



AN ALTERNATIVE APPROACH TO DISINFECTION USING CHLORINE DIOXIDE

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ABSTRACT

The use of oxidizing biocides is among the most cost effective means of disinfecting water. Chlorine dioxide has various benefits compared to other oxidizing biocides, but its stability, properties and characteristics necessitate that “in situ” generation, typically using precursor solutions, in a Chlorine Dioxide Generator is a common practice. Apart from chlorine dioxide gas or vapor, the precursor solutions can pose a potential health and safety hazard and require appropriate safety precautions to be incorporated in the design and operation of generation and dosing equipment. The use of solid precursors can simplify the generation of chlorine dioxide, eliminate some of the potential hazards encountered with other generation methods, and produce stable chlorine dioxide solutions which can be used in many types of disinfection applications. Attributes of chlorine dioxide, its generation and applications are discussed in this paper.

INTRODUCTION

Chlorine dioxide is not new in the realm of disinfectants. However, there are many different ways to bring chlorine dioxide to better fit end-user’s functional requirements, safety of handling and application. Cooling water treatment is one of the fields of application that has very specific end-user requirements as to viability and of disinfecting agents related to safety, practicality, efficacy and economics. The main differences revolve around precursors, which may utilize liquid, gaseous or solid state chemicals, or “stabilized chlorine dioxide solutions”.

COOLING WATER TREATMENT REQUIREMENTS

Cooling of a process or products of a process using water results in an increase in the temperature of the water used for the cooling process. The increase in temperature would typically increase the corrosion and scaling potential within the cooling water. If the cooling water system utilizes evaporation for dissipation of the heat picked up by the cooling water then in addition to an increase in temperature, a concentration of dissolved solids in the water, these solids entering the system as components or contaminants in the water used to make up or maintain the water volume in the system. The increase in concentration of dissolved solids in the cooling water will further increase the potential for scale formation and corrosion. The evaporation of water within the cooling system would typically be accomplished by passing the warm cooling water across a cooling tower, the cooling medium in the tower being air. The cooling tower not only functions to cool the water but also acts as an air scrubber. Therefore a further source of contaminants in the cooling water is from the air. These would typically be particulate matter and microbiological material. Therefore evaporative cooling systems need to be designed, operated and/or treated to control corrosion, scaling, fouling and microbial activity within the cooling

system, in order to minimize damage to equipment through corrosion and loss of heat transfer or performance due to scaling or fouling. This evolves into the use of treatment chemicals whose functionalities are corrosion inhibitors, scale inhibitors, dispersants, surfactants and biocides/disinfectants. Although all of the concerns are of vital importance with respect to protection of the plant and performance, the microbiology of the system can cause fouling of heat exchangers and tower packing (Biofilm), and subsequent loss of efficiency, corrosion within heat exchangers, pumps and distribution pipework (Microbiologically Induced Corrosion - MIC) may also be a Health and Safety concern (pathogens such as Legionella pneumophila - Legionnaires Disease).

Cooling water or cooling systems offer a somewhat ideal environment for the support and proliferation of microbial populations. Typically nutrients are present in significant concentrations, pH of the water is typically between 7 and 9, and the water is warm but typically below 60°C (140°F). In some cases process leaks or contamination can provide additional organic nutrient material which can dramatically increase the rate of growth of microbial species. Operation of certain systems can lead to stagnant water in the cooling system or create dead-legs which promote localized growth of microbial species and biofilm formation, which can create a rapid contamination of the entire cooling system when this stagnant water or dead-legs are brought back into the system's cooling water recirculation.

CONTROL OF MICROBIOLOGY IN A COOLING SYSTEM

Biocides or disinfectants are used to control microbial populations and biofilm within a cooling system. The biocide treatment may be based on an oxidizing biocide, a non-oxidizing biocide or a combination of both. Each of these approaches has its own virtues, but in many, if not most, cases an oxidizing biocide based program is the most effective in terms of efficacy, as defined by speed of kill, is broad spectrum, as defined by efficacy against different types of organism, and economics. Intermittent use of non-oxidizing biocide(s) to supplement and enhance a baseline oxidizing biocide program may be regarded as best practice.

Typical oxidizing biocides used to treat cooling water are chlorine, bromine, and chlorine dioxide. Hydrogen peroxide, ozone and peracetic acid are also effective but less commonly used. Again each has its own inherent advantages and disadvantages.

Much of the concerns with regard to oxidizing biocides are related to safely in storage handling and application. Because of the nature of some of the oxidizing biocides or their precursors, a potential fire hazard may be created by spillage and/or decomposition. Some require generators or special dosing equipment. These concerns and issues have to be addressed and facilities specifically designed and constructed to ensure safety. This can add significant cost to what initially appears to be a "cheap approach". Oxidizing biocides used for microbiological control in evaporative cooling systems are given in Table 1

Table 1
Oxidizing Biocides

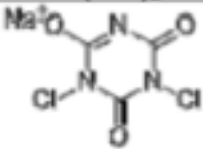
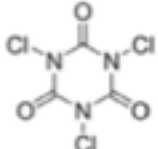
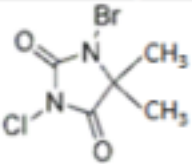
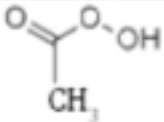
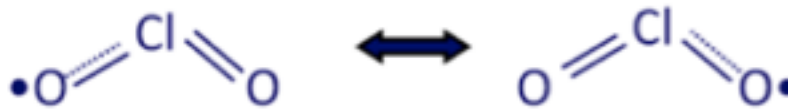
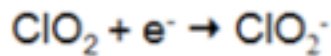
Chemical	Form	Molecular Formula
Chlorine gas	Gas	Cl ₂
Sodium hypochlorite	Aqueous solution	NaOCl
Calcium hypochlorite	Solid powder	Ca(OCl) ₂
Sodium dichloroisocyanurate	Solid pellets	
Trichloroisocyanurate	Solid pellets	
Sodium Bromide	Aqueous solution	$\text{NaBr} + \text{HOCl} \rightarrow \text{HOBr} + \text{NaCl}$ <i>Activated with Cl₂ gas or NaOCl</i>
Bromochlorodimethylhydantoin	Solid granules or pellets	
Bromine chