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## **Low Maintenance Water Treatment for Heating and Cooling Systems**

Review of Technologies and Guidelines for Implementation

Kent W. Smothers, Susan A. Drozd, and Vincent F. Hock

September 2007



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**Abstract:** Manufacturers of chemicals and treatment programs for new and existing heating and cooling systems continuously discontinue old products and introduce new ones onto the market. To be “smart buyers” of these products, Army installations require periodic technology reviews to stay informed about advances and new capabilities of water treatment products available in the marketplace. This work reviewed current state-of-the-art treatment schemes and technologies, and summarized general guidelines for developing chemical treatment programs in heating and cooling systems.

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## **Preface**

This study was conducted for Directorate of Military Programs, Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162784AT41, "Military Facilities Engineering Technology," under Work Units 0079X4 and 008BBF, "Low Maintenance Water Treatment for Heating and Cooling Systems." The technical monitor was William D. Goran, CEERD-CV-T.

The work was performed by the Materials and Structures Branch (CF-M) of the Facilities Division (CF), Construction Engineering Research Laboratory (CERL). The CERL principal investigator was Vincent F. Hock. Kent W. Smothers is affiliated with the Illinois State Water Survey. Martin J. Savoie is Chief, CEERD-CF-M, and L. Michael Golish is Chief, CEERD-CF. The Director of CERL is Dr. Ilker R. Adiguzel.

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## Unit Conversion Factors

Multiply	By	To Obtain
British thermal units (International Table)	1,055.056	joules
centipoises	0.001	pascal seconds
centistokes	1.0 E-06	square meters per second
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees (angle)	0.01745329	radians
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
foot-pounds force	1.355818	joules
gallons (U.S. liquid)	3.785412 E-03	cubic meters
horsepower (550 foot-pounds force per second)	745.6999	watts
inches	0.0254	meters
inch-pounds (force)	0.1129848	newton meters
miles (U.S. statute)	1,609.347	meters
ounces (mass)	0.02834952	kilograms
ounces (U.S. fluid)	2.957353 E-05	cubic meters
pints (U.S. liquid)	4.73176 E-04	cubic meters
pints (U.S. liquid)	0.473176	liters
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter
pounds (mass) per cubic inch	2.757990 E+04	kilograms per cubic meter
pounds (mass) per square foot	4.882428	kilograms per square meter
pounds (mass) per square yard	0.542492	kilograms per square meter
quarts (U.S. liquid)	9.463529 E-04	cubic meters
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square yards	0.8361274	square meters
tons (2,000 pounds, mass)	907.1847	kilograms
tons (2,000 pounds, mass) per square foot	9,764.856	kilograms per square meter
yards	0.9144	meters



# **1 Introduction**

## **1.1 Background**

The development of up-to-date selection and guidance is necessary to help Army installations be “smart buyers” of water treatment for new and existing heating and cooling systems. This includes central plant heating and cooling systems, and building heating, ventilating, and air conditioning (HVAC) systems. Specifically, treatment for cooling towers, steam boilers, condensate return systems, and closed heating and cooling systems needs to be addressed. Manufacturers continue to introduce new chemicals and treatment programs onto the market, and old products have been discontinued. The Corps of Engineers (COE) and Army have not evaluated these new chemicals in over 10 years, therefore Army installations may be uninformed as to new advances, and may be unable to make informed choices regarding products promoted by chemical vendors.

The lack of current and consistent guidelines has resulted in poor control of water treatment at many facilities. Poor control has resulted in reduced system reliability and efficiency, and increased maintenance costs due to premature failure of systems and components.

This document will discuss some of the more common treatment strategies in use today for heating and cooling systems, and provide general guidance on the performance that a successful treatment program should be expected to achieve in these systems. It will also provide some guidance on how to evaluate the effectiveness of a water treatment program.

## **1.2 Objective**

The objective of this work is to evaluate current state-of-the-art treatment schemes and technologies, to develop guidelines for chemical treatment programs in heating and cooling systems, and to confirm the effectiveness of selected treatment programs in field installations.

## **1.3 Approach**

1. A literature review was conducted to identify new and/or environmentally friendly treatment chemicals and to evaluate their potential for application at Army installations.

2. A preliminary approach was developed, and presented to a User Group Meeting comprised of representatives from several Army installations and an Industry Expert Panel, which further modified the scope and approach of the study to include the following principal elements:
  - a. A general review of open heating/cooling system treatments (Chapter 2, p 3)
  - b. A general review of closed heating/cooling system treatments (Chapter 3, p 10)
  - c. A general review of steam boiler/condensate treatments (Chapter 4, p 14)
  - d. A discussion of initial conditioning and storage considerations (Chapter 5, p 19)
  - e. A description of the steps involved in selection and specification of a chemical treatment program (Chapter 6, p 23)
  - f. A description of the steps involved in evaluating a chemical treatment program (Chapter 7, p 26).

#### **1.4 Mode of Technology Transfer**

This report will be made accessible through the World Wide Web (WWW) at URL: <http://www.cecer.army.mil>

## 2 Treatment of Open Heating and Cooling Systems

### 2.1 Open Cooling System Treatment

Open cooling systems (Figure 1) present a wide range of problems from a chemical treatment standpoint. Since these systems accomplish cooling by evaporation, minerals and dissolved solids present in the makeup water are constantly concentrated to levels that can far exceed their solubility in a very short time. Evaporation also concentrates corrosive species, making corrosion control critically important. The relatively high concentration of nutrients and generally warm temperatures make these systems an ideal environment for many forms of biological growths, including bacteria, algae, and (when wood is used in construction) fungi. Cooling towers also effectively scrub fine particulate matter from the air, accumulating large quantities of fine, silt-like material, which is often rich in organic matter. The first, and perhaps the most important step of any cooling water treatment program, is to establish good maintenance practices, and to *keep the system clean*. Most open cooling system chemical treatment blends will, as a minimum, include a copper/yellow metal corrosion inhibitor, a steel corrosion inhibitor, a polymer with scale inhibition and/or dispersant capabilities, and a biocide. A discussion of various ways to control these problems follows.



**Figure 1. Cooling towers.**

## 2.2 Corrosion Control

The most common construction materials used in open cooling systems are steel (piping and tube sheets) and copper (condenser tubes). Various copper alloys are sometimes used instead of copper for the condenser tubes. The cooling towers themselves can be constructed of fiberglass, galvanized steel, stainless steel, or even wood. Galvanized steel is by far the most common, but fiberglass and stainless steel are gaining popularity in certain areas and applications. It is absolutely essential to determine all of the materials of construction, system size and operating conditions, and the makeup water quality before selecting the proper corrosion control program. Table A1 (see Appendix A, p 40) lists chemicals widely used and recognized as effective corrosion inhibitors for open cooling systems.

The most commonly used corrosion inhibitors for copper and yellow metal alloys are tolytriazole (TT), benzotriazole (BZT), and mercaptobenzothiazole (MBT). (Tolytriazole is by far the most common.) Although these compounds are extremely effective copper corrosion inhibitors, their main drawback in cooling systems is their sensitivity to attack by oxidizing biocides. Also, the relatively new phosphonate, manganese/aminophosphonic acid (MAPA) has shown some promise as a copper corrosion inhibitor.

