The tendency for calcium carbonate scale formation can be lessened by reducing pH. However, this may increase the tendency for carbon steel corrosion and may require a more robust corrosion inhibition program, which may use a phosphorous-containing chemical. In addition, pH reduction with sulfuric acid may lead to calcium sulfate deposition.

Scale vs. Cycles of Concentration

Most waters used as cooling tower makeup contain some of the ions that can contribute to scale formation. Primarily, these are calcium, magnesium, and silica. Barium and strontium are less common but are present in some waters and can lead to scale formation.

Corrosion Control – Significant Phosphorous

Many of the most common corrosion control agent contain significant levels of phosphorous. These have been a mainstay of water treatment for the past 40 to 50 years.

Stabilized Phosphate

The stabilized phosphate treatment regimen was discussed in Section 4. In most cases, phosphate levels of 5 to 20 ppm as PO_4 (1.6 to 6.5 ppm P) are applicable.

Polyphosphates

A discussion of polyphosphates is also found in Section 4. In most cases, phosphate levels of 5 to 10 ppm as PO_4 (1.6 to 3.3 ppm P) are applicable.

Calcium Carbonate Scale Control – Significant Phosphates

For electric utility power plants and other large industrial facilities, conventional scale control programs will use a combination of concentration control, pH control and a scale inhibitor. The specific operating cycles of concentration, pH range, scale inhibitor, and scale inhibitor concentration will be a function of makeup water quality and operating conditions.

What is defined here as "conventional" scale control programs use chemicals such as polyphosphates or organo-phosphorous compounds. Many of these contain phosphorous in excess of 20% by weight.

Summary of Scale Inhibitors Containing Significant Phosphorous

Table 4-1 shows the typical calcium carbonate scale inhibition products that contain significant phosphorous ("high-phosphorous" products). These range from 20% to 31% phosphorous by weight.

Table 5-1
Summary of Scale Inhibitors Containing Significant Phosphorous

Name	Acronym	Formula	MW	Weight P	%P
Aminotris-methylenephosphonic acid	ATMP	$C_3P_3O_9H_{12}N$	298.91	92.91	31%
1-Hydroxyethylidene-1,1-diphosphonic acid	HEDP	$C_2O_7P_2H_7$	204.94	61.94	30%
Sodium tripolyphosphate	NATPP	$Na_5P_3O_{10}$	367.91	92.91	25%
Tetrapotassium pyrophosphate	KTPP	$K_4P_2O_6$	314.34	61.94	20%
Sodium hexametaphosphate	SHMP	$Na_6P_6O_{18}$	449.91	92.91	21%

6

BASICS OF LOW-PHOSPHOROUS SCALE AND CORROSION CONTROL PROGRAMS

What is Considered Low-Phosphorous?

There is no single definition of what is a “low-phosphorous” treatment program. The definition will be driven by site-specific environmental regulations. In many cases “low-phosphorous” will be defined as a program that contributes less than 1.0 mg/l of total phosphorous (3 mg/L of PO_4) or even as low as 0.5 mg/l of total phosphorous (1.5 mg/L of PO_4) to the cooling system discharge stream. This document focuses on approaches to reducing the amount of phosphorous in corrosion and scale control programs rather than setting a single discharge value. Designing a low-phosphorous cooling water treatment program goes beyond just selecting low-phosphorous treatment products. Another factor that may need to be factored in is the presence of phosphate in the makeup water of an evaporative cooling system. For example, if the makeup water contains 0.2 ppm PO_4 (0.17 ppm P), the makeup water will contribute 0.8 ppm PO_4 (0.27 ppm P) in a cooling tower that is operated at 5 cycles of concentration,

Considering the Total Program

There are many ways of implementing a low-phosphorous program. These may include:

- Makeup treatment
- Adjustments in concentration/blowdown control
- pH adjustments
- Use of low-phosphorous treatment products

These are discussed below. A low-phosphorous program may make use of a combination of these methods.

A low-phosphorous water treatment program takes the total program into account. This includes all of the chemicals that are used in the program. All of the phosphorous entering the cooling water must be considered. In addition to the phosphorous contained in the water treatment “molecules” used in the program, it must include any “tramp phosphorous” that is in the product as a result of manufacture.

Corrosion and scale control are usually interrelated. Parameters that impact calcium carbonate scale formation also usually impact corrosion rates. Reducing pH will decrease scale potential but will make the water more corrosive toward carbon steel. Increasing cooling tower cycles of concentration will usually make the water less corrosive toward carbon steel but will increase calcium carbonate scale potential.

Impact of Makeup Treatment

Treatment of water used as makeup to cooling water systems can impact corrosion potential, mineral scale potential, and suspended solids fouling potential. From the standpoint of corrosion and mineral scale in cooling water systems, the makeup treatment processes that are most relevant are hardness removal (softening) and alkalinity reduction/pH control. Since calcium carbonate is the most prevalent scaling species in cooling water systems, hardness removal and alkalinity reduction both reduce the tendency for calcium carbonate scale formation and reduce the need for calcium carbonate scale inhibitors. In addition, in cooling tower systems hardness removal may allow the system to operate at higher cycles of concentration and/or higher pH. Operation at higher pH may reduce the corrosiveness of the cooling water and reduce the need for corrosion inhibitors.

Softening

The softening methods applicable to cooling water makeup treatment are precipitation softening, ion exchange softening, and membrane treatment (nanofiltration/reverse osmosis).

Precipitation Softening

The most common form of precipitation softening is lime softening or lime-soda softening.

For lime softening, calcium hydroxide, $Ca(OH)_2$, is added to the process. It is either added as a lime slurry or produced from calcium oxide in a lime slaker to produce the calcium hydroxide.

The lime slaker reaction is:

$CaO + H_2O \rightarrow Ca(OH)_2$

The most basic chemical reaction in a cold lime softening process is the reaction of calcium bicarbonate with lime to precipitate calcium carbonate.

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

If sufficient alkalinity is present, the cold lime process can reduce calcium hardness to about 50 ppm.

In addition, some magnesium (about 10%) can be removed via the reaction:

$Mg(HCO3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$

Calcium that exceeds the stoichiometric quantity of alkalinity cannot be precipitated by lime alone. Additional alkalinity must be added. This typically is in the form of soda ash (Na_2CO_3). This is called lime-soda softening

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$

The equipment used to separate the precipitated solids from the liquid product is typically a solids-contact clarifier or equivalent.

Membrane Processes – Reverse Osmosis and Nanofiltration

Reverse is a membrane process by which dissolved salts are removed by applying pressure across the membrane. The simplified concept is shown in Figure 5-1

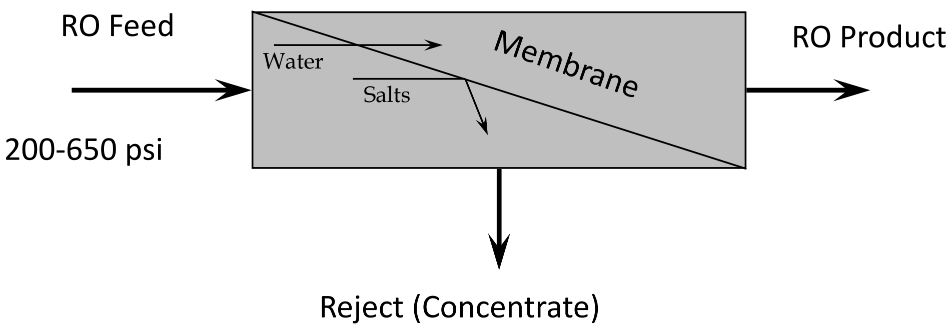


Figure 6-1
Reverse Osmosis Schematic

The pressurized concentrated solution enters the membrane chamber and part of the pure water passes through the semi-permeable membrane and becomes the product. The concentrated solution is discharged to waste.

While a small percentage each ion will pass through the membrane along with the water, the majority are removed. By removing the much of the hardness ions (calcium and magnesium) and silica, the water will not have as much of a tendency to form mineral scale.

The membrane will have a different rejection characteristic for each ion. The salt passage is the portion of an ion (usually expressed as percentage) to pass through the membrane and the salt rejection is the percentage rejected by the membrane. Salt Passage is:

$$\text{SP\%} = 100 \text{ X } \frac{\text{Concentration of Ion in Product}}{\text{Concentration of Ion in Feed}} \qquad (6\text{-}1)$$

Salt rejection (SR) is expressed as:

$$\text{SR\%} = 100 - \text{SP} \qquad (6\text{-}2)$$

The percent recovery (R) of an RO system is the percentage of feedwater that is converted into product.

$$\text{R(\%)} = 100 \text{ X } \frac{\text{Product Flow}}{\text{Feed Flow}} \qquad (6\text{-}3)$$

Recovery needs to be normalized to account for changes in feed pressure and temperature. Appropriate factors are available from each membrane manufacturer.

The concentration factor (similar to cooling tower cycles of concentration) is calculated by the formula:

$$\text{CF} = \frac{Feed\_Flow}{\text{Re}\,ject\_Flow} \qquad (6\text{-}4)$$

Nanofiltration membranes are reverse osmosis membranes that remove a limited proportion of dissolved solids. They remove a higher percentage of divalent ions than monovalent ions and are thus often called “softening membranes.” Nanofiltration membranes may remove only 50-65%

of monovalent ions but up to 90% of divalent ions. Nanofiltration membranes operate at lower pressures (50-100 psig) than RO membranes.

