TwinOxide®

for Disinfection

of Cooling Systems

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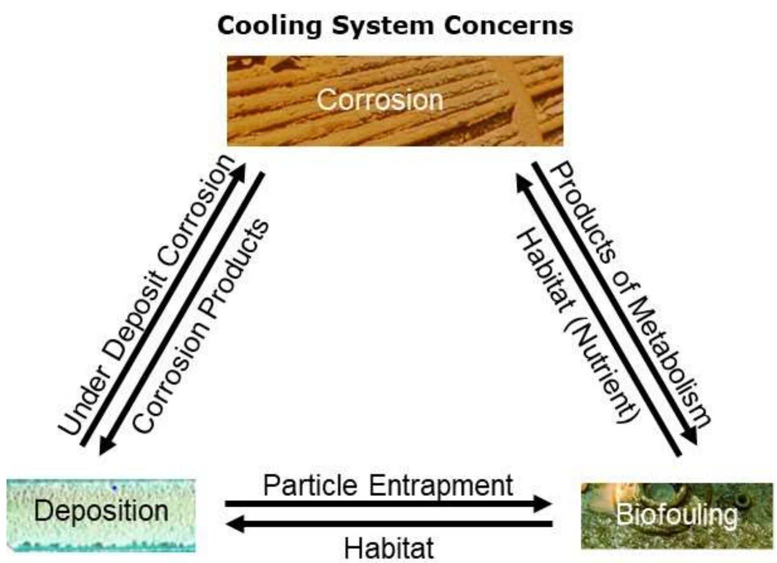
Cooling Water presents three major concerns with respect to its potential effect and damage it can cause to equipment within the Cooling System Circuit.

- **Corrosion**
- **Deposition**
- **Microbiological Activity**

These are interrelated and therefore all must be under control and minimized.



The essential point is *"under control and minimized"*. Although this normally involves the use of Water Treatment Chemicals and Programs, design and selection of materials of construction can help to minimize the potential for some of the negative concerns.

The use of corrosion resistant materials such as Titanium and GRP can help minimize corrosion, although it will be at a cost. Basically, for cost reasons Mild Steel is used for much of the piping and heat exchange equipment in cooling systems. Sometimes process side compatibility will dictate that material other than mild steel, such as Stainless Steel is required for some water-cooled process equipment or heat exchangers. For improved heat transfer, Copper or Copper Alloy heat exchangers are used, where suitable and compatible with the medium being cooled. Although more corrosion resistant than Mild Steel, Stainless Steel can suffer chloride stress corrosion cracking (SCC), which may lead to a need to limit Chloride concentration in the cooling water. Copper or Copper Alloys require a corrosion inhibitor, normally an Azole, to be used.

Designing cooling equipment with a large, larger than theoretically required, heat transfer surface area can result in a low(er) water side skin temperature, which will help minimize scaling and deposit. Such designs can result in low water velocity which potentially defeats the objective of minimizing deposition and fouling. Designing equipment with high water velocity can help minimize deposition and fouling, but can, depending on the metallurgy, cause erosion. turbulent water flow should be avoided as it impedes heat transfer. Water can be softened to remove potential scale forming calcium and magnesium salts, however, this results in producing a water which has a higher corrosion potential than the original unsoftened water

Microbiological activity, biofilm formation and Microbiologically Influenced Corrosion (MIC), are not easily “designed out”. To control these a biocide is normally required. Although biocides may have a bad connotation or perception with some people because they “kill living material” and are “toxic”, there are various aspects of some biocides, such as low(er) use concentration and low(er) environmental impact, which make these biocides more “environmentally friendly” and therefore more acceptable than others. There are several “Non-Chemical Devices” (NCD’s) on the market with claims of ability to control the microbiology within a cooling system, these having a better implied image than chemicals by many people. Claimed mechanism of the control by some of the techniques is questionable or not easily proven, some have a limited capacity of water flow that they can treat per unit so only a proportion of the recirculated cooling water is “treated”, many have no “retention” across the cooling tower and do not effectively control microbiological fouling and activity within the cooling tower, a major concern here is harboring and propagating pathogens such a Legionella and Pseudomonas. Studies of many any of the “Non-Chemical Devices” have shown that they “may not be achieved using a non-chemical device as the sole method of water treatment .

Biocides used in Cooling Systems

Biocides used in cooling systems can be divided into two basic categories, oxidizing biocides and non-oxidizing biocides. There are features and benefits associated with both types of biocide.