Steel corrosion inhibitors are more varied, but most fall into two categories: anodic or cathodic. Put simply, anodic inhibitors work by forming a barrier at the anode, and cathodic inhibitors form a barrier on the cathode. Anodic inhibitors include orthophosphates, nitrite, and molybdate. When using anodic inhibitors, it is important to always maintain adequate concentrations in the bulk water. Failure to add sufficient chemical to form a passive coating on all of the anodic sites can lead to increased localized corrosion rates. Cathodic inhibitors include polyphosphates and zinc salts. A number of phosphonates are also effective as steel corrosion inhibitors. The most common of these is hydroxyphosphono acetic acid (HPA). Phosphono carboxylate mixtures and derivatives have also started to see widespread use as steel corrosion inhibitors in cooling systems.

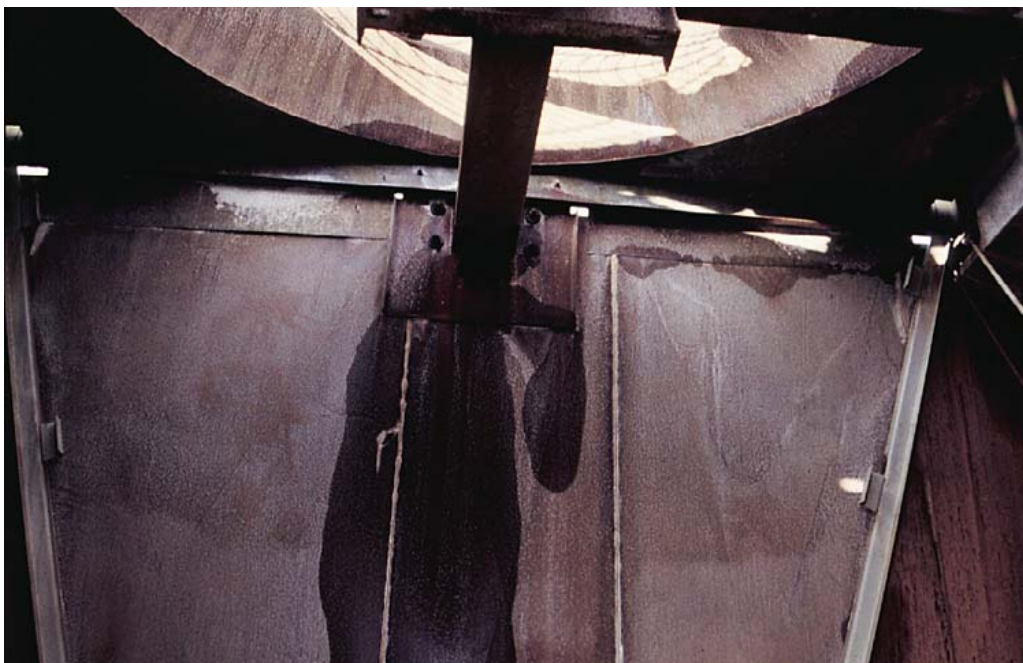
The Association of Water Technologies (AWT) Cooling Water Subcommittee has established and published standards (Boffardi 2000) for quantitatively classifying corrosion rates obtained under their established guidelines in open and closed cooling systems for steel and copper/copper alloys (see Tables B1 and B2, respectively, in Appendix B to this report, p 42). The corrosion rates that any specific system can achieve depend on many factors, including water quality, temperature, nature and amount of con-

taminants present, and the type and level of treatment. At times, the cost of achieving “excellent” versus “very good” corrosion control may not be warranted. The level of protection expected for a specific system should be identified and agreed on before selecting a treatment program.

### 2.3 Mineral Scale Control

The most common mineral scale in open cooling systems is calcium carbonate, although other calcium salts, magnesium salts, and silicates are not uncommon. The use of sulfuric acid was a common form of scale control for many years, but it has become fairly uncommon with the banning of the use of chromate as a corrosion inhibitor in open cooling systems, and the development of more effective scale inhibiting compounds. The potential for catastrophic damage if an overfeed of acid occurs (Figure 2), and the existence of economical and effective alternatives, have caused most facilities to discontinue acid usage.

The most effective and frequently used calcium carbonate inhibitors are phosphonates, with the following compounds most frequently used: 1-hydroxyethylidene, 1-2-diphosphonic acid (HEDP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), and aminotri(methylenephosphonic acid) (AMP). Phosphonates can be loosely defined as any molecule containing at least one phosphonic acid group. Table A2 (p 40) lists the phosphonates most commonly used for scale control in open cooling systems.



**Figure 2. Galvanized tower damaged by sulfuric acid.**

One of the oldest forms of scale inhibition, which is still in use for very small (<50 tons) cooling towers or evaporative condensers, is slowly soluble polyphosphate. This product will allow for some cycling and provide some corrosion inhibition as well. It is available in plastic mesh bags or containers that are suspended in the basin, and dissolves very slowly, providing a crude form of dosage control. For small towers that receive very little day-to-day attention, this is sometimes a viable treatment alternative.

In addition to phosphonates, a number of polymers are used either separately or in combination with phosphonates to achieve overall scale control. While polymers are generally less effective at inhibiting calcium carbonate scale, they are more efficient when it comes to preventing other salts like calcium sulfate, silicates, and calcium phosphate or phosphonate. Many of the common polymers used in cooling tower formulations also act as dispersants with suspended solids. The more effective they are at this task, the more forgiving the treatment formulation will be in preventing scale build-up during temporary upsets in water chemistry.

The first class of polymers that found widespread use and success were the polyacrylates, which are homopolymers of acrylic acid. A variety of polyacrylates are available, and the specific properties of any individual product are largely tied to its molecular weight. Lower molecular weight polyacrylates are, in general, good calcium carbonate and calcium sulfate inhibitors and very good dispersants. Higher molecular weight polyacrylates are used as flocculating agents, and are unsuitable for use in cooling systems. These products are also usually fairly economical in comparison to some of the more recently developed and more complex polymers.

These first molecules were all homopolymers, having only one functional group. Today, there are a number of copolymers (two functional groups), terpolymers (three functional groups), and even a quadpolymer (four functional groups) on the marketplace. Virtually all of these new polymers, with the exception of polymaleic acid derivatives, are at least partially based on a polyacrylic acid component. New products continue to be introduced into the marketplace, and most of these find a niche where they can provide a competitive advantage. Table A3 (p 40) lists some of the most common polymers in use today.

## **2.4 Fouling Control**

The ability to control fouling depends largely on the effectiveness of corrosion, scale, and biological control. Fouling can be defined in many ways,

but for the purposes of this report, it is defined here as “the accumulation of suspended solids, biomass, corrosion products, or mineral scale on heat exchanges surfaces.” An effective chemical treatment program that controls corrosion, scaling, and biological growth can prevent fouling in most cases. Many of the polymers commonly used in cooling water treatment formulations are excellent dispersants. However, cooling towers are very efficient at scrubbing particulate matter from the air, and this can make fouling control very problematic. One of the best tools that can be used to supplement chemical treatment is side-stream filtration. Filtration improves the overall performance of almost any cooling water treatment formulation.