Ion Exchange Softening

Ion exchange softening uses a cation exchange resin made of a water insoluble styrene-divinylbenzene polymer with negatively charged sulfonic acid sites. The ion exchange vessel contains a bed of the cation exchange resin in the sodium form. The ion exchange softening process exchanges hardness ions in the water, primarily calcium and magnesium, for sodium. Once the bed is exhausted (has exchanged most of its sodium for hardness ions, the bed is regenerated with a strong sodium chloride solution.

The softening reaction is represented by the following formula.

$$2R^{-}Na^{+} + Ca^{++} \leftrightarrow R_2^{=}Ca^{++} + 2Na^{+}$$

Where R is the water-insoluble cation exchange resin

Since this is a reversible reaction, the hardness ions can be eluted from the exchange sites and replaced with sodium by regenerating with a strong solution of sodium chloride. The regenerant solution is usually about 8% sodium chloride.

The regeneration process consists of:

1. Backwash to remove suspended material and loosen the bed.
2. Regenerant introduction which routes the regenerant solution through the bed at a slow rate to displace the hardness ions.
3. Rinsing of the remainder of the regenerant brine from the bed and preparing the softener to return to the service cycle.

For more detailed information on makeup treatment processes, refer to the EPRI Revised Guideline for Makeup Water Treatment[24] and the EPRI Open Cooling Water Chemistry Guideline (Reference 1).

Impact of Concentration Control (Cycles of Concentration) on Calcium Carbonate Scaling

Cooling tower cycles of concentration (COC) have a direct relationship to deposit potential, usually calcium carbonate deposition potential. Table 6-1 shows a simulated cooling tower makeup water supply with moderate calcium hardness, magnesium hardness, and total alkalinity and low silica. The simulated cooling tower makeup water is shown in Table 6-1.

Table 6-1
Simulated Cooling Tower Makeup Water

Calcium Hardness mg/L as $CaCO_3$	80.0
Magnesium Hardness mg/L as $CaCO_3$	40.0
Sodium as mg/L Na	22.0
Potassium as mg/L K	3.0
Total Alkalinity mg/L as $CaCO_3$	110.0
Sulfate as mg/L SO_4	40.0
Chloride as mg/L Cl	14.5
Silica as mg/L SiO_2	5.0
pH	7.8
Conductivity, µS/cm	308

This makeup water was used as the basis for calculations using a commercially available software program commonly used for calculating water characteristics, scaling potential, and scale inhibitor dosages.[1] These calculations are based on cycling up a cooling tower with the simulated makeup water shown in Table 5-1 without any sulfuric acid feed for alkalinity/pH control. For this example, HEDP was chosen as the calcium carbonate scale inhibitor. HEDP contains 30% phosphorous. The impact of concentration control is shown in Table 6-2 and Figure 6-2.

Table 6-2
Impact of COC on Scale Inhibitor Dosage
Simulated Makeup Water

Cycles of Concentration (Concentration Ratio)	pH	HEDP, mg/L	Total P, mg/L
2.0	7.85	0.14	0.04
3.0	8.10	0.41	0.12
4.0	8.28	0.84	0.25
5.0	8.41	2.34	0.70
6.0	8.53	5.96	1.79
7.0	8.62	(13.00)	(3.90)
8.0	8.70	(23.00)	(6.90)

Note: Figures in parentheses represent unrealistic HEDP dosages per calculation.

---

[1] WaterCycle Rx, French Creek Software.

The same data are shown graphically in Figure 6-2.

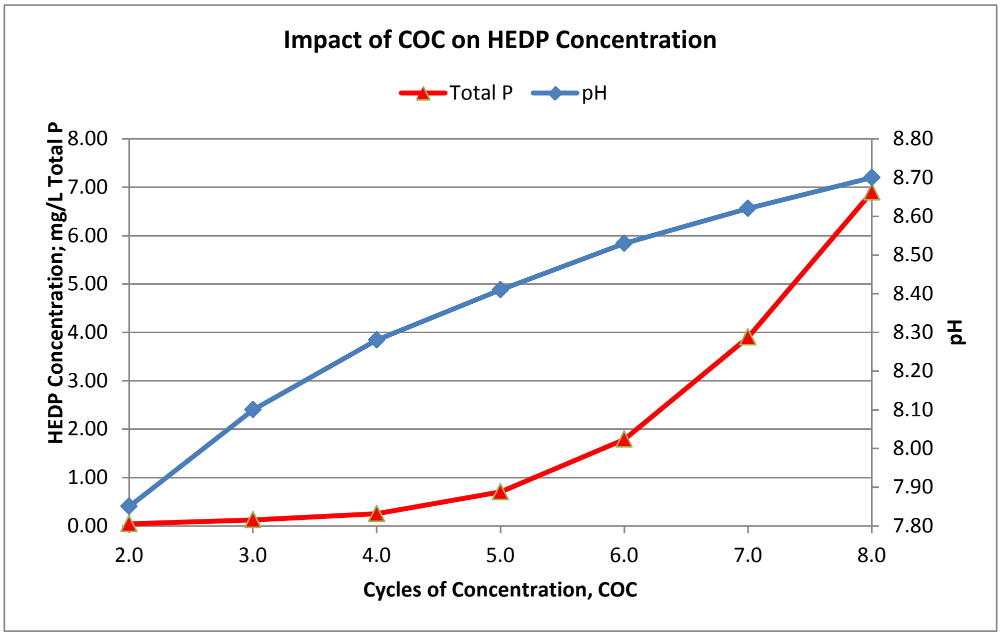


Figure 6-2
Plot of Impact of Cycles of Concentration on HEDP Concentration

In this case, a cooling tower blowdown discharge of less than 0.5 mg/L as P can be achieved by keeping COC below about 4.5.

This is just a simple example to demonstrate the impact of concentration control. It is important to note that this example deals only with the scale inhibitor program and does not take into account any phosphorous that may be present as part of the corrosion control program.

Impact of Alkalinity/pH Control on Calcium Carbonate Scaling

The addition of sulfuric acid, or other mineral acid, to a system reduces pH by destroying alkalinity in accordance with equations 6-1 through 6-3.

$$2Na_2CO_3 + H_2SO_4 \rightarrow 2NaHCO_3 + Na_2SO_4 \qquad (6\text{-}5)$$

$$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2CO_3 \qquad (6\text{-}6)$$

$$H_2CO_3 \leftrightarrow CO_2\uparrow + H_2O \qquad (6\text{-}7)$$

It takes approximately one ppm of sulfuric acid to destroy one ppm of bicarbonate alkalinity.

Reduced pH can have a significant impact on the amount of a given scale inhibitor needed in a system. Table 6-3 and Figure 6-3 show an example. These calculations are based on cycling up a cooling tower with the simulated makeup water. For this example, HEDP was also chosen as the calcium carbonate scale inhibitor.

Table 6-3
HEDP Needed With and Without Acid Feed

Cycles of Concentration (Concentration Ratio)	pH Without Acid Feed	mg/L HEDP Without Acid Feed	mg/L Total P Without Acid Feed	pH With Acid Feed	mg/L HEDP With Acid Feed	mg/L Total P With Acid
2.0	7.85	0.14	0.04	7.85	0.14	0.04
3.0	8.10	0.41	0.12	8.10	0.41	0.12
4.0	8.28	0.84	0.25	8.28	0.84	0.25
5.0	8.41	2.34	0.70	8.30	0.85	0.26
6.0	8.53	5.96	1.79	8.30	0.92	0.28
7.0	8.62	(13.00)	3.90	8.30	0.97	0.29
8.0	8.70	(23.00)	6.90	8.30	1.09	0.33

Note: Figures in parentheses represent unrealistic HEDP dosages per calculation.

The data shown in Table 6-3 are shown graphically in Figure 6-3.

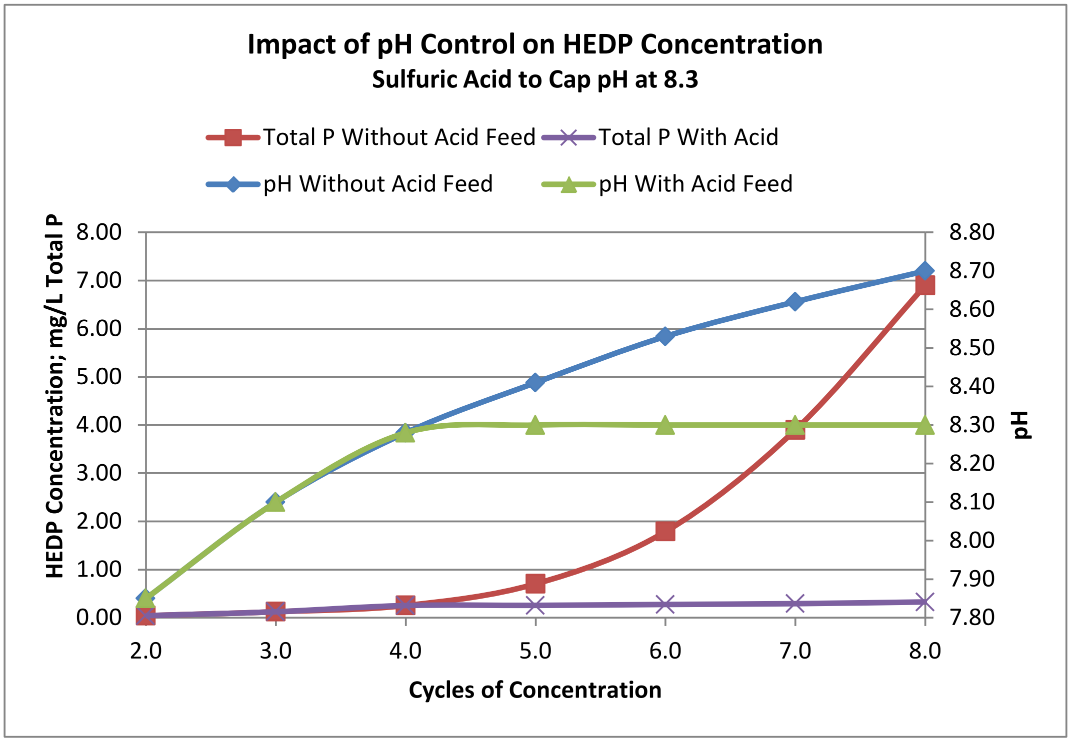


Figure 6-3
Plot of Impact of pH on HEDP Requirement

In this example, holding the pH at 8.3 keeps the HEDP level (as P) below 0.5 ppm. However, the reduced pH increases the corrosivity of the water toward carbon steel.