- Oxidizing Biocides are typically more rapid at effecting a kill.
- Oxidizing Biocide programs tend to be lower cost than sole Non-oxidizing Biocide programs.
- Most Oxidizing Biocides can be quantitatively analyzed at use concentration by relatively simple and easy methods. This feature can also be used to control the addition and concentration of the Oxidizing Biocide in the cooling water.
- Oxidizing Biocides tend to be less persistent in the environment than Non-oxidizing Biocides.
- Oxidizing Biocides are less prone to organisms developing a resistance or acclimatization to the biocide. Microorganisms can mutate to develop acclimatization to Non-oxidizing Biocides, which is why more than one type of Non-oxidizing Biocide is often used, normally applied alternatively.

An effective and efficient biocide program would typically comprise of a baseline Oxidizing Biocide Program, either applied continuously or intermittently, supplemented by infrequent intermittent shot doses of Non-oxidizing Biocide(s).

Oxidizing Biocides commonly used are

- **Chlorine**
  - Chlorine gas
  - Sodium Hypochlorite
  - Calcium Hypochlorite
  - Dichloroisocyanurate
  - Trichloroisocyanurate

- **Bromine**
  - Bromochlorohydantoin
  - Activated Bromide
  - Stabilized Bromine Chloride

- **Hydrogen Peroxide**
- **Peracetic Acid**
- **Chlorine Dioxide**
- **Ozone**

Historically Chlorine Gas or Hypochlorite has been used in many cooling systems. Chlorine is an effective Oxidizing Biocide but not the most efficient and it has negative environmental impact consequences. Equipment, namely a Chlorinator is required to use and inject Chlorine Gas, these are relatively expensive, require maintenance and are susceptible to breakdown, particularly as they get older. Maintenance and repair requires the chlorinator to be purged and made safe before work can begin.

Sodium Hypochlorite degrades with time particularly in sunlight and relatively high ambient temperatures, by a factor of 3.5 times for every 10ºC increase in storage temperature. Concentrated solutions of Sodium Hypochlorite can degrade by about 15% in 30 days. Calcium Hypochlorite is only sparingly soluble and not easy to effectively dose.

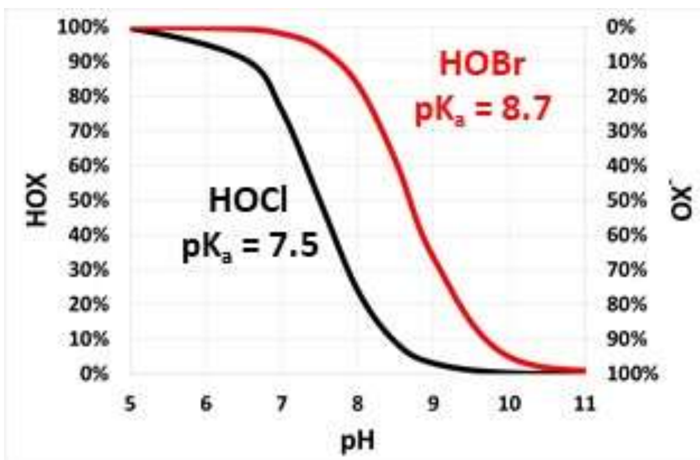
The efficiency of Chlorine decreases as pH increases, because it dissociates by a reversible reaction into biocidal Hypochlorous Acid and much lower biocidal efficient Hypochlorite Ions. At a cooling water pH of 7.5, 50% of the Sodium Hypochlorite is present as biocidal Hypochlorous Acid and 50% and Hypochlorite Ions.

$Cl_2 + H_2O \rightarrow HOCl + HCl$

$NaOCl + H_2O \rightarrow HOCl + NaOH$

$Ca(OCl)_2 + H_2O \rightarrow HOCl + Ca(OH)_2$

$HOCl \rightleftarrows H^+ + OCl^-$



Chlorine is an oxidizing agent that reacts by oxidation through Chlorination, forming chlorinated molecules, and is reactive to certain inorganic compounds and many organic compounds, which create a chlorine demand which results in higher dose concentrations being required. It reacts with ammonia to form Chloramine, the reaction taking over 7 ppm of Available Chlorine for every 1 ppm of Ammonia.