## 2.5 Microbiological Control

The control of biological growth in open cooling systems can be very problematic as the conditions are almost ideal for the propagation of microbes and algae. Bacteria, protozoa, algae, and fungi all thrive in the warm, nutrient-rich water systems. The failure to control that biological growth can make controlling scale, corrosion, and fouling almost impossible, in addition to creating the potential for serious health risks. While Legionnaire’s disease is perhaps the best known health condition associated with cooling towers, there are a host of other pathogenic organisms that could potentially present health risks if not controlled. Biocides used in open cooling systems are generally divided into two classes, oxidizing and non-oxidizing, both of which can be effective in controlling biological growth. An effective biological control program can be developed using either oxidizing or non-oxidizing biocides, or a combination of both types. *The most important part of any successful biocide program is to keep the system clean.* Visual inspection of the tower basin and fill is required one to four times per month (depending on size, location, etc.) to determine if physical cleaning is necessary.

Oxidizing biocides include various forms of chlorine and bromine, hydrogen peroxide, and ozone. All of these products are effective against *Legionella*, with chlorine generally preferred at lower pH levels (<8.0), and bromine at higher pH levels. Oxidizing biocides react very quickly with any biological material in the system, which also means that they deteriorate very quickly. Also, note that oxidizing biocides react with many of the treatment chemicals mentioned earlier. Since most phosphonates, polymers, and azoles are attacked to some degree by oxidants, selecting the appropriate oxidant, the necessary concentration, method of feeding, etc., all require careful consideration to minimize impacts on other treatment

chemicals. Table A4 (p 41) lists some of the more common oxidizing biocides.

Non-oxidizing biocides are more persistent, and will remain in the system until removed by blowdown. They can be applied continuously, or in slugs. Since a tolerant strain of microbes will sometimes become problematic when using a single non-oxidizing biocide, it is common practice to alternate with another non-oxidizing biocide and/or an oxidizing biocide. Many non-oxidizing biocides are more effective at penetrating biomass than oxidizing biocides. This makes them very effective tools in fighting the fouling problem addressed earlier. Some of the newer non-oxidizing biocides are much more environmentally friendly than earlier compounds, e.g., tetrakis (hydroxymethyl) phosphonium sulfate (THPS), the winner of the 1999 President's Green Chemistry Challenge Award. Some of these compounds can also be used to target specific problems. For example, Terbutylazine has very little efficacy towards bacteria, but is extremely effective in managing algae problems. Table A5 (p 41) lists some of the more common forms of non-oxidizing biocides.

## 2.6 Treatment Monitoring and Control Requirements

Open cooling system chemistry can change very rapidly, so control of blowdown and chemical feed (including biocides) needs to be as automated as possible. Conductivity controllers that can accept multiple inputs from makeup meters, conductivity meters, pH probes, etc. are required. These controllers will maintain the conductivity within a predetermined range, and control the metered addition of chemicals and biocides. General specifications for chemical treatment equipment are provided in *Smart Corrosion Control Monitoring and Control Systems for Heating and Cooling Applications* (Hock et al. 2006).

While automated treatment systems provide a convenient and effective way to maintain cooling water chemistry and treatment within the desired range, the performance of the system needs to be confirmed by periodic on-site testing. This is critical to ensuring the success of any treatment program. The exact tests that need to be performed and the frequency with which they need to be done will vary depending on the system, makeup quality, and specific chemical program employed. This testing criteria needs to be established before the implementation of the program, and the system needs to be checked regularly to confirm the criteria are being adhered to. A control chart should be developed to detail any actions that



need to be taken in response to the test results. As a *minimum*, the following regular tests are required:

- a hardness and/or conductivity test should be done to confirm operating cycles of concentration and potential for scaling
- an inhibitor or tracer test to confirm chemical treatment concentration.

Molybdate, commonly used as a corrosion inhibitor, can be easily tested with a simple comparator. Phosphonate and polymer test kits exist, but are more time consuming and sometimes subject to interferences. Metal concentrations should be monitored periodically as well (iron and copper as a minimum, others may be required depending on materials of construction). Corrosion rate monitoring is also strongly recommended.

Some biocides have test kits to determine their concentration as well, and where applicable this should be done. Additionally, another means of evaluating biocide effectiveness is in the use of test kits to determine approximate concentrations of different microbes. A number of commercially kits are available to test for aerobic bacteria, anaerobic bacteria, slime-formers, iron bacteria, etc. These good screening tools can at least provide an indication of the overall effectiveness of the biocide program, and of the effectiveness of the biocide program towards planktonic (or mobile) bacteria. However, they may not provide accurate information on the efficacy of the program towards the sessile (non-mobile, the colonies that form on the pipe surfaces) microbe populations. Deposit/fouling monitors and bio-probes are commercially available to test the effectiveness towards sessile colonies. Monitoring for *Legionella* is more difficult, and requires an expensive laboratory test.

### 3 Treatment of Closed Heating and Cooling System

Closed recirculating systems are commonly used for both heating and cooling in building HVAC systems. They can be very small, local systems of less than a hundred gallons, or central systems containing several hundred thousand gallons. At one time, there was a conception that these systems did not require chemical treatment. Since there is no concentration of salts in closed systems, as occurs in open cooling systems or steam boilers, most of these systems do not require any kind of mineral scale inhibitors in their treatment formulations. Some high temperature systems may need zeolite softening to prevent scale formation, particularly if makeup rates are excessive. Nevertheless, these systems are all susceptible to corrosion, and chilled systems are subject to microbiological problems similar to cooling towers. Closed systems typically contain mixed metallurgy that makes galvanic corrosion control a prime concern. Figure 3 shows an example of oxygen pitting that occurred in a closed heating system boiler experiencing high makeup rates.

#### 3.1 Corrosion Control

Corrosion control in closed systems has traditionally incorporated a mild steel inhibitor and copper/copper alloy inhibitor. Elevation of system pH is usually, but not always, a part of the treatment. The most common steel inhibitors include nitrite, molybdate, and silicates. Corrosion and biological control in closed systems can be aided by properly designed and maintained side-stream filtration.



**Figure 3. Hot water boiler tube pitting.**

Nitrite forms a passive film on steel surfaces, and is usually coupled with a buffering agent like borax to supplement the pH and buffering capacity. An azole is normally added to provide copper corrosion inhibition, most commonly tolytriazole. While nitrite is a very effective corrosion inhibitor when properly applied, it can also become a food source for bacteria in chilled water systems. A good biocide program is absolutely critical when using nitrite in chilled water systems. Figure 4 shows an example of how effective the nitrite/borate/azole program can be. This pipe was removed from a closed heating system after more than 25 years of service with consistent treatment using the nitrite/borate/azole program.