Low Phosphorous Treatment Products – $CaCO_3$ Scale Control

Calcium Carbonate Scale Control

Use of low-phosphorous treatment products can be an important part of reducing phosphorous discharge. In addition to total phosphorous content of a treatment product, its “efficiency” or needed use level in a given situation should be considered.

Table 5-1 showed some common scale inhibitor compounds that can be considered “high phosphorous.” Those range from 20% to 31% phosphorous by weight. There are several compounds that are effective calcium carbonate scale inhibitors that contain less than 20% phosphorous by weight. Table 6-4 shows the higher phosphorous scale inhibitors along with the lower phosphorous scale inhibitors.

Table 6-4
Common High & Low-P Calcium Carbonate Scale Inhibitor Products

Name	Acronym	Formula	MW	Weight P	%P
Aminotris-methylenephosphonic acid	ATMP	$C_3P_3O_9H_{12}N$	298.91	92.91	31.1%
1-Hydroxyethylidene-1,1-diphosphonic acid	HEDP	$C_2O_7P_2H_8$	205.94	61.94	30.1%
Sodium tripolyphosphate	STPP	$Na_5P_3O_{10}$	367.91	92.91	25.3%
Tetrapotassium pyrophosphate	KTPP	$K_4P_2O_6$	314.34	61.94	19.7%
Sodium hexametaphosphate	SHMP	$Na_6P_6O_{18}$	449.91	92.91	20.7%
Hydroxyphosphonoacetic acid	HPA	$C_3O_6P_1H_5$	167.97	30.97	18.4%
Phosphonobutane tricarboxylic acid	PBTC	$C_7O_9P_1H_{11}$	269.97	30.97	11.5%
Phosphinosuccinic oligomer	PSO	$C_8P_1O_{10}H_{11}$	297.97	30.97	10.4%
Polyamino polyether methylene phosphonate	PAPEMP	$C_{10}P_4O_{13}N_2H_{27}$	~600	123.90	20.6%

The use of a lower phosphorous scale inhibitor can reduce total phosphorous in the discharge significantly. For example, 1 mg/L of HEDP will contribute 0.3 mg/L total phosphorous while 1 mg/L of PBTC will contribute 0.1 mg/L total P. In addition, there are differences in efficiency between some of these calcium carbonate scale inhibitors. An example, using the same makeup water, is shown in Table 6-5 and Figure 6-4. This shows the effect of both lower phosphorous in the molecule and the fact that PBTC is considered to be more efficient than HEDP under these conditions. Again, this is a theoretical case and not an actual cooling system.

The use of low-phosphorous calcium carbonate products can significantly reduce the concentration of phosphorous in the discharge of a cooling tower system. Table 6-5 compares HEDP and PBTC dosages required for calcium carbonate scale inhibition using the same theoretical makeup water that was used in the other examples. The same information is shown in graphical form in Figure 6-4.

Table 6-5
Comparison of HEDP and PBTC Dosages and Total P

Cycles of Concentration (Concentration Ratio)	pH	HEDP, mg/L	Total P from HEDP, mg/L	PBTC, mg/L	Total P from PBTC, mg/L
2.0	7.85	0.14	0.04	0.44	0.05
3.0	8.10	0.41	0.12	0.98	0.11
4.0	8.28	0.84	0.25	1.69	0.19
5.0	8.41	2.34	0.70	2.49	0.29
6.0	8.53	5.96	1.79	3.35	0.39
7.0	8.62	(13.00)	(3.90)	4.24	0.49
8.0	8.70	(23.00)	(6.90)	(5.10)	(0.59)

Note: Numbers in parentheses represent unrealistic concentrations per calculation

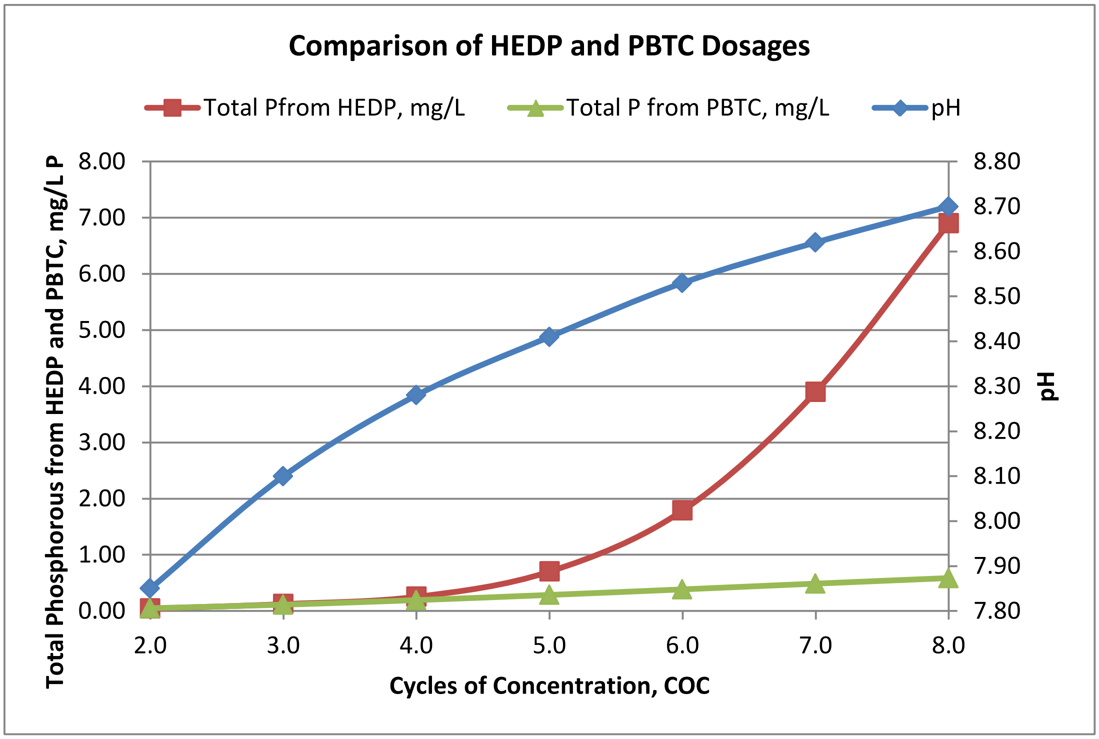


Figure 6-4
Comparison of HEDP and PBTC Dosages

Control of Other Scales

Control of calcium sulfate, silica, magnesium sulfate, and iron deposits relies primarily on non-phosphorous containing polymers. Refer to the information in Section 4.

Corrosion Control Considerations

Scale control and corrosion control are interrelated. Many of the steps discussed above to mitigate scaling will likely have an impact on corrosion. For example:

- Softening cooling tower makeup will reduce scaling potential but may make the makeup water more corrosive. This may be somewhat offset by the fact that operating at higher cycles of concentration may reduce corrosion potential.
- Operating at a lower pH in order to reduce scaling potential will likely make the cooling water more corrosive.

Phosphates have been a keystone of steel corrosion control since the end of the chromate “era.”

Alkaline Cooling Water Programs

As noted above, reducing pH minimizes scale deposition but increases corrosion potential. Conversely, raising pH reduces corrosion potential. One approach that can be used to reduce steel corrosion is to allow pH to rise and control scaling by means of an effective low-phosphorous scale inhibitor.

Summary

Reducing phosphorous discharge in an evaporative cooling system may involve using one of the techniques discussed above or combining these techniques to meet the required goal.

7

BASICS OF NON-PHOSPHOROUS SCALE AND CORROSION CONTROL PROGRAMS

What is Considered Non-Phosphorous

For purposes of this document "non-phosphorous" is defined as a corrosion or scale inhibiting molecule that does not contain the phosphorous atom. It also does not contain any phosphorous in the overall blended product. Of course, there is always the possibility that there is some phosphorous contained in the makeup water supply. This must be accounted for and may contribute to phosphorous in the discharge but is beyond the control of this document.

Non-Phosphate Corrosion Inhibitors

The following is a discussion of corrosion inhibitors that are considered "non-phosphorous" in accordance with the above definition.

Zinc

The basis of zinc as a cathodic corrosion inhibitor for carbon steel was discussed in Section 4. Zinc is typically used in conjunction with an anodic corrosion inhibitor. While zinc itself is "non-phosphorous," the anodic corrosion inhibitor most often associated with zinc is phosphate.

Zinc can be toxic to aquatic life. There are environmental discharge restrictions in some locations.

Molybdate

Molybdate, discussed in Section 4, can be a building block in a non-phosphorous water treatment program.

While molybdate is not considered highly toxic, discharges are often regulated. Many public treatment works regulate the discharge of molybdate to sewer systems to limit its concentration in sludge intended for land application.

Polysilicates (Sodium Silicate)

Polysilicates were also discussed in detail in Section 4. The advantages of polysilicates are that they do not contain phosphorous and there are few environmental restrictions.