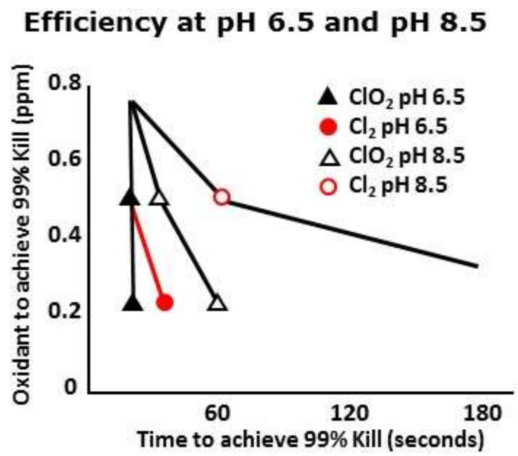
Within many Regulatory Water Companies and Associations, there is a growing concern over the disinfection by products (DPBs) of halogens in general, chlorine in particular, and this leads to legislation and discharge limits in some areas and Countries. The concern is the formation of halogenated organic molecules. The mechanism of Chlorine is by oxidative substitution or addition, hence production of Chlorinated By-Products generally classified as Trihalomethanes (THM), Halo-acetic acids (HAAs), and other molecules such as Mutagen X (MX). These compounds are of concern because they can be harmful to human beings if they end up in or contaminate drinking water, some being known carcinogens. TwinOxide does not produce Halogenated Organic Molecules such as THM, HAA, or MX and is therefore "more environmentally friendly" than Chlorine or other Halogens when used as a disinfectant in Cooling Systems, and in other applications such as Drinking Water, Food and Beverage Applications etc.

TwinOxide

TwinOxide employs a simple and safe technique to produce a 0.3% Chlorine Dioxide Solution using free flowing solids, without the need for relatively expensive generators. Because both Chlorine Dioxide and Chlorine contain the word or chemical Chlorine, many people think that the two molecules are similar. This is far from the truth, they are entirely different molecules, have significantly different characteristics and properties, and disinfect water through different mechanisms.

A lot of material and data has been published on Chlorine and Chlorine Dioxide. Collation and correlation of this material can be used to compare and contrast Chlorine Dioxide and Chlorine when used as disinfectants, biocides or sterilizers. TwinOxide exhibits all of the attributes of Chlorine Dioxide, and provides some additional benefits with respect to Health, Safety, Environmental and Capital Expenditure, compared to Chlorine Dioxide produced by generators which are required when using liquid precursors.

There are several parameters that may be used to compare the "strength" or "efficacy" of a biocide. One of these, "speed of kill", which, as can be seen in the diagram to the right, is more rapid for Chlorine Dioxide than for Chlorine



In terms of Oxidation Capacity, Chlorine Dioxide is 2.6 times greater than Chlorine. This is derived from the fact that in the redox reaction for Chlorine Dioxide, Chlorine Dioxide accepts a total of 5 electrons.

$$ClO_2 + e^- \rightarrow ClO_2^-$$

$$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + 2H2O$$

Overall combined reaction = $ClO_2 + 4H^+ + 5e \rightarrow Cl^- + 2H2O$

In the redox reaction for Chlorine, Chlorine only accepts 2 electrons. $Cl_2 + 2e^- \rightarrow 2Cl^-$

Taking Atomic and Molecular Weights, Chlorine Dioxide contains 52.56% Cl, which, taking into account the 5 electron change, equates to 263% Available Chlorine. Chlorine is, by convention, taken as 100% Available Chlorine, which makes Chlorine Dioxide more than 2.6 times the Oxidation Capacity of Chlorine.

Chlorine dioxide attacks the electron-rich centers of organic molecules. One electron is transferred and Chlorine Dioxide is reduced to Chlorite (ClO_2^-).

By comparing the oxidation strength and oxidation capacity of different disinfectants, one can conclude that Chlorine Dioxide is effective at low residual disinfectant concentrations. Chlorine Dioxide is not as reactive as Chlorine and only reacts with Sulfuric substances, Amines and a few other reactive Organic substances. In microbiology Amines or Amino type compounds are molecules such as Amino Acids, Proteins and Enzymes, all of which are important in the metabolism and biochemical reactions of Microorganisms. Chlorine Dioxide destroys or inactivates these molecules, thus disrupting the metabolism and results in mortality of the organism.

Chlorine Dioxide reacts with Pyrrole, which is present in the structure of Chlorophyll. The break-down of the Pyrrolic Ring and the consequent deactivation of the Chlorophyll enables Chlorine Dioxide to become effective in the control of Algae growth. In many Algae the main structural element of the cell wall is Cellulose, which makes the cell wall “tougher” than the cell wall of Bacteria and relatively difficult for biocides, such as Halogens and many other biocides to penetrate and kill the Algae. Control of Algae can be best achieved by biocides, herbicides or algaecides that disrupt or block Chlorophyll reactions, for which, as mentioned above, Chlorine Dioxide is very efficient.