Molybdate is an anodic inhibitor that is effective at limiting steel corrosion. Molybdate is typically used in high concentrations when used in closed systems. The addition of an oxidizer like nitrite makes molybdate more effective at lower concentrations. Since molybdate is a relatively expensive product, it is common to see nitrite and molybdate used in combination in closed system treatment blends, especially in heating systems. Molybdate blends normally incorporate an azole for copper inhibition as well. An effective blend would incorporate 60 to 80 parts per million molybdate in combination with an inhibiting agent such as tolytriazole.

Silicates form a protective film on metallic surfaces, and will protect both steel and copper/copper alloys. Silicates can be used alone, or in combination with nitrite, molybdate, and azoles. One advantage silicate has is the ability to form a protective film over existing corrosion products on steel piping. However, silicate programs require careful management since there is the potential for the formation of an insulating deposit on heat exchange surfaces.



**Figure 4. System piping treated with nitrite/borate/azole.**

High temperature closed systems (>350 °F) can sometimes be treated effectively with only pH adjustment and an oxygen scavenger. The pH is normally adjusted with sodium hydroxide, and sodium sulfite is added as an oxygen scavenger. As long as the system does not develop excessive makeup rates, this treatment scheme is very effective.

Organic inhibitors are also more commonly used in closed system treatment, either as dispersants with compounds such as polyacrylates, or as true corrosion inhibitors. Thermal polyaspartate is one compound that has already been proven in open cooling systems and is sometimes used in closed systems as well.

Note that many closed heating and cooling systems are filled with either ethylene glycol or propylene glycol. These systems require attention to corrosion inhibition as well. While most glycols will be purchased with some form of an inhibitor added, it is not uncommon to find systems filled with uninhibited glycol. Glycol solutions, while relatively non-corrosive initially, will degrade to organic acids over time. For this reason, inhibited glycol solutions will normally contain a buffering agent to neutralize any acids generated in addition to other corrosion inhibitors. Inhibitors can and should be added to any uninhibited glycol solutions.

### **3.2 Microbiological Control**

Microbiological control in closed chilled water systems and heating systems operating under 131 °F is critical to accomplish corrosion and fouling control, and to avoid potential health problems. A biocide program should be selected to complement the corrosion inhibitor program in use. The system pH must always be considered since many biocides have a limited effective pH range.

Most of the non-oxidizing biocides used in open cooling systems (see Table A5, p 41) are used in closed systems as well. Oxidizing biocides are also used, of which bromine and chlorine dioxide are probably the most common. Oxidizing biocides are not compatible with treatment programs containing nitrite, since they will oxidize the nitrite to nitrate. Closed system biocide programs should be designed to control both sessile and planktonic bacteria.

### 3.3 Treatment Monitoring and Control Requirements

Closed heating and cooling systems usually require less sophisticated treatment monitoring and control equipment than open cooling systems since they do not concentrate solids, and they do not normally require frequent additions of chemical treatment and/or makeup water. However, they may benefit from a pH or conductivity monitor that can sometimes be used to control chemical treatment as well, depending on the specific system and treatment employed.

As with open cooling systems, treatment levels and system chemistry must be monitored by periodic on-site testing to confirm the presence of sufficient inhibitor concentration. Some basic tests must also be done to ensure the success of the treatment program. As with open systems, the exact tests that need to be performed and the frequency with which they need to be done vary depending on the system, makeup quality, and specific chemical program employed. Generally, closed systems will require less frequent and comprehensive testing than open cooling system or boilers, because the water quality does not change as quickly. At a minimum, an inhibitor or tracer test to confirm chemical treatment concentration needs to be done. It is usually advisable to monitor pH, conductivity, and metal concentrations (iron and copper) periodically. Corrosion rate monitoring is also strongly recommended.

For chilled water systems, if the biocide in use has a test kit, the concentration should be monitored regularly. In any case, microbiological test kits should be used to monitor bacterial populations in chilled water systems. Sulfate reducing bacteria and other anaerobic bacteria can be especially problematic in chilled water.

## 4 Steam Boiler/Condensate Treatment

### 4.1 Steam Systems – Makeup Pretreatment

Steam boilers evaporate water, concentrating any dissolved solids in the makeup water. To control the dissolved solids content, boilers are regularly “blown down.” Various types of pretreatment equipment, such as softeners, demineralizers, and reverse osmosis, are used to remove dissolved solids from the water. The type of pretreatment required depends on such parameters as makeup quality, makeup rates, operating pressures, and boiler design. As a minimum, most boilers benefit from softening to remove calcium and magnesium.

Additionally, larger systems use a deaerator to remove dissolved gases from the makeup train. This is one of the most critical pieces of equipment in any steam plant, and should be monitored daily to ensure that it is operating properly. The operating principle is simple. Boiler feedwater is heated with steam, and a portion of the steam is allowed to vent to the atmosphere, carrying any dissolved gases with it. A simple check can be performed to confirm that the temperature and pressure agree, indicating efficient deaerator operation. The following formula provides an easy way to determine the correct operating temperature:

$$T = 212 + (3 \times P) \quad \text{Eq 1}$$

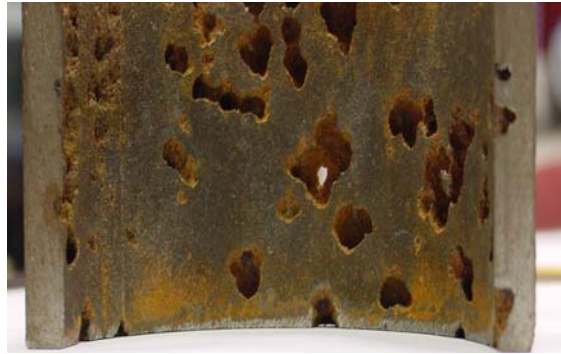
where:

T (temperature) is expressed in °F for a given pressure

P (pressure) is expressed in psig, gauge pressure above atmospheric pressure.

Also, simple test kits are available to monitor dissolved oxygen in boiler feedwater. However, great care must be taken in collecting the sample. Sample collection lines and the sample cooler should be constructed of stainless steel. Dissolved oxygen concentrations should be monitored weekly (at least).

The failure to maintain a deaerator in efficient operating condition can result in a rapid failure of the deaerator and feedwater piping, since the reaction of oxygen with the steel piping is almost instantaneous at the elevated temperatures in boiler feedwater. Figure 5 shows a section of feedwater piping that failed in less than 1 year due to a faulty deaerator.



**Figure 5. Feedwater piping failure from oxygen pitting.**

## **4.2 Steam Systems – Internal Treatment**

Chemical treatment of non-utility steam boilers usually consists of an oxygen scavenger for the boiler, dispersant/scale inhibitors, an anti-foam agent, and a treatment to protect the steam distribution and condensate return system. The most common types of programs would be chelant, all organic, and phosphate residual programs.

Chelant programs can be effective, and provide good control of high iron and copper concentrations, but require very careful monitoring and control. Overfeed, or locally high concentrations of the chelant, can result in a severe corrosion attack. The extremely corrosive nature of the concentrated solution can also make handling and application of a chelant problematic. For those reasons, and because other effective options exist, chelant programs are not usually the best choice for most installations.

