

COOLING TECHNOLOGY INSTITUTE

Application of Oxidizing Biocides



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This guideline document summarizes the best current state of knowledge regarding the specific subject. This document represents a consensus of those individual members who have reviewed this document, its scope and provisions. It is intended to aid all users or potential users of cooling towers.

Approved by the CTI Executive Board.



This document has been reviewed and approved as part of CTI's Five Year Review Cycle. This document is again subject to review in 2016.

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Preface to Application of Oxidizing Biocides

Safety and environmental requirements continue to have a dramatic impact on the methods used to treat recirculating cooling waters. Legislation such as that prohibiting the use of hexavalent chrome, the “Clean Water Act” and the Superfund Amendments Reauthorization Act (SARA) have all represented strong driving forces to consider alternative treatment technologies. These changes have had a direct impact on the choice and application of oxidizing biocides. Safer alternatives to gaseous chlorine and better application technology for oxidizing biocide alternatives have become major topics of concern.

This document will cover the use and application of the four major oxidizing biocides used in treating cooling waters: chlorine, bromine, chlorine dioxide, and ozone. The document will help end users and all personnel involved in treating cooling systems to better understand the chemistry, the application methods and the safety and environmental issues concerning oxidizing biocides.

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Application of Oxidizing Biocides

Chapter I: Chlorine

I. Introduction

Chlorine, which is an element of the halogen family, was first discovered in its gaseous state in 1774 by the Swedish chemist Karl W. Scheele. Chlorine gas is readily compressible into a clear amber liquid, has an unmistakable pungent odor and is extremely irritating to mucous membranes.

Due to its chemical properties, chlorine is an unusual and extremely versatile substance. Chlorine is considered to have more diverse uses than any chemical known - from the manufacture of food products to rocket fuels. The largest single use for chlorine is in the manufacture of ethylene oxide and glycol used to make antifreeze fluids and synthetic fibers. As an oxidizing agent, chlorine also is extremely effective as a disinfectant and microbiological control agent.

The first known use of chlorine as a disinfectant was in 1846 when Semmelweis used chlorine water for the scrubbing and cleansing of hands in maternity wards. In the 1850's in London, chlorine was first used as a germicide in a water and waste treatment application. Today, chlorine is by far the most widely used disinfectant for water and wastewater treatment in both municipal and industrial applications. Chlorination is also the most commonly used microbiological control approach used in cooling towers.

As a cooling system microbiological agent, chlorine is both effective and economical. It is relatively easy to apply, measure and control. However, as a toxic material, chlorine must be handled and used with extreme caution.

This chapter will discuss the use of chlorine as a biocide in cooling water systems. The chapter will include sections on chlorine chemistry, biocidal effectiveness, and guidelines for the effective use and application of chlorine. Environmental and safety concerns will also be discussed along with a summary on the relative costs for different forms of chlorine.

II. Chlorination Chemistry

When chlorine is added to cooling water, a variety of reactions occur. The reactions depend on the components present in the cooling water and on the system water characteristics. In the case of gaseous chlorine, the process begins with the hydrolysis of molecular chlorine (Cl_2) to

form a mixture of hypochlorous (HOCl) and hydrochloric (HCl) acids:



The HOCl formed then undergoes a pH dependent partial dissociation to form hypochlorite and hydrogen ions:



The relative distribution of chlorine species described by equations (1) and (2) is shown in figure 1. At pH values encountered in cooling water, free chlorine exists as mixtures of HOCl and OCl^- .¹

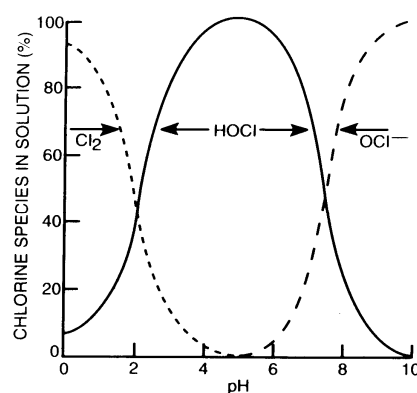
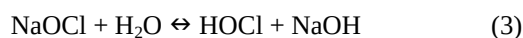


FIGURE 1. Relative concentrations of chlorine compounds vs. pH

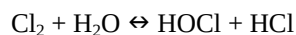
Chlorination methods other than gaseous chlorine such as sodium hypochlorite (3),



Calcium hypochlorite, chlorinated isocyanurate, and chlorinated hydantoin, all react with water to form HOCl and OCl^- (Table I). Hence, regardless of chlorination method, hypochlorous acid and hypochlorite ion are the biocide species formed.