The disadvantages of polysilicates are that the protective film is slow to form and is fragile. It can be disrupted by corrosive chloride and sulfate ions. The use of polysilicates can result in the formation of silicate deposits when used in conjunction with high background silica levels.

Polymers

Some of the non-phosphorous polymers discussed in Section 4 have some corrosion control properties.

Softened Makeup and High pH

There is a scale and corrosion control program that has found some use in commercial, institutional, and light industrial cooling tower systems that consists of softening the cooling tower makeup and operating at high cycles of concentration. Mineral scale control is a result of softening the cooling tower makeup. According to claims made for the program, carbon steel corrosion control is the result of both operating at elevated pH and increased silicate levels. Microbiological control is the result of the osmotic pressure created by the high total dissolved solids. It should be noted that an upset in the makeup softening system could lead to rapid deposition of calcium carbonate and calcium/magnesium silicates.

Non-Phosphorous Scale Inhibitors

There are several non-phosphorous scale inhibitors that are effective for calcium carbonate, calcium sulfate, calcium phosphate, and silicates. These polymers were discussed in Section 4. Some of these materials are available from most WTSCs while some are favored by specific WTSCs.

PAA

PAA (polyacrylic acid) primarily inhibits calcium carbonate and calcium sulfate scales. It is not particularly effective as a calcium phosphate inhibitor.

PMA

PMA (polymaleic acid) is primarily a calcium carbonate scale inhibitor.

AEC

AEC (alkyl epoxy carboxylate) is primarily a calcium carbonate scale inhibitor.

PASA

PASA (polyaspartic acid) is claimed to control calcium carbonate, calcium sulfate, barium sulfate, and calcium phosphate deposition.

Sulfonated Polymers

As noted in Section 4, sulfonated polymers are primarily used for calcium phosphate control. However, they are important building blocks in most of the copolymers and terpolymers that are also important for calcium carbonate, calcium sulfate, and even silicate control.

8

PROPRIETARY LOW-PHOSPHOROUS CORROSION AND SCALE CONTROL PROGRAMS

This section provides information on the proprietary low-phosphorous programs currently offered by the water treatment service companies that have agreed to provide information for this document. Information was requested from companies that provide a significant amount of chemicals and service to the electric utility industry. **This information is provided for informational purposes only. EPRI does not validate, recommend, or endorse any particular proprietary programs.** The companies that provided information are listed in alphabetical order. Each company presented information in a somewhat different format. Text provided by the companies is shown in italics.

Applied Specialties, Inc.

Applied Specialties, Inc. (ASI) indicated that they successfully use phosphino succinic oligomer (PSO) in low-phosphorous scale control programs. They also note that the PSO is free of residual phosphate as a result of the manufacturing process.

Buckman

Introduction

Buckman provided information on one low-phosphorous program. Text in italics is directly from the Buckman submittal.

Buckman PCA Plus: *The product is presented as a low-phosphorous product that is not based on phosphonate technology. It controls calcium carbonate, calcium phosphate, and calcium sulfate deposition and scale in high stress conditions and is stable in the presence of halogens.*

Technical information was limited to the product bulletin.

ChemTreat

Introduction

ChemTreat made significant contributions to this document as a whole.

ChemTreat did not separate information on Low-Phosphorous and Non-Phosphorous products. Their combined submittal is in Section 9.

GE Water and Process Technologies

Introduction (from GW Response)

This introduction, provided by GE Water & Process Technologies (GEWPT), applies to both low-P and non-P programs. Text in italics was provided directly by GEWPT.

Thank you for considering GE Water and Process Technologies in EPRI's effort to determine and understand current Non-P and Low-P cooling water treatment methodologies. We appreciated your patience as we worked to develop a meaningful response. Our Technology, Product Management, and Product Applications teams have collaborated to provide the information contained in this document. We have provided, to the best of our ability, information regarding current treatment capabilities and methodologies in response to your questions, while minimizing the amount of proprietary information divulged.

As you know, Non-P treatment requires specific approaches and technologies, some of which are new to the marketplace. GE Water has developed and continues to expand our Non-P and Low-P capabilities for both scale and corrosion inhibition. One area where we are currently quite active is in trying to better understand the protective films that form with these programs. We believe that the best way to improve corrosion performance and take a major step forward is to gain a deep understanding of what's happening at the surface.

For the purposes of this document, Non-phosphorous is defined as not having phosphorous in the molecule or in the overall product. Background phosphorous may be present in the makeup water and does not "count against" a non-phosphorous program. Low-Phosphorous is defined as having <1.5 ppm phosphorous (as PO4) in the treatment product. Given the wide variety of water conditions found globally, each application involving Non-P or Low-P treatment must be reviewed individually. The technical and cost considerations are balanced to provide the customer with the most cost-effective approach to meet their target inhibition goals. Target pH, cycles, and salt saturation values are carefully balanced with appropriate chemical addition during this case-by-case evaluation, handled by the experienced Cooling Application Engineers at GEWPT.

Other factors must also be considered when it comes to selecting which specific Non-P or Low-P based product is used. Some of these factors include:

- *S-value and target cycles*
- *Plant configuration and operating mode*
- *Past history of condenser scaling problems*
- *Need for inhibition of other species such as suspended solids, calcium phosphate, iron, manganese, calcium sulfate, barium, strontium, copper, zinc, aluminum.*
- *Inhibitor stability in the presence of high calcium levels*
- *Feed and control capabilities*
- *State permitting and discharge requirements*

Performance problems and/or risk of failure can develop when one or more of the following occur:

- *Feed rates fall below prescribed levels or are not adjusted as operating conditions change.*
- *Products are fed in the wrong location*
- *Frequent loss of pH control*
- *Cycles are frequently above prescribed limits*

Specific treatment products and control strategies are discussed in the sections below. While molecular weights, mole ratios, and distribution are critical to performance, these are considered proprietary and are not included. Product bulletins and additional MSDS's will be provided at a later date.

Proven in multiple case studies, we are excited to offer these technologies to the power industry.

Non-Phosphorous Calcium Carbonate Scale Inhibition Programs

GEWPT has experience with Non-P based $CaCO_3$ inhibition in fresh water (river, lake, well, etc), brackish water, seawater and reuse water. A proprietary polymer approach is typically recommended; employing either a single polymer or a proprietary blend from our Depositrol, or GenGard series of products. Homopolymers and copolymers incorporating carboxyl or ethoxylated acrylic functional groups are most effective at inhibiting pure $CaCO_3$ deposition. There are no lower limits when it comes to inhibiting CaCO3. Upper limits are handled on a case by case basis. Please refer to Table 1 in the appendix for details. In general, a second level engineering analysis is done when any of the following conditions exist:

- *LSI > 2.7*
- *Calcite S-value exceeds ~240.*
- *Calcium hardness exceeds 2,000 ppm as CaCO3*
- *Tube wall temperatures greater than 150F (e.g. service water exchangers)*
- *History of CaCO3 scaling problems*
- *Low velocities, shell side or plate and frame design.*

In the case of low-P, calcium carbonate scale inhibition a program combining phosphonate and polymer is often recommended as described in Table 2 in the appendix.

Non-P and Low-P Scale Inhibition Programs for Other Scales

For calcium sulfate, GEWPT similarly recommends a proprietary polymer based approach employing either a single polymer or a proprietary blend from our Depositrol, or GenGard series of products. Silica and magnesium silicate can precipitate at neutral and alkaline pH ranges respectively. In the Non-P Program, they are controlled by maintaining cycles of concentration in the cooling tower to stay below their limits. In a Low-P program, a proprietary blend is used to specifically extend the solubility of silica. Please refer to the appropriate tables for details.

Non-Phosphorous Programs for Steel Corrosion Control

The approach to Non- and Low-P treatment for steel corrosion inhibition is dependent on the amount of soluble phosphate in the makeup water to the cooling water system. With the presence of a small amount of PO4 in the makeup source, an all-polymer approach is preferred.

GEWPT employs a variety of programs and treatment schema for Non-P steel corrosion inhibition. Typically these programs exploit the natural corrosion inhibition of higher pH and employ a proprietary polymer to promote protective films. The typical conditions and approaches are discussed in Table 3 in the appendix. The proprietary polymer based approach, employing either a single polymer or a proprietary blend from our Depositrol PY, or GenGard series of products is recommended.

Low-Phosphorous Programs for Steel Corrosion Control

Products chosen from the Depositrol PY series for this application will work in conjunction with the PO4 in the makeup to both maintain the solubility of the PO4 and provide direct steel corrosion inhibition. Should a Low-P approach be desired where the makeup water contains no measurable PO4, the Depositrol BL series of products contains several blends to address the increased corrosive nature of the makeup water. Please refer to the appropriate tables in Section 8 and Section 9 for a sampling of several approaches to effectively treating a cooling system requiring mild steel corrosion protection and a Low-P approach.