The all-organic (or all-polymer) programs have become much more common, and can be effective for controlling scale and for iron and copper transport through the boiler. All-organic programs typically combine several types of organic polymers such as polyacrylic acid, polymaleic acid, and copolymer and terpolymer derivatives of those compounds.

The most common program is the phosphate residual program. In this program, phosphate is added to react with calcium salts. Organic polymers are added to act as calcium phosphate deposit inhibitors, and also to act as dispersants to prevent sludge accumulation and aid in iron and copper transport. This is a fairly robust program, and (unlike the all-organic program) can handle a fair amount of hardness in-leakage and remain effective at preventing scale buildup or sludge accumulation. The phosphate residual test is also quick, easy, and economical, in contrast to tests available for polymer concentrations.

The type of program and individual components chosen for any specific application will depend on boiler design, level of staff supervision and training, makeup quality and rate, steam usage, and environmental and regulatory issues. Steam that is used for cooking of food must comply with Food and Drug Administration (FDA) and/or U.S. Department of Agriculture (USDA) guidelines. These regulations are very specific, and allow for only certain chemicals to be used.

The most common oxygen scavenger used is sulfite. Sulfite is economical to use, reacts quickly, and is easy to handle and apply. The test for residual sulfite is also quick and easy. However, at higher pressures, the dissolved solids added by sulfite can be of concern. One disadvantage of sulfite is that it is not effective as a steel passivator, or as an oxygen scavenger in the condensate return line. Other available oxygen scavengers are erythorbic acid or sodium erythorbate, diethylhydroxylamine (DEHA), and methylethylketoxime (MEKO). These compounds are also effective passivators, and DEHA and MEKO both protect the condensate return system.

Condensate treatment is used to prevent oxygen corrosion and CO<sub>2</sub> attack. Carbonate alkalinity in the boiler makeup that is not removed by pre-treatment will break down in the boiler to form CO<sub>2</sub> that travels out of the boiler with the steam and forms carbonic acid in the condensate. This can cause a very aggressive grooving type of a corrosion attack in condensate return lines (Figure 6). Neutralizing amines are basic compounds that react with the carbonic acid formed by CO<sub>2</sub> from the makeup. The most common neutralizing amines are cyclohexylamine, morpholine, and diethylaminoethanol. These compounds are often used in combination, since they will tend to concentrate differently in different parts of the system due to the variance in volatility of the three compounds.



**Figure 6.** CO<sub>2</sub> attack of condensate return line.





**Figure 7. Iron oxide and filming amine buildup on feedwater piping.**

DEHA and MEKO are both effective at controlling oxygen corrosion in condensate return systems. Another method of controlling oxygen corrosion is the use of filming amines. These compounds (most commonly octadecylamine) form a protective barrier on the metal surface. Filming amines can perform very well at preventing oxygen corrosion, but they tend to loosen and remove existing oxides, and can cause maintenance problems if not properly applied. The loosened oxide material becomes bound together by the filming amine compound, and can make steam traps and other equipment inoperable. Figure 7 shows a piece of feedwater piping removed from a system where octadecylamine had been added at an excessive rate. This deposit consisted of iron oxide loosened from the condensate return system and filming amine. The feedwater piping was new, and there was no corrosion of the underlying piping. However, in less than 1 year, a deposit formed that was heavy enough to significantly reduce the capacity of the feedwater pump.

### **4.3 Steam Systems – Monitoring and Control**

Steam system chemistry can change very rapidly, so control of continuous blowdown and chemical feed needs to be automated. Conductivity controllers that can accept multiple inputs from makeup meters, conductivity meters, pH probes (for condensate), etc. are required. These controllers will maintain the conductivity within a predetermined range, and control the metered addition of chemicals. Hock et al. (2006) provide general specifications for chemical treatment equipment.

While automated treatment systems provide a convenient and effective means of maintaining boiler water chemistry and condensate treatment, confirmation of the performance of the system needs to be achieved by periodic on-site testing. This is critical to ensuring the success of any treat-

ment program. The exact tests that need to be done and the frequency they need to be done will vary depending on the system, makeup quality, pretreatment equipment, operating pressures, and specific chemical program employed. This testing criteria needs to be established before implementing the program. Regular checks need to be done to confirm that criteria are being adhered to, and a control chart should be developed to detail any actions that need to be taken in response to the test results. As a *minimum*, the following tests are required regularly for boiler water:

- conductivity
- oxygen scavenger residual
- phosphate (if used)
- polymer (if used)
- hardness
- pH or alkalinity.

The condensate should be tested for conductivity, pH, alkalinity, and hardness. Other tests, such iron and copper in boiler water or condensate, or neutralizing amines in condensate, may be required less frequently. The deaerator should have a dissolved oxygen test performed at least weekly. Pretreatment equipment, such as ion exchange, reverse osmosis, etc., should have tests done to confirm that it is operating as desired. The exact tests required, and the acceptable levels for those tests, should be identified by the chemical contractor. The control of suspended solids is usually accomplished by manual “flash” blowdown, performed as-needed, or at prescribed intervals.

## **5 Initial Conditioning and Storage Considerations**

### **5.1 Initial Conditioning of Equipment**

#### **5.1.1 Before Operation (New Systems)**

New systems should always be cleaned and passivated before start-up and before any final adjustments to system controls are made. New piping may contain mill scale, flash rusting from exposure to the elements, oils, or other contaminants that should be removed before operation. Particular attention should be paid to boilers, stainless steel or galvanized cooling towers, and large piping systems.

Boiler manufacturers usually recommend an alkaline boil-out, generally consisting of an alkaline phosphate solution such as disodium or trisodium phosphate, and a surfactant, which is circulated in the boiler for a prescribed amount of time with frequent blowdown from the “mud” drum to remove suspended solids. The exact formulation and procedure used varies with the specific equipment. The chemical vendor should be responsible for determining the correct formulation and ensuring that proper procedure is followed to comply with local sanitary sewer discharge ordinances.

Cooling towers require a somewhat different cleaning procedure. Stainless steel cooling towers require thorough flushing to remove surface deposits and debris, since the presence of any deposits will interfere with the replenishment of the protective oxide layer and allow pitting to occur. New galvanized steel towers are subject to a form of corrosion known as “white rust” under alkaline conditions, and need pre-conditioning to prevent this attack. White rust is a form of zinc oxide, which is white in color, and can lead to the failure of the tower within a very short time frame if not controlled. The Cooling Technology Institute (CTI) recommends operation of new towers with a pH of 7.0-8.0 and an alkalinity of 100-300 mg/L for the first 45 to 60 days of operation to allow time for a resilient passive oxide layer to develop on the surface.

Since this is impossible with many water supplies, an alternative has been developed. Circulation of a neutral-pH blend of ortho-phosphate, a surfactant, and a dispersant for a prescribed amount of time can allow formation

of the passive oxide layer within a few days. The exact formulation, circulation time, and dosage will vary according to makeup water quality, materials of construction, and equipment design. The chemical vendor should be responsible for determining this information and certifying the proper procedure is followed.