Table I Summary - Chlorine Hydrolysis Reactions

Gaseous Chlorine



Sodium Hypochlorite



Calcium Hypochlorite



Sodium Dichloro-s-triazinetriene (Sodium Dichloroisocyanurate)

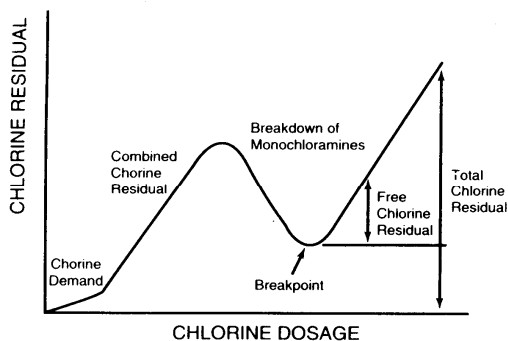


FIGURE 3. Breakpoint chlorination curve

Reaction with Inorganics:

Chlorine will readily oxidize certain inorganic constituents. Some of these include ferrous iron (Fe^{++}), manganese (Mn^{++}), and sulfides (S^{--}). These reactions with inorganic constituents can significantly increase the chlorine demand of the water and consequently the quantity of chlorine required for microbiological control. Oxidation of inorganics can also lead to unwanted cooling water deposit problems.⁷

Reaction with Oxidizable Organics:

Non-microbiological organic materials present in cooling water may also be oxidized by chlorine. These compounds include hydrocarbons, process chemicals, humic substances, and airborne contaminants such as leaves and pollen. Chlorine can react with many of these contaminants to form chlorinated organics, i.e., chlorinated hydrocarbons and trihalomethanes (THM's). These reactions can also create toxic effluents and additional chlorine demand. Effluent toxicity and environmental concerns will be discussed in Section VIII.

Reaction with Treatment Components:

Cooling water treatment components also can adversely react with chlorine. Components investigated most thoroughly include phosphonates used for scale and corrosion control and azoles used for yellow metal corrosion protection.^{8,9} Research with these materials has generally shown that if properly maintained at low residuals, chlorine is not a problem. However, at high chlorine residuals, problems can occur due to the degradation of phosphonate to form orthophosphate, and to the addition of chlorine to the azole to form the chlorinated azole species. Other treatment compounds that can react with chlorine include polymeric dispersants, nitrite and certain non-oxidizing biocides.

Volatility:

A significant and frequently underestimated loss of chlorine in a cooling system is stripping due to volatility. The rate of stripping is strongly pH dependent-HOCI being more volatile with OCl- relatively non-volatile.^{4,6} For a typical cooling system operating at pH6.5, up to 30-40% of the chlorine residual can be flashed off due to stripping in the tower. For the same tower at pH 8.5, less than 10-15% would be lost.⁵ This can have a dramatic impact on the chlorine consumption of a system and on the quantity of chlorine feed required to maintain a desired residual.³ An even more dramatic loss can occur due to stripping of combined residual chlorine. Chloramines are more volatile and require much longer contact time for efficacy compared to free residual chlorine.

The reactions and losses discussed above, in addition to other factors such as UV decomposition and temperature, all affect the chlorine consumption and chlorine effectiveness for a particular system. The next few sections of this chlorine chapter will focus on guidelines for the actual use of chlorine including application methods, monitoring and control, and environmental discharge concerns.

V. Application Methods - Slug Chlorination

Historically, slug chlorination was the predominant method of applying chlorine to cooling systems. Slug chlorination typically consists of applying chlorine one to three times a day for one to three hour periods, with maximum target free residuals of up to 1.0-2.0 ppm free residual chlorine. Slug chlorination offers the advantage of minimizing the duration of chlorine discharge.

The practice of slug chlorination may be necessary in cooling systems where system blowdown is discharged directly into a receiving stream and chlorine discharge is regulated by environmental discharge constraints. Other than discharge regulations, slug or intermittent chlorination offers no performance advantages.³ Several disadvantages to slug chlorination, however, do exist including the following:

- Operator intensive due to increased chlorination equipment maintenance
- Variability in pH due to intermittent production of acid
- Reduced effectiveness at alkaline pH due to short contact times