Program Summary – Low-Phosphorous Scale Control Programs

Table 8-1
GE Water & Process Technologies Low-P Scale Control Programs

Salt	**P as PO_4 (ppm)**	**Control Program**	**Actives**	**Ion Product limit**	**Concentration limit (ppm)**
Calcium Carbonate	<1.5 ppm at cycles	Depositrol BL or Gengard	Combination of phosphonate and	Note LSI and Calcite S-values in Introduction	
Calcium Sulfate	<1.5 ppm at cycles	Depositrol BL series	Blend of Acrylate or Sulfonate based polymer	4,000,000-50,000,000 * (Ca as $CaCO_3$ and Sulfate as SO_4)	-
Silica	<1.5 ppm at cycles	Gengard 6000 series	Blend	-	275 ppm *
Magnesium Silicate	<1.5 ppm at cycles	Cycles of Concentration	-	Varies with pH and Temperature	-
Manganese	<1.5 ppm at cycles	Make up oxidation with Depositrol PY	Sulfonate based polymer		< 2 ppm **
Ba/Sr salts	<1.5 ppm at cycles	Depositrol PY Series	Multiple	Required engineering analysis	
Zinc, Iron, Al, TSS	<1.5 ppm at cycles	Depositrol PY or Gengard series	carboxyl or ethoxylated acrylic based	Required engineering analysis	

* Second level engineering analysis required for higher values
** Cost benefit analysis required for higher values

Low Phosphorous Steel Corrosion Control Programs

Table 8-2
GE Water & Process Technologies Low-P Steel Corrosion Control Programs

Calcium as $CaCO_3$ (ppm)	P as PO_4 in Makeup	P as PO_4 in blowdown (ppm)	Typical pH	Typical Approach	Actives
<250	Yes	<1.5 ppm at cycles	8.7 – 9.0	Depositrol BL Series	No-P Optimal Polymer Blend
250 - 1000	Yes	<1.5 ppm at cycles	8.0 – 8.7	Depositrol BL Series	No-P Optimal Polymer Blend
<250	No	<1.5 ppm at cycles	8.7 – 9.0	Depositrol BL Series	Low-P Optimal Polymer Blend
250 - 1000	No	<1.5 ppm at cycles	8.0 – 8.7	Depositrol BL Series	Low-P Optimal Polymer Blend
100 - 1000	No	<1.5 ppm at cycles	8.0 – 8.5	FloGard MS Series w/ Depositrol PY Series	Zinc / Low-P Polymer
100 – 1000	Yes	<1.5 ppm at cycles	8.0 – 8.5	FloGard MS Series	Zinc Based
250 – 1000	Yes	<1.5 ppm at cycles	8.0 – 8.5	Inhibitor SL Series	Silicate / Polymer Blend

Nalco, an Ecolab Company

Introduction

Nalco submitted information in tabular format on both low-phosphorous and non-phosphorous programs.

Program Summary – Low-Phosphorous Scale Control Programs

General Program Description	Nalco has several low-P options for scale control. Products containing PSO can prevent calcium carbonate scale where the saturation index is less than 60. For higher calcite saturation index conditions, we would use product containing PBTC phosphonate for low-P situations. These are considered low P in that they contribute ~ 1/3rd the amount of phosphate compared to traditional phosphonate scale inhibitors like HEDP or AMP.
Applicable Conditions (pH range, calcium hardness etc.)	For PSO products, max Calcite Saturation index (SI)= 60. For PBTC products, max Calcite SI = 110
Target Deposits	$CaCO_3$, $CaSO_4$
Application History (Operating Experience)	Multiple power plants using this chemistry, specific locations considered confidential
Program Limitations	

Program Summary - Low Phosphorous Corrosion Control Programs

General Program Description	Several products using PSO chemistry as a cathodic corrosion inhibitor, which doubles as a scale inhibitor. PSO also provides an anodic inhibitor effect at higher dosages, but the most cost effective treatment is when PSO is fed with an orthophospahte source. Example products are 3DT179, 3DT180. Considered low-P in that PSO is 29% PO4, compared to more traditional polyphosphate or hexametaphosphate (>50% PO_4).
Applicable Conditions (Metallurgy, pH range, calcium hardness etc.)	For mild steel corrosion control, requires ortho-PO_4 levels of 3 ppm, or higher, or higher alkalinity (>300 ppm) and calcium (>80 ppm) levels, or soluble zinc (0.5 - 1.0 ppm)
Application History (Operating Experience)	Multiple power plants using this chemistry, specific locations considered confidential
Program Limitations	Treatment may require an ortho-PO_4 source to achieve acceptable mild steel corrosion rates (<3 mpy) for higher anion waters (Cl + SO_4 total >300 ppm). If PSO is only scale inhibitor, maintain calcium carbonate saturation index <60

Program Component 1

Description	PSO (phosphinosuccinic oligomer)
Active Level	Considered proprietary

Solenis

Introduction

Solenis is the former Ashland Water Technologies.

The following charts represent the program descriptions provided by Solenis for low-phosphorous programs.

Low-Phosphorous Scale Control Programs

General

General Program Description	These are blends of various polymers of varying molecular weights (1000 to 7000) and functionality. Where-in the functioal groups can be carboxylate, sufonate, phosphinate or nonionic in nature. The polymers may be homo-, co-, ter- and quad- in nature. They may also use phosphinate backbone functionality and be clended with oxidate stable phosphonates. These descriptors will be used for the individual products listed below.

Program Product 1 Drewsperse 752

Description	Mid range molecular weight polycarboxylate with a sequestation agent that is extremely effective on calcium carbonate and very good on calcium sulfate deposit control. The sequestrant is for iron and manganese control.

Program Product 2 Drewsperse 6980

Description	Mid range molecular weight carboxylated sulfonated phosphinated copolymer that is extremely effective on calcium carbonate and very good on calcium phosphate and sulfate deposit control. Stabilizes zinc, zinc phosphate and disperses suspended iron and manganese oxides. .

Program Product 3 Amersperse 7963

Description	Mid range molecular weight carboxylated sulfonated phosphinated copolymer that is extremely effective on calcium carbonate and very good on calcium phosphate and sulfate deposit control. Stabilizes zinc, zinc phosphate and disperses suspended iron and manganese oxides. Plus Ultra low

Program Product 4 Millsperse 8440

Description	Ultra low molecular weight polycarboxylate with a complex phosphonate that provides excellent control of calcium carbonate, calcium floride and silicates. Good on calcium sulfate and provides iron and manganese sequestration.

Program Product 5 Performax Millennium 6925

Description	Complex phosphonate that provides iron and manganese squestration and can be used as supplement with other specialized polymeric dispersants to provide calcium floride and silicate control

Program Product 6 Performax Millennium 6945

Description	Mid range molecular weight copolymer, quad polymer, and an oxidant stable carboxylated phosphonate. Used where additional calcium carbonate deposit control is required.

Program Product 7 Ameroyal 710

Description	Complex Phosphonate, carboxylated phosphonate and a mid range molecular weight terpolymer. Used in cooling waters, geothermal brines and R/O applications.

Program Product 8 Drew 11-608

Description	Carboxylated phosphonate and a mid range molecular weight terpolymer.

Program Product 9 Drew 11-697

Description	Complex Phosphonate, carboxylated phosphonate, ultra low molecular weight polycaboxylate and a mid range molecular weight terpolymer. Used in cooling waters, geothermal brines and R/O applications.

Low-Phosphorous Corrosion Control Programs

General

General Program Description	See sheet 2 for multi purpose blends and applications of low ortho phosphate (≤ 5 ppm) and low additions of poly phosphate (≤ 2 ppm) to any of the Non-P Scale control additives that complies with the site discharge allowances. Or zinc and silicate additions to the Low-P Scale control additives that complies with the site discharge allowances..

Program Product 1 Enviroplus 6150

Description	A ratioed blend of oxidantly stable organic compunds that produce a dianodic corrosion control mechanism. An organic zinc substitute containing carboxylated and phosphonated functionality.

Program Product 2 Amersperse 5111

Description	Stablized Zinc Phosphate dinodic corrosion inhibitor with Drewsperse 6980 coplymer (see Low P Scale).

9

PROPRIETARY NON-PHOSPHOROUS CORROSION AND SCALE CONTROL PROGRAMS

Introduction

This section provides information on the proprietary non-phosphorous corrosion and scale control programs offered by the water treatment service companies that have agreed to provide information for this document. **This is provided for informational purposes only. EPRI does not recommend or endorse and particular proprietary programs.** The companies that provided information are listed in alphabetical order. Each company presented information in a somewhat different format.

Applied Specialties, Inc.

Applied Specialties, Inc. (ASI) indicated that they successfully use polyacrylic acid (PAA) technology as a non-phosphorous calcium carbonate scale inhibitor. They note that supplementary approaches may be required if significant iron is present in the water.

Buckman

Introduction

Buckman provided information on one non-phosphorous program.

Bulab 7185 Scale Inhibitor: According to the product bulletin, Bulab 7185 effectively controls calcium carbonate, calcium phosphate, and calcium sulfate. It maintains effectiveness under stressed conditions. The product also provides performance in the presence of fouling due to iron and other suspended solids. The Safety Data Sheet (SDS) lists maleic acid as an ingredient.

ChemTreat

Introduction

ChemTreat has published extensively on non-phosphorous cooling technology.[25] [26] [27] [28] [29] The non-phosphorous product line promoted by ChemTreat is the PhosFree™ line. ChemTreat provided the material below to describe both their Low-Phosphorous and Non-Phosphorous products.

Material Submitted by ChemTreat

Initially in response to increasing concerns over the role of phosphate as an environmental nutrient, ChemTreat embarked on a comprehensive research effort to develop substitutes for *phosphorus based cooling water chemistries. In the post-chromate era, phosphate chemistries have come into widespread use as both antiscalants and corrosion inhibitors. Organic phosphates such as phosphonates and phosphinates are the most widely used calcium carbonate antiscalants, and also offer some measure of cathodic carbon steel corrosion control. Inorganic ortho phosphate and polyphosphates are predominantly used as anodic and cathodic carbon steel corrosion inhibitors, respectively. The development of phosphorus free cooling water chemistries required the development of both effective non-phosphorus (non-P) scale inhibitors and corrosion inhibitors. The best performing non-P scale inhibitors developed from the research program are able to maintain LSI values as high as 2.96 and provide carbon steel and copper corrosion inhibition rates of <1 mpy and <0.1 mpy respectively (Post, 2010).*

Untreated – 60 mpy **Non-P program < 1 mpy**

Table 9-1
Corrosion Coupons - Untreated and Treated

The non-P chemistry has been successfully applied in power industry cooling systems (Post, 2011) as well as in wide range of industrial and commercial cooling systems (Post, 2014).