Again, when selecting the proper cleaning method and formulation for any system, it is important to ascertain all of the materials of construction, types of equipment, and local sanitary system discharge rules and limitations. It is the responsibility of the vendor/contractor that provides this service to certify that the proper procedure is followed and all local, state, and Federal ordinances are complied with during the procedure. However, since the system owner/operator will need to operate and maintain the system in question, it is important to monitor this process and confirm that the approved specifications are followed.

#### **5.1.2 After Storage or Lay-up (Return to Service)**

Systems returned to service may require some cleaning, especially cooling towers, which will accumulate silt and organic material during seasonal lay-ups. Towers should be cleaned and inspected before being returned to service. Towers also require disinfection with chlorine after flushing and before applying corrosion inhibitor/passivator blend.

## **5.2 Seasonal Lay-up or Storage**

Heating and cooling system equipment is often taken out of service for extended periods, either due to a scheduled seasonal lay-up, or because the equipment capacity is not needed at that time. Systems can be stored wet (with appropriate corrosion inhibitors), or dry. The storage option selected for any particular application will be selected based on the individual operating requirements. For example, a boiler that is stored wet can be placed in service much more quickly than one that is stored dry.

#### **5.2.1 Boiler Storage**

Boilers may also be stored wet or dry. If the boiler may be needed for backup capacity in an emergency, it is usually stored wet. For long-term storage, dry may be the better option. When placing a boiler in dry storage, it should be drained as completely as possible. Low heat from a secondary heating source, such as a small wood fire, can aid in drying the boiler. A desiccant such as lime or silica gel can be placed in the boiler before seal-

ing to remove water vapor. Another option is to introduce a vapor phase inhibitor (VCI) for corrosion protection. These materials are usually blown in as a powder, and since they are relatively low in toxicity, they can be left in the boiler when it is returned to service.

Boilers that are placed in wet storage should be blown down to remove any suspended solids and lower the conductivity, and then filled completely with water. It is critical to maintain an elevated pH ( $> 9.5$ ) and a high concentration of an oxygen scavenger such as sodium sulfite while the boiler is in storage. Most cases of boiler tube failures due to pitting can be attributed to improper storage practices. The addition of a small circulating pump and pot feeder to a line connecting the continuous blowdown and manual blowdown lines will provide a convenient method for maintaining circulation, testing, and adding chemicals as needed.

### **5.2.2 Open Cooling System Storage**

Cooling towers are often drained to prevent freezing during the heating season in the cooler regions of the country where comfort cooling is not a year-round requirement. Before taking a cooling system off-line for storage, it is important to clean and flush the system to reduce the potential for corrosion. Water, with appropriate corrosion inhibitors and microbicides, may be retained in equipment such as piping and chillers that can be isolated from the cooling tower. When systems are stored wet, the circulating pumps should be operated periodically to replenish inhibitor and biocide concentrations and prevent particulate matter from settling and promoting under-deposit pitting. Systems that can be properly sealed in this way may employ VCI compounds, much like a boiler.

### **5.2.3 Closed System Storage**

Closed systems are normally stored wet, although in areas that experience freezing chilled water heat exchange coils in air-handling units and associated parts of the system may be drained. It has been a common practice to fill coils with glycol and then drain them to prevent water from accumulating in the coils and freezing. This should never be done unless a commitment is made to flush the coils thoroughly with water before returning to service. The dilute glycol makes an ideal food source for bacteria, and will make biological control problematic if introduced to the chilled water system.

When closed heating and cooling systems are stored wet, corrosion inhibitors and biocides should be applied and tests should be done regularly to ensure adequate concentrations are maintained. The circulating pumps should be operated periodically to replenish corrosion inhibitor and biocides in areas where they may have been depleted.

## 6 Selecting and Specifying a Chemical Treatment Program

A variety of chemical treatment programs are currently available for heating and cooling systems. The best selection for any specific location will vary depending on water quality, equipment operating parameters, materials of construction, and environmental constraints. Additionally, new treatments are constantly being developed, particularly in the area of green chemistry alternatives. However, there are criteria for an effective chemical treatment program that are common to all locations.

A general guideline for the critical components, requirements, and performance specifications that should be addressed by any consultant, contractor, or chemical vendor that supplies chemical treatment to a U.S. Army facility follows:

- The contractor should conduct a complete inspection of the facility, developing an inventory of equipment (including size, design, materials of construction, and operating parameters) and systems that require treatment. While viewing schematics and diagrams may prove helpful in this process, it cannot replace the requirement of a physical, on-site inspection of the facility. Operating information that should be gathered includes, but is not limited to, water and fuel usage, steam production, chemical usage, and auxiliary equipment.
- The contractor should collect water and deposit samples from the systems to be treated to identify any existing problems that need to be addressed with the chemical treatment program, and to establish a benchmark for future analysis. Existing problems that are identified should be specifically addressed in the treatment plan. Many supplies have variable water quality in the cold distribution. Past records, particularly of makeup water quality, should be investigated to determine any recent changes in water quality and associated system performance. The contractor should investigate and identify any local ordinances or environmental regulations that may constrain which chemical treatment will be employed.
- Once adequate background information has been accumulated, the contractor should meet with facility personnel and establish goals and milestones that the treatment programs will achieve. This may include specific issues such as acceptable corrosion rates and bacterial counts, maintaining heat exchanger rates, or goals for water and fuel savings.

- The contractor should then be prepared to submit a detailed chemical treatment and maintenance program that specifically addresses how the established goals will be accomplished. The following issues should all be addressed:
  - Identify water treatment equipment needs and specify as needed.
  - Identify pretreatment equipment needs for boilers when appropriate.
  - Specify chemical formulation to be used for each system, identifying which components are for corrosion control, scale control, and/or fouling.
  - Specify microbiocides for chilled water and cooling water systems.
  - Specify maintenance and treatment procedures for control of *Legionella* and other problem microbes.
  - Specify proper chemical feed application points.
  - Specify what control tests are required for each system, and with what frequency they should be done.
  - Provide Control Charts for each system showing acceptable ranges for required control tests, and detailing what actions should be taken when tests results fall outside the recommended range.
  - Review existing maintenance procedures and recommend changes where appropriate and required to facilitate the success of the treatment program. This should include detailed recommendations for start-up and lay-up of all systems. The contractor should also provide a daily log sheet for operators to record the results of any control tests, water and fuel usage, chemical usage, and other appropriate operating information such as temperature and pressure. This information is critical in diagnosing any problems that may develop.
- The contractor should conduct on-site training during the initial visit, explaining the chemical treatment program in use, demonstrating the required control tests, and discussing and recommending changes to existing maintenance procedures. The contractor should also inspect all associated mechanical pretreatment equipment (such as ion exchange units, reverse osmosis units, and deaerators) and confirm that maintenance personnel are properly trained in the operation and maintenance of that equipment. If they are not, appropriate training should be provided. This should be reinforced during subsequent site visits on a regular basis. The goals and format of this training should be clearly detailed, including a means for evaluating its relative effectiveness.