In comparison to Chlorine, less Chlorine Dioxide is required to obtain an effective residual disinfectant.

In one application in a Cogeneration Power Plant Cooling System which uses Secondary Treated Sewage Water as Make Up Water, effective control of the microbiology of the Cooling Water and Cooling System was obtained using an average Chlorine Dioxide concentration of 0.03 ppm ClO_2 in the Cooling Water (2).

It can also be very effective when a large amount of Organic and/or Ammoniacal Matter is present in the water to be treated, such as in polluted Waste Waters and Cooling Water contaminated with Ammonia, such as in Urea and Ammonia Plant Cooling Systems.

Efficacy and “speed of kill” are related to the concentration of active disinfectant used. This leads to an important concept that a lethal Concentration (C) of disinfectant must be maintained for a given Contact Time (t). This is known as the Ct Value with units typically mg minute/Liter or ppm minute, or, mg hour/Liter or ppm hour/lLiter.

Ct Value = C x t

CT Values to obtain a 99% Kill[3]

Organism	Chlorine	Chlorine Dioxide
Bacteria	$Ct_{99\%}$ 3.3 ppm minute	$Ct_{99\%}$ 0.19 ppm minute
Viruses	$Ct_{99\%}$ 8.0 ppm minute	$Ct_{99\%}$ 2.8 ppm minute
Giardia (Protozoa)	$Ct_{99\%}$ 41 ppm minute	$Ct_{99\%}$ 7.3 ppm minute
Cryptosporidium (Protozoa)	Not Killed	$Ct_{99\%}$ 40 ppm minute

Biofilm Control

“Chlorine Dioxide is beside Ozone the only suitable disinfectant able to control and remove is efficient and effective in the kill and removal of biofilm” (4).

Chlorine Dioxide, or more correctly Chlorine Dioxide solutions, such as prepared using TwinOxide, are not solutions of ionic compounds but a solution of Chlorine Dioxide Gas. Similarly, Ozone solutions are solutions of Ozone Gas. This phenomenon enables Chlorine Dioxide to penetrate Biofilm Structures whereas other biocides have difficulty penetrating Biofilm or are consumed or deactivated by the matrix of hydrated extracellular polymeric substances (EPS), which mainly consists of polysaccharides, proteins, nucleic acids and lipids, which microorganisms form in their immediate local environment, resulting in what is called Biofilm. Chlorine or Sodium Hypochlorite do not accomplish biofilm control and removal as effectively as Chlorine Dioxide because Hypochlorous Acid has difficulty penetrating the Biofilm, and, the organic content of the Biofilm reacting with the Residual Chlorine or creating a Chlorine Demand, makes the Chlorine or Sodium Hypochlorite less effective killing organisms associated with the Biofilm. Chlorine Dioxide is a better disinfectant than Chlorine because Chlorine Dioxide effectively controls and removes biofilm. Chlorine Dioxide is dissolved Chlorine Dioxide Gas and can penetrate the slime layer protecting the bacteria in a biofilm. Because it is a powerful oxidizing agent it 'dissolves' the slime layer and kills the exposed bacteria.

Within Biofilms Acid Producing Bacteria (APB) exist and proliferate. These are effectively killed by Chlorine Dioxide and if the Biofilm tries to reform, Chlorite, which can be formed by the reactions involved when Chlorine Dioxide acts as a disinfectant, is reactivated by the acids produced by these bacteria and Chlorine Dioxide is formed, thereby impeding the recolonization of surfaces by Biofilm.

Biofilm and products of metabolism, such as acids as mentioned above or sulfide as produced by Sulfate Reducing Bacteria (SRB), can result in Microbiologically Influenced Corrosion, which can seriously and rapidly damage equipment. The Biofilm also blocks tubes and pipework in the Cooling Circuit, and the Packing or Fill of Cooling Towers.

A Cooling System suffered severe corrosion of side panels of its Cooling Tower which required high costs related to replacement of the Cooling Tower Cladding, shutdown and loss of production. The corrosion was found to be associated with heavy microbiological fouling, Biofilm and MIC within the tower. After repair and replenishment of the Tower, the Cooling Water Biocide Treatment Program was changed to TwinOxide. The microbiology of the system has subsequently been under control since switching to TwinOxide and to date no biofilm or MIC has been experienced within the Cooling System.

Biofilms attached to heat exchanger surfaces impede heat transfer and reduce Cooling System efficiency because they contain a high percentage of water, and act as a stagnant layer of water on the heat transfer surface. Water is 25-80 times less heat conductive than steel and as a result, 1mm of biofilm is equivalent to a 25- 80 mm increase in heat exchanger tube wall thickness.