Although the initial intent of the research effort was environmentally focused, it rapidly became apparent that the non-phosphorus chemistries which were being developed offered many significant advantages over conventional phosphorus-based corrosion control chemistries for power industry cooling systems. Those advantages included, but were not limited to:

- ***Reduced microbiological treatment cost.** Phosphorus is the limiting nutrient for algae, and even bacteria require some phosphorus for ATP processes. For power plants, typically sodium hypochlorite used for microbiological control is the largest cooling water chemical expense and one of the thorniest discharge issues. Non-P programs reduce antimicrobial usage and related discharge issues.*
- ***Non-phosphorus programs are non-fouling with respect to calcium phosphate.** Effective phosphate-based corrosion inhibitor programs require a delicate balance between the applied phosphate concentration, calcium, pH, temperature, and dispersant polymer concentrations. All five factors must be in balance at all points in the system and at all times. That is difficult to achieve without fouling higher temperature exchangers and requires precise control to maintain all five factors in balance. By contrast, the ChemTreat non-P technology is non-fouling and cannot be overfed, similar to the chromate programs of the past.*

- ***Reduced polymeric dispersant levels**. All phosphate-based programs operate in excess of calcium phosphate saturation and require a polymeric dispersant to stabilize the calcium phosphate. Such programs are vulnerable to fouling should there be a loss of the polymeric dispersant due to stress on or underfeed of the polymer. The ChemTreat non-P technology does not require such super-saturation and subsequently require less dispersant to maintain overall program efficacy.*
- ***Effectiveness in low- or no- calcium waters.** The ChemTreat non-P technology directly passivates the metal surface and does not require the presence of calcium to form a protective film. The independence on calcium makes it particularly cost effective in low hardness water.*
- ***Effective in closed cooling systems.** In the Power industry, closed cooling systems typically use demineralized water or condensate for makeup. The ChemTreat non-P program is non-nutrient contributing and is effective in no-calcium closed loop water.*
- ***Excellent aquatic effects profile.** In addition to simply being non-phosphorous, the non-P chemistry developed by ChemTreat has a very high LD50 on aquatic life forms. It has been possible to discharge this product into sensitive aquatic ecosystems where other conventional treatments have not been allowed to discharge.*
- ***Effective on steel, copper, and aluminum.** The ChemTreat non-phosphorus chemistry is also effective on aluminum and copper alloys.*
- ***Particularly effective for layup, standby, and initial passivation.** ChemTreat's non-phosphorus chemistry forms a durable protective film directly onto metal surfaces. The film is resistant to upset conditions, and also provides excellent protection for the metal during layup and standby conditions, which have become increasingly common due to the management of the US power grid. Metal specimens passivated with the ChemTreat non-phosphorous chemistry show excellent resistance to corrosion based on open circuit potential measurements and copper plating tests (Post, 2014).*

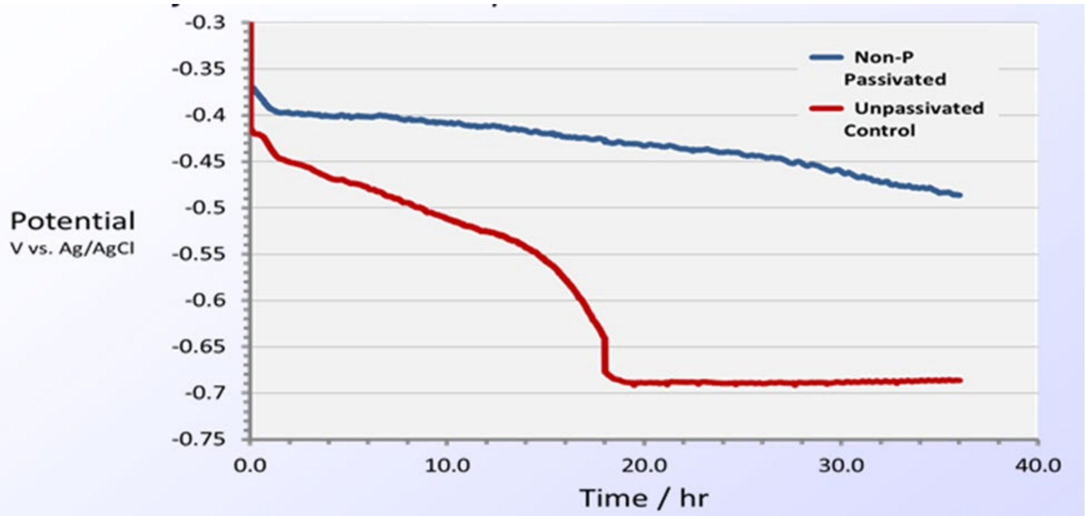


Figure 9-1
Open Circuit Potential Electrochemical Results After Steel Coupon Is Placed In Untreated Water

ChemTreat has created a full range of cooling water treatment products under the FlexPro® trade name to take advantage of the unique advantages of their non-phosphorus chemistry as shown in the table below.

Table 9-2
ChemTreat Low-P and Non-P Products

FlexPro® Product	Application	Non-N	Non-P	Low-P	pH Non-Hazardous
CL5634	Cooling Tower	X	X		X
CL5644	Cooling Tower	X	X		X
CL5632	Cooling Tower		X		X
CL5638	Cooling Tower		X		
CL5639	Cooling Tower		X		
CL5640	Cooling Tower			X	X
CL5641	Cooling Tower			X	
CL5643	Cooling Tower			X	
CL2632	Closed Loop		X		
CN5600	Cleaning & Passivation		X		

References:

Post, R.M., Tribble, R.H., and Richardson, J.R., Development of Next Generation Phosphorus-Free Cooling Water Treatment Technology, International Water Conference paper 10-23, 2010.

Post, R.M., Cerra, H.R., and Tribble, R.H., Development and Application of Phosphorus-Free Cooling Water Treatment Technology, Electric Utility Chemistry Workshop, Champaign, IL, June 7-9-, 2011.

Post, R.M., Kalakodimi, R.P., and Tribble, R.H., The development and Application of Phosphorus Free Cooling Water Technology, Cooling Technology Institute, Feb. 3, 2014.

Post, R.M., Kalakodimi, R.P, and McIninch, G., Cooling System Startup, Layup, and Passivation, Southwest Chemistry Workshop, San Diego, CA, Aug 4, 2014.

GE Water & Process Technologies

Introduction

GE Water & Process Technologies (GEWPT) provided an extensive introduction/discussion which is included in Section 8 (Proprietary Low-Phosphorous Corrosion and Scale Control Programs). Non-phosphorous programs are shown in tabular format below.

Program Summary – Non-Phosphorous Scale Control Programs

Salt	P as PO_4 (ppm)	Control Program	Actives	Ion Product limit	concentration limit (ppm)
Calcium Carbonate	0	Depositrol PY or Gengard series	carboxyl or ethoxylated acrylic based polymer	Note LSI and Calcite S-values in section 1.	
Calcium Sulfate	0	Depositrol PY series	Acrylate or Sulfonate based polymer	1,000,000 – 4,000,000* (Ca as $CaCO_3$ and Sulfate as SO_4)	-
Silica	0	Polymer and Cycles of Concentration	-	-	225ppm *
Magnesium Silicate	0	Cycles of Concentration	-	Varies with pH and Temperature	-
Manganese	0	Make up oxidation with Depositrol PY	Sulfonate based polymer		< 2 ppm **
Ba/Sr salts	0	Depositrol PY Series	Multiple	Required engineering Analysis	
Zinc, Iron, Al, TSS	0	Depositrol PY or Gengard series	carboxyl or ethoxylated acrylic based polymer	Required engineering analysis	

* Second level engineering analysis required for higher values
** Cost benefit analysis required for higher values

Program Summary – Non-Phosphorous Steel Corrosion Control Programs

Calcium as $CaCO_3$ (ppm)	Phosphate as PO_4	Typical pH	Typical Approach	Actives
<250	0	8.8 – 9.2	Depositrol PY Series	Single Polymer
250 - 1000	0	8.4 – 8.8	Depositrol PY Series	Single Polymer
250 - 1000	0	8.2 – 8.7	Inhibitor SL Series	Silicate Based
100 – 1000	0	8.2 – 8.5	FloGard MS Series with Depositrol PY	Zinc / MS Corrosion Inhibition Polymer

Nalco, an Ecolab Company

Introduction

Nalco submitted information in tabular format on both low-phosphorous and non-phosphorous programs.

Program Summary – Non-Phosphorous Scale Control Program (1)

General Program Description (attach sheets if needed)	**3DT138** This product uses a proprietary blend of polymers to control iron, manganese, calcium carbonate, calcium phosphate, calcium sulfate, zinc and suspended solids deposition in High Stress cooling water systems. This product contains both a tagged polymer (tHSP2) and the inert TRASAR #2 component that enables automated dosage control either by product or by active polymer to ensure the proper amount of actives are always in the system for varying water quality and operating conditions. This product is designed to be used with a 3D TRASAR monitoring and control system.
Applicable Conditions (pH range, calcium hardness etc.)	Treatment is capable as calcium carbonate scale inhibitor up to calcite saturation index of 90
Target Deposits	$CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, Fe, Mn, Zinc, TSS
Application History (Operating Experience)	Multiple power plants using this chemistry, specific locations considered confidential
Program Limitations	Calcium carbonate saturation < 90, Mn < 2 ppm, Tri-calcium phosphate saturation < 70,000. Maximum active polymer concentration < 15 ppm.