- The frequency and scope of site visits should be specified in the contractor's bid submission, based on the requirements established by the facility. Site visits should include testing of all systems being treated, and a written report should be submitted to responsible facility personnel. This report should: provide an evaluation of treatment and operator performance, identify problems, and recommend corrective actions. Water and deposit samples may be collected by the contractor or submitted by the facility for more detailed analysis when needed. Sufficient laboratory samples will be analyzed to confirm accuracy of field tests and identify any trends in changing system water quality that could indicate developing corrosion, scaling, or microbial problems. Provision for this service should be included in the terms of the contract. Selected systems will require the installation of corrosion coupon loops to evaluate the level of corrosion inhibition being achieved. The chemical treatment contractor should be responsible for the installation of a corrosion coupon loop with appropriate coupons. Installation, removal, and evaluation of the corrosion coupons may be detailed to the contractor or handled by the facility, depending on the facility's preference. Provisions for emergency site visits should be specifically addressed as well.
- All chemicals and testing reagents should be accompanied by Material Safety Data Sheets (MSDS), and chemical drums or containers should be stored in an area with an appropriate spill containment system. The contractor should assist in the development of a chemical safety plan that contains MSDS information, emergency contact and notification information in the event of a spill or accident, appropriate first aid information, etc. Any safety equipment and precautions required for the handling of chemicals used should be identified as well.
- Provisions for routine communication between site visits should be identified. This may include weekly submission of operator logs by mail or email, submission of water samples from problem systems, consultation by phone or email, etc. The responsible individuals and contact information for both the contractor and the facility should be clearly identified and agreed on to ensure effective communication.

## 7 Evaluating the Chemical Treatment Program

The chemical treatment program should be evaluated regularly, at least on a semi-annual basis. Failure to provide adequate service or to achieve the stated goals should be grounds for the early termination of the contract, at the discretion of the facility. Questions and concerns in the following areas should all be considered when evaluating the success of a chemical treatment program.

### 7.1 System Operating Efficiency

An effective chemical treatment program not only maintains existing efficiencies, but can result in significant savings in water, fuel and power usage. Relevant questions include:

- Were identified goals in this area met?
- Did the systems or equipment experience more or less downtime for maintenance?
- Did fouling or deposits reduce the rates for critical heat exchanger application like chillers?
- Were tests for bacterial counts and *Legionella* acceptable?

### 7.2 Corrosion Rates

- Were established corrosion rate goals met?
- Were corrosion coupons installed and evaluated according to guidelines established by a recognized technical or professional society such as the American Society for Testing and Materials (ASTM) or the National Association of Corrosion Engineers (NACE) International?

### 7.3 “Consumer” Complaints

- Did the facility see a difference in the level and nature of building occupant complaints related to heating and cooling systems?

### 7.4 Communication/Responsiveness

- How effective was the chemical treatment provider in communicating with the responsible facility representatives and maintenance personnel?

- Was the treatment provider responsive to requests from facility personnel in a reasonable time frame?
- Did they follow up on verbal recommendations and observations with written recommendations and procedures for correcting the problem?

## **7.5 Proactive Program Review**

Chemical treatment programs should be reviewed and re-evaluated by the contractor and facility representatives on an ongoing basis to ensure optimal performance.

## **8 Conclusion**

Manufacturers continue to develop new treatment chemicals for reducing corrosion, scale, and microbiological growth in heating and cooling systems, and automated systems to aid in their implementation. The developmental trend is toward formulas that ensure cleaner systems that pose fewer health and environmental risks, and harbor fewer biological hazards such as Legionnaire's disease. Such automated treatment systems offer convenient and effective ways to maintain a balanced treatment program, but still need to be supplemented with periodic testing to confirm performance, and with frequent monitoring until it is established that performance parameters are being met.

This work reviewed current state-of-the-art treatment schemes and technologies, and summarized general guidelines for developing chemical treatment programs in heating and cooling systems. No single treatment program is suited to all Army heating and cooling systems, as water quality, equipment operating parameters, and environmental constraints vary widely. Still, implementing these general guidelines summarized here at Army heating and cooling plants will improve control corrosion, scale, and microbiological growth in heating and cooling systems, enabling the equipment to work with fewer breakdowns, greater energy efficiency, and a longer overall service life.

## Acronyms and Abbreviations

<u>Term</u>	<u>Spellout</u>
AMP	aminotri(methylenephosphonic acid)
ASTM	American Society for Testing and Materials
AWT	Association of Water Technologies
BZT	benzotriazole
CERL	Construction Engineering Research Laboratory
COE	Chief of Engineers
CTI	Cooling Technology Institute
DEHA	diethylhydroxylamine
ERDC	Engineer Research and Development Center
FDA	Food and Drug Administration
HEDP	1-Hydroxyethane
HPA	hydroxyphosphono acetic acid
HQUSACE	Headquarters, U.S. Army Corps of Engineers
HVAC	heating, ventilating, and air conditioning
IWC	International Water Conference
MAPA	manganese/aminophosphonic acid
MBT	mercaptobenzothiazole
MEKO	methylethylketoxime
MSDS	Material Safety Data Sheet
NACE	National Association of Corrosion Engineers
PBTC	2-Phosphonobutane-1,2,4-Tricarboxylic Acid
PVC	polyvinyl chloride (PVC)
THPS	tetrakis (hydroxymethyl) phosphonium sulfate
TT	tolytriazole
UK	United Kingdom
URL	Universal Resource Locator
USDA	U.S. Department of Agriculture
VCI	vapor phase inhibitor
WWW	World Wide Web

# Bibliography

## Overview

The following bibliography resulted from a review of the Proceedings from the International Water Conference (IWC) and the NACE International for the past several years to identify effective treatment chemicals for corrosion, mineral scaling, fouling, and biological control. (The bibliography to this report includes the papers selected for review.) A significant number of new chemicals were introduced over that time, most notably in the areas of new, highly effective polymers (many with multiple functional groups), phosphonates and phosphonate alternatives, and microbiocides.

Phosphonates have long been used for calcium carbonate inhibition, and to a lesser extent, corrosion control in open cooling systems. New phosphonates have been developed (Sullivan and Hepburn 1995; Parsons 1996; Ferguson Undated) for scale and corrosion control, and our understanding of the mechanisms by which they work has been improved (Vanderpool 1997; Gill Undated) during the past 10 years. While work continues on developing new molecules of these highly versatile phosphonate compounds (Downward et al. 1997; Failon and Gabriel 1998; Failon et al. 1999), there is also considerable effort to find alternatives to phosphorus containing compounds due to phosphorus discharge limitations in certain applications and locations. Alternatives to phosphorus-based compounds have been developed for both calcium carbonate scale (Geiger 1995; Chagnard undated), and corrosion inhibition (Dallmier undated).

Polyacrylates and polymaleates have been used as inhibitors for calcium phosphate, calcium carbonate and silicate for many years. Many advances and variations from the original base compounds have been introduced over the years. Copolymers (two different functional groups) and terpolymers (three functional groups) were introduced in the 1980s. Recently, new versions of some polymers that are testable in the field have been introduced (Hann et al. 1998) and there are even quad polymers (Richardson and Trulear 2000; Wolfe undated) (four functional groups) available in the marketplace.