Biofilms harbor, provide nutrients and protect other microorganisms from biocides. Of great concern in this area are pathogens such as Legionella, E. Coli, and Protozoa, which can act as a host for Legionella.

Effective control and removal of Biofilm is obviously of prime importance in Cooling System.

Spectrum of Biocidal Effectiveness

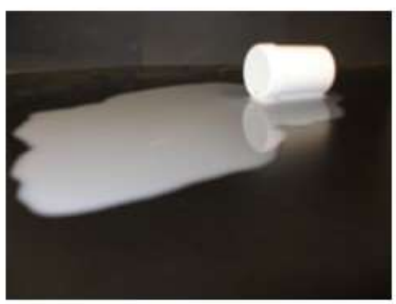
Chlorine, Sodium Hypochlorite and Chlorine Dioxide are all effective for controlling Bacteria, Fungi and Yeast. However, Chlorine Dioxide tends to be much more efficient and effective for controlling Algae, Pathogens, Viruses, Parasites, Spores and Biofilm. Control and eradication of Biofilm, which is fundamental for minimizing the Risk of Legionnaires Disease, which is required by many Authorities, particularly in Cooling Systems, and, Hot and Cold Water Systems.

TwinOxide 0.3% Chlorine Dioxide Solution

TwinOxide 0.3% Chlorine Dioxide Solution exhibits the characteristics, properties and efficacy of Chlorine Dioxide, as mentioned above. TwinOxide 0.3% Chlorine Dioxide Solution has some other benefits compared to Chlorine Dioxide produced by other techniques. Classic techniques to produce Chlorine Dioxide use concentrated liquid precursors. In the event of a leak or spillage, the liquids will spread, unless they are used and stored within separate containment bunds. Spread and flow of a liquid oxidizing precursor may allow the oxidant to come in contact with reducible and/or flammable material and can result in combustion and fire. Spread and flow of a liquid Mineral Acid precursor may result in corrosion of material it comes in contact with, and in the case of come metals this corrosion can liberate Hydrogen. The TwinOxide technique uses free flowing solid, precursors which are less likely to spread in the event of spillage and they are spillage, and they are not in the same reactive form as liquid precursors.

Spillage of Liquids and Free Flowing Solids

Leakage of Solution



Spillage of Solution

Spillage of Solid

Designing a TwinOxide Program

When designing a TwinOxide Biocide Treatment Program there is some vital information about the Cooling System and its Operation that is required in order to implement and apply an optimal and cost effective program.

Make Up Water

- Source and type of water, essentially differentiate between ground water, surface water, such as river water, canal water, stream water lake water, and, if applicable, reused water such as process water, process condensate, steam condensate, boiler blowdown water, waste water, or sewage.
- Any Pretreatment used for the Make Up Water, such as clarification, filtration, softening, demineralization.
- Make Up Water quality, and If applicable, any seasonal variation in quality and/or contamination.
- Chemical and microbiological analysis of the Make Up Water.

Cooling Water

- Chemical and microbiological analysis of the Cooling Water.
- Potential Process Side Contaminants

System Design and Operation

- System water Volume.
- Cooling water Recirculation Rate.
- Make Up Rate.
- Blowdown Rate.
- Cooling Water cold supply and hot return temperatures
- System half-life.
- System Metallurgy.
- System operation (hours per day, days per week, week per year).
- Critical equipment such as high skin temperature, low water velocity, and/or where water flow through equipment, piping or parts of the cooling circuit that may be throttled or stopped at times.

Where possible data should be verified and confirmed. Given appropriate data TwinOxide personnel can design and propose a suitable and practical TwinOxide Biocide Program for the Cooling System.

Benefits of TwinOxide®

In summary, TwinOxide® 0.3% Chlorine Dioxide Solution provides many important benefits.

- Simple, easy and safe preparation and dosage of disinfectant.
- Solid precursors, therefore low risk of "spreading" in the event of leakage or spillage of precursors.
- Non-fuming precursors.
- No THM or HAA formation.
- Efficient and rapid disinfectant.
- 2.6 times more oxidation capacity than Chlorine.
- Effective biofilm control and removal.
- Effective on all types of microorganism.
- Low residual disinfectant concentrations.
- At use concentration, no corrosion of metals, and compatible with elastomers.

References

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4) *Wolfgang M. Chlorine dioxide as effective biocide for microbiological and antifouling control water system. Periphyton and fouling conference, Saint. Petersburg, October, 2008.*