Program Component 1

Description	Polymaleic anhydride (PMA)
Active Level	Considered proprietary

Program Component 2

Description	tHSP2 (tagged high stress polymer AA:AMPS). This polymer has a fluorescent tag on it so dosage can be automated and active polymer levels continuously measured using a 3D TRASAR control system
Active Level	Considered proprietary

Program Component 3

Description	TRASAR TR2. This is the inert TRASAR fluorescent component that enables continuous measurement and feed automation via a 3D TRASAR controller
Active Level	Considered proprietary

Program Summary – Non-Phosphorous Scale Control Program (2)

General Program Description	**3DT137** This is the same as 3DT138, but includes a yellow metal corrosion inhibitor
Applicable Conditions (pH range, calcium hardness etc.)	Treatment is capable as calcium carbonate scale inhibitor up to calcite saturation index of 90
Target Deposits	$CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, Fe, Mn, Zinc, TSS
Application History (Operating Experience)	Multiple power plants using this chemistry, specific locations considered confidential
Program Limitations	Calcium carbonate saturation < 90, Mn < 2 ppm, Tri-calcium phosphate saturation < 70,000. Maximum active polymer concentration < 15 ppm.

Program Component 1

Description	Polymaleic anhydride (PMA)
Active Level	Considered proprietary

Program Component 2

Description	tHSP2 (tagged high stress polymer AA:AMPS). This polymer has a fluorescent tag on it so dosage can be automated and active polymer levels continuously measured using a 3D TRASAR control system
Active Level	Considered proprietary

Program Component 3

Description	TRASAR TR2. This is the inert TRASAR fluorescent component that enables continuous measurement and feed automation via a 3D TRASAR controller
Active Level	Considered proprietary

Program Component 4

Description	BZT (sodium benzotriazole) for yellow metal corrosion inhibition
Active Level	Considered proprietary

Program Summary – Non-Phosphorous Scale Control Program (3)

General Program Description	Several other non-P scale inhibitor products using all organic polymer chemistries: HSP, HSP2 & PAA. Example products include: 1389, 3DT (HSP, or 4500, 3DT120 & 3DT121 (HSP2) and PAA products, such as 9354 and 1383.
Applicable Conditions (pH range, calcium hardness etc.)	These products are capable of preventing calcium carbonate scale up to a saturation index (SI) = 60. For SI>60, the 3DT138/3DT137 products should be used in non-P treatment programs.
Target Deposits	$CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, Fe, Mn, Zinc, TSS
Application History (Operating Experience)	Multiple power plants using this chemistry, specific locations considered confidential
Program Limitations	Calcium carbonate saturation < 60, Mn + Fe < 12 ppm, Tri-calcium phosphate < 70,000

Solenis

Introduction

Solenis provided a generic discussion outlining applicable conditions, stressors and limitations of non-phosphorous cooling water programs. Text in italics is taken directly from the Solenis submittal.

Provided below is a generic discussion outlining applicable conditions, stressors and limitations of non-phosphorous cooling water programs. While, under some conditions, "Non-Phosphorus" type programs have demonstrated sub-standard performance, many of these issues can be mitigated through system-specific analysis and program design. Solutions are typically developed on a "case by case" basis and require increased solution engineering experience, compared to traditional treatment. The separate or individual generic additives that are available from Solenis or other raw material suppliers are not part of our disclosure. Deposit or scale control needs can typically be evaluated using saturation modeling software. Mild steel corrosion control is somewhat more difficult to achieve but can be accomplished with generic and proprietary additives, when applied to a dynamic cooling system. As with any cooling program, the concentrations and ratios of active components can be adjusted to improve performance. This will be discussed here-in and only the proprietary products will be provided in the spread sheet questionnaire.

Deposit Control

Effective deposit control can be achieved utilizing non-phosphorus products. Non-Phosphorus deposit control will typically come at the same or higher use-cost as phosphorus containing compounds, depending on water chemistry. The bulk of phosphorous based, deposit control additives in cooling water are low molecular weight, organic phosphates or "phosphonates." These products are known sequestrants and antiprecipitants. There are a few synthetic polymeric dispersants that contain organo phosphonate or phosphinate functionality which enhance certain types of deposit control and/or corrosion inhibitory stabilization via delivery of the inhibitor to the system metal surfaces. Also, some deposit control products, though termed Non-P in their end state, contain phosphorus due to the manufacturing method. Each of these candidates are not considered for "No P" applications, however; in low-phosphorous programs they can be blended in at low levels to achieve very positive performance improvement results.

Program limitations will vary depending upon the potential deposit formation that may exist in the cycled cooling water which can very geographically/globally. Performance capabilities of the many generic additives are available for the control of calcium, magnesium, carbonate, sulfate, phosphate, silicate as well as silica and barium and strontium sulfate. The use of acid may or may not be required depending upon the cycled terminal pH. Polymer performances are strictly additive, while polymer fed in combination with other low molecular weight deposit control additives may have a synergistic effect that allows for improved performance at lower use concentrations and ratios for deposit control applications. All the data developed from such testing or ion pairing and computer simulation are used as application guidelines for deposit control. Deposit control without the use of phosphorous containing compounds can be easily engineered to achieve the targeted performance.

Corrosion Control

The use of organic substitutes for inorganic precipitating corrosion inhibitors can be costly and difficult to achieve if equivalent corrosion control performance compared to inorganics is required. Inorganic phosphates, ortho (anodic corrosion control) and polyphosphate (cathodic corrosion control) are low cost and excellent performers in highly corrosive waters, when paired with the proper polymeric stabilizing dispersant. Other low cost precipitating inorganic corrosion inhibitors that are in use include; zinc (cathodic corrosion control) and ortho or reactive silicates (anodic corrosion control). Again, the performance of these additives can be enhanced by pairing them with the proper polymeric stabilizing dispersant.

The majority of the organic substitutes used for corrosion control rely on chemiadsorption of the compound, followed by selective or controlled diffusion of dissolved oxygen to allow for the preferred, protective oxide film build underneath. Thus, they are more susceptible to the impact of other counter or interfering anions (i.e. chlorides, sulfates, dissolved surface corrosion products coordinated with these anions) which can interfere with development of the desired protective film. It is therefore recommended that the Larson Skold index be evaluated for such waters to determine if some inorganic inhibitor may be required to achieve the targeted corrosion control performance without the presence of pitting. The inorganics maybe added to achieve the blowdown outfall restricted value or added to just achieve a detected residual in the cooling water. For sites with clarification of waste or evaporators and crystallizer for ZLD, the use of inorganics may be of little concern as they are not being discharged to a receiving water stream, but land filled as sludge. The simplest inorganics for use in corrosion control include zinc or polyphosphate for cathodic control and ortho-silicate or ortho-phosphate for anodic control.

The following represent some corrosion improvements for various metallurgies:

Avoid suspended solids, organic and biological fouling.

Aluminum, copper/copper alloys, and galvanized steel are all pH and ORP sensitive. Avoid excessively high pH (i.e. > 8.5) or low pH (below 6) unless specific corrosion inhibitors (i.e. azoles, silicates and phosphates, zinc) are added. Avoid free dissolved copper ≥200 ppb for aluminum and galvanized steel. Avoid ORP values greater than + 600 mV.

Stainless Steels - halide concentration allowed is % molybdenum content, temperature and pH dependent. Avoid negative ORP, heat check or stain and iron/manganese deposition.

Titanium - avoid negative ORP and the presence of reducing compounds including organic acids.

Program/Product Design Considerations

Cooling water treatment programs can be divided into three basic types. Properly applied programs and products ensure that the risks of each type are effectively mitigated. These programs typically employ proprietary blended products with a focus on corrosion control, deposit control, or a combination of both.

Corrosion Intensive Waters

These are typically coastal inland fresh waters, snow melt run-off waters, captured rain waters, evaporator, reverse osmosis, or cold lime softened waters that are cycled with or without pH control from acid addition. The cooling waters can be low in calcium and total alkalinity. Or they can be high in chloride and sulfates, thus resulting in high Larson Skold value cooling waters. Specific issues will change, depending on the number of cycles at which the cooling system operates.

Deposit Intensive Waters

These are typically cycled cooling waters that are high in hardness and alkalinity. They can be cycled well waters, process or reclaimed/recycled high hardness high alkalinity waters, waters found in very arid areas, and some surface waters. Primary stressors can include calcium carbonate, magnesium silicate and calcium magnesium silicate. Hence, the Larson Skold values are reduced compared to corrosion intensive waters, effectively making corrosion control easier. Secondary stressors can include phosphate found in the make-up water or high silica levels. Sulfates are easily handled by polymer dispersants.

Balanced Waters

These are cycled cooling waters that have very little corrosion stress and deposit control stress is inherently calcium carbonate, at reasonable calcite saturation levels.

Specific Non-Phosphorous Products

Information on product families has been provided by the supplier. The information is here for informational purposes only. EPRI does not endorse any particular products of any suppliers. Suppliers frequently introduce new products and blends so this information may be valid for a limited time only.

Millsperse: This family contains some products that are zinc-based for cathodic corrosion protection of carbon steel, galvanized steel, copper/copper alloys. .

CIL / DWS: This family contains some anodic corrosion control products consisting of ortho silicates and buffered ortho silicates used in corrosion protection of carbon steel, galvanized steel, copper/copper alloys, and aluminum.

Enviroplus: This family contains some polycarboxylate based corrosion inhibitors. It is claimed to be a mixed potential corrosion inhibitor with primarily cathodic control at pH ≤8.0 and primarily anodic corrosion control at pH ≥8.3.