Biocides used for the control of algae and microbial populations in cooling systems have seen increased attention with the outbreaks of Legionnaires

Disease that continue around the world. Biocides are usually grouped into two categories, oxidizing and non-oxidizing. Variants of established oxidizing biocides, like “stabilized” bromine (Moore et al. 1997; Howarth et al. 1999) and “mixed-oxidant” solutions (Bradford and Petersen 2000) are being marketed. Non-oxidizing biocides are being introduced, either as refinements (Gaffney and Wiatr 1998) of existing biocides like isothiazolin, or entirely new products like THPS.

There has been an increased interest and emphasis on environmentally friendly chemicals in the last few years as well, and some of these are addressed in this report. Recent work has shown environmentally friendly chemicals such polycarboxylates and carboxylate derivatives (Hater and Schweinsberg 1999) demonstrate great promise as corrosion inhibitors. One of these carboxylate derivatives, thermal polyaspartate, has shown efficacy for both scale and corrosion inhibition (Ross et al. 1995; Bain et al. 1999) in cooling systems. Work has been done on existing compounds like tolyltriazole to produce less toxic, more stable versions (Given et al. 1998; Cheng et al. 1999). New, more environmentally friendly biocides have been developed (Talbot and Downward 1998; Dallmier undated) as well.

While there have been fewer new chemicals introduced for boiler and steam systems in the last few years, there have been a few new developments. One area in particular where there has been some work, is in the development of environmentally friendly condensate corrosion inhibitors. A few new oxygen scavenger chemicals are available, but sulfite remains the workhorse for the boiler pressures found in most Army facilities.

The literature review undertaken for this work makes it apparent that the water treatment industry is in a constant state of flux. New chemicals are being introduced on a regular basis. It often takes several years for these new treatment technologies to be fully evaluated. Virtually all treatment schemes in use today have both strengths and limitations that one must consider in choosing the correct treatment for a given application. It would be impossible to develop a single specification for the treatment of heating and cooling systems at all Army facilities.

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## Appendix A: Water Treatment Chemicals

**Table A1. Open cooling system corrosion inhibitors.**

Corrosion Inhibitor (Acronym)	Steel Inhibitor*	Copper Inhibitor
Benzotriazole (BT)	N	Y
1-Hydroxyethylidene, 1-2-diphosphonic acid (HEDP)	S	N
Hydroxyphosphono acetic acid (HPA)	Y	N
Manganese/aminophosphonic acid (MAPA)	Y	Y
Mercaptobenzothiazole (MBT)	N	Y
Molybdate	Y	N
Nitrite	N	Y
Orthophosphate	Y	N
Phosphonocarboxylic acid (POCA)	Y	N
Phosphono carboxylate mixtures (PCM)	Y	N
Thermal polyaspartate (TPA)	Y	Y
Tolytriazole (TT)	N	Y
*Y = Yes, N = No, S = Some		

**Table A2. Common phosphonates for open cooling system scale inhibition.**

Phosphonate	Common Acronyms
Aminotri(methylenephosphonic acid)	AMP/ATMP
Bis(hexamethylene)triamine(pentamethylenephosphonic acid)	BHMT/BHMTMP
Diethylenetriaminepenta(methylenephosphonic acid)	DTPMP/DETPMP
Diethylenetriamine(methylenephosphonic acid)	DTMP/DETPMP
H1-Hydroxyethylidene, 1-2-diphosphonic acid	HEDP
Hexamethylenediaminetetra(methylenephosphonic acid)	HMP/HDTMP
Phosphonobutane carboxylic acid	PBTC

**Table A3. Common polymers for open cooling system treatment.**

Homopolymers	Acronym
Polyacrylic acid	PAA
Polymaleic acid	PMA
<b>Copolymers</b>	
Acrylic acid/maleic acid	AA/MA
Acrylic acid/sulfonic acid	AA/SA
Sulfonated Styrene/maleic anhydride	SS/MA
<b>Terpolymers</b>	
Acrylic acid/methacrylic acid/itaconic acid	AA/MAA/IA
Acrylic acid/sulfonic acid/non-ionic	AA/SA/NI
Acrylic acid/sulfonic acid/sodium styrene sulfonate	AA/SA/SSS
Maleic anhydride/ethyl acrylate/vinyl acetate	MA/EA/VA



**Table A4. Common oxidizing biocides.**

Oxidant	Commonly Available Forms
Bromine	Liquid (Sodium bromide solution activated by chlorine)
	Solid (Hydantoins)
	Solid ("stabilized" bromine/chlorine product)
Chlorine	Gas (Cl <sub>2</sub> )
	Solid (Calcium Hypochlorite)
	Liquid (Sodium Hypochlorite)
Chlorine Dioxide	Liquid (ClO <sub>2</sub> )
Isocyanurates	Solid (chlorinated or chlorinated w/ bromine)
Ozone	Gas (O <sub>3</sub> )
Peroxides	Liquid (Hydrogen peroxide)
	Liquid (Peracetic acid)

**Table A5. Common non-oxidizing biocides.**

Biocide*	Effective pH Range	Effective for <i>Legionella</i>
2-Bromo-2-nitro 1,3 propanediol	>7.5	
Decylthioethane amine hydrochloride	6.0-8.5	
Dibromo nitrilopropion amide	6.5-8.5	Y
Dodecyl guanadine hydrochloride	6.5-9.5	
Glutaraldehyde	6.0-10.0	Y
Glutaraldehyde/quaternary ammonium compound	6.0-10.0	Y
Isothiazolone	4.5-9.3	Y
Methylene bis thiocyanate	4.0-8.0	
Dithiocarbamates	7.0-9.5	N
Octyl-isothiazolin-one	4.5-9.3	Y
Quaternary ammonium compound	6.5-9.2	N
Terbutylazine	6.5-9.3	N
Tetrakis hydroxy methyl phosphonium sulfate	7.0-10.0	Y

\*Several of these biocides have multiple variants under the same general name.

## Appendix B: Corrosion Rate Standards

**Table B1. Quantitative classification of corrosion rates for open cooling water systems.**

Description	Carbon Steel*	Copper/Copper Alloys*
Excellent	≤ 1	≤ 0.1
Very Good	1 - 3	0.10 - 0.25
Good	3 - 5	0.25 - 0.35
Fair	5 - 8	0.35 - 0.50
Poor	8 - 10	0.50 - 1.0
Severe	> 10	> 1.0
*Corrosion rates expressed as mpy (millimeters penetration per year)		

**Table B2. Quantitative classification of corrosion rates for closed cooling water systems.**

Description	Carbon Steel*	Copper/Copper Alloys*
Excellent	≤ 0.2	≤ 0.1
Good	0.20 - 0.50	0.10 - 0.25
Fair	0.50 - 0.80	0.25 - 0.35
Poor	0.80 - 1.0	0.35 - 0.50
Severe	> 1.0	> 0.50
*Corrosion rates expressed as mpy (millimeters penetration per year)		

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