Non-Phosphorous Scale Control Program Summary

General

General Program Description	These are blends of various polymers of varying molecular weights (1000 to 7000) and functionality. Where-in the functioal groups can be carboxylate, sufonate or nonionic in nature. The polymers may be homo-, co-, ter- and quad- in nature. These descriptors will be used for the individual products listed below.

Program Product 1 Drewsperse 747A

Description	Ultra low molecular weight polycarboxylate antiprecipitant that is extremely effective on preventing calcium carbonate scaling very good on calcium phosphate deposit control..

Program Product 2 Drewsperse 6910

Description	Ultra low molecular weight carboxylated terpolymer antiprecipitant that is extremely effective on preventing calcium carbonate scaling very good on calcium phosphate deposit control and provides zinc stablization.

Program Product 3 Drew 11 - 541

Description	Mid range molecular weight polycarboxylate that is extremely effective on calcium sulfate and very good on calcium carbonate deposit control

Program Product 4 Amersperse 6946

Description	Mid range molecular weight copolymer of polycarboxylate and sulfonate that exhibts both strong acid and weak acid functionality. It is extremely effective on calcium phosphate and very good on calcium carbonate, calcium sulfate deposit control. Stablizes zinc and is used to disperse suspended solids and iron / manganes oxides/hydroxides.

Program Product 5 Drew 11 - 644

Description	same as Amerspesre 6946 but with lower acid functionality to increase calcium carbonate deposit control performance and lowering calcium sulfate and suspended solids performance

Program Product 6 Drew 11 - 804

Description	Mid range molecular weight copolymer of carboxylate and sulfonate and a terpolymer of carboxylates and sulfonate. Extremely good on Calcium carbonate and phosphate deposit control. Very good on calcium sulfate and suspended solids dispersency. Stablizes zinc and is used to disperse suspended solids and iron / manganes oxides/hydroxides.

Program Product 7 Enviroplus 6950

Description	Polycarboxylate with inherent bodegradability. Mixed potential corrosion inhibitor with primary cathodic control at ≤ 8.0 pH and primarily anodic control at ≥ 8.3 pH. Effective on Carbon Steel and Copper/Copper Alloys. Very effective on Calcium Carbonate, good on calcium sulfate and phosphate. Provides some suspended solids despersancy. Will disperse Iron and manganese oxides hydroxides.

Program Product 8 Drewsperse 6935

Description	Mid range molecular wieght quad polymer of carboxylated, sulfonated and non ionic functionality.

Non-Phosphorous Corrosion Control Summary

General

General Program Description	These are adjunct products to be used with deposit control additves to enhance the inhibitor delivery to the meatal surface. The cooling water chemistry to be adjusted to optimize the natural cathodic and anodic half cell enviroment as discussed in the seperate introduction.

Program Product 1	Millsperse 955; Millsperse 957TR
Description	Zinc chloride and Zinc sulfate respectively. Cathodic corrosion control for Carbon Steel, Copper/Copper Alloys, Galvanize.

Program Product 2	CIL : DWS 4005
Description	ortho silicates and buffered ortho silicates respectively. Anodic corrosion control of Carbon Steel, Copper/Copper Alloys, Galvanize, and Aluminum.

Program Product 3	Enviroplus 6950
Description	Polycarboxylate with inherent bodegradability. Mixed potential corrosion inhibitor with primary cathodic control at ≤ 8.0 pH and primarily anodic control at ≥ 8.3 pH. Effective on Carbon Steel and Copper/Copper Alloys.

10

CURRENT STATE OF RESEARCH INTO NON-PHOSPHOROUS PROGRAMS

WTSC's are actively pursuing non-P (and non-Zn) corrosion inhibitors with environmental profiles suitable for direct discharge.

One company has reported considerable success with non-phosphorous corrosion inhibitor cooling water treatment programs, with several commercial applications including power plants. (See references 27-31). A non-P, non-nitrogen program (no nitrogen containing polymers, phosphonates, or azoles) is also commercially available. The still-proprietary chemistry is said to be a synergistic blend of non-P corrosion and scale inhibitors that form a reactive polyhydroxy complex on the surface of the metal. The corrosion inhibitor has the advantage of being easier to control than phosphate based programs, since it is non-fouling and independent of calcium, pH, and temperature. Since it contains no phosphorus in any form, it does not contribute to algae growth in the tower or the environment. It is reportedly effective on steel, copper, and aluminum alloys. The reported environmental data indicate approximately a 30x safety factor between the typical usage concentration and aquatic effects levels, which facilitates direct discharge of the treated cooling water in sensitive areas.

11
REFERENCES

---

[1] *Open Cooling Water Chemistry Guideline*, EPRI, Palo Alto, CA, 2012, 1025318.

[2] C. Frayne, *Cooling Water Treatment: Principles and Practices*, Chemical Publishing Company, 1999.

[3] J. N. Tanis, *Procedures of Industrial Water Treatment*, LTan Inc., Ridgefield, CT.

[4] *The Nalco Water Handbook, Third Edition*, McGraw-Hill, 2009.

[5] *Handbook of Industrial Water Treatment*, GE Water & Process Technologies, online at http://www.gewater.com/handbook/index.jsp

[6] *Drew Principles of Industrial Water Treatment*, Drew Chemical Corporation, Boonton, NJ, 1990.

[7] *Kurita Handbook of Water Treatment*, Kurita Water Industries, 4-7 Nishi-Shinjuku 3-chome, Shinjuku-ku, Tokyo 160.

[8] *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs*, United States Environmental Protection Agency.

[9] Clean Water Act, Section 303(d).

[10] *Service Water System Corrosion and Deposition Sourcebook*, EPRI, Palo Alto, CA, 1993, TR-103403.

[11] *Service Water System Piping Guideline*, EPRI, Palo Alto, CA, 2005, 1010059.

[12] *Life Cycle Management Sourcebook for Nuclear Plant Service Water Systems*, EPRI, Palo Alto, CA, 2005, 1008282.

[13] *Sourcebook for Microbiologically Influenced Corrosion in Nuclear Power Plants.* EPRI, Palo Alto, CA: 1988. NP-5580.

[14] H. Herro and R. Port, *The Nalco Guide to Cooling Water Systems Failure Analysis*, McGraw-Hill, 1993.

[15] Frayne, C., *Cooling Water Treatment Principles and Practice*, Chemical Publishing Company, 1999.

[16] J. M. Brooke, "Magnesium Silicate Scaling in Circulating Cooling Systems*,"* NACE International, Corrosion '84, Paper No. 327 (1984).

[17] *Treatment of Silica Limited Cooling Water*, EPRI, Palo Alto, CA: 1984, CS-4212, Vols. 1-3.

[18] Z. Amjad, ed., *The Science and Technology of Industrial Water Treatment*, CRC Press, 2010.

[19] T. Larson, R. Skold, "Laboratory Studies Relating Mineral Quality of Water to Corrosion of steel and Cast Iron," Corrosion, (1958).

[20] R. Pisigan and J. Singley, "Evaluation of Water Corrosivity Using the Langelier Index and Relative Corrosion Rate Models," Corrosion 84, New Orleans LA, (1984).

[21] L. Lehrman, H. L. Shuldener, Journal of the American Water Works Association, 43, 175, (1951).

[22] L. Lehrman, Journal of the American Water Works Association, 56(8), 1009, (1964).

---

[23] N. Asrar, U. M. Anees, A. Shahreer, “Corrosion Prevention with Sodium Silicate”, Technical Report No. TR3804/EVP95013, 1998.

[24] Revised Guideline for Makeup Water Treatment, EPRI, Palo Alto, CA, 1999, TR-113692.

[25] R.M. Post, R.H. Tribble, H. R. Cerra, and T. Banks, “Meeting Environmental Aquatic Challenges for the Next Generation of Nuclear Plant Construction”, Proceedings International Water Conference, IWC 09-17, 2009

[26] R.M. Post, R.H. Tribble, and J.R.Richardson, “Development of Next Generation Phosphorus-Free Cooling Water Treatment Technology”, Proceedings International Water Conference, IWC 10-23, 2010

[27] R.M.Post, H.R.Cerra, and R.H.Tribble, “Development and Application of Phosphorus-Free Cooling Water Treatment Technology”, Procedings of the 31st Annual Electric Utility Chemistry Workshop, 2011

[28] J. Richardson, H. Cerra, R. Tribble, “Nutrient Control – The Key to a Low Environmental Impact Cooling Water Program,” Proceedings of the International Water Conference, IWC 11-15, 2011.

[29] R.M.Post, P. Kalakodimi, R. Tribble, “Development and Application of Phosphorus Free Cooling Water Technology” Proceedings of the Cooling Technology Institute, TP14-14, 2014.

Export Control Restrictions
Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute, Inc. (EPRI, www.epri.com) conducts research and development relating to the generation, delivery and use of electricity for the benefit of the public. An independent, nonprofit organization, EPRI brings together its scientists and engineers as well as experts from academia and industry to help address challenges in electricity, including reliability, efficiency, affordability, health, safety and the environment. EPRI also provides technology, policy and economic analyses to drive long-range research and development planning, and supports research in emerging technologies. EPRI's members represent approximately 90 percent of the electricity generated and delivered in the United States, and international participation extends to more than 30 countries. EPRI's principal offices and laboratories are located in Palo Alto, Calif.; Charlotte, N.C.; Knoxville, Tenn.; and Lenox, Mass.

Together...Shaping the Future of Electricity

Program:
Water Mangement Technology

© 2014 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute, EPRI, and TOGETHER...SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

3002001276

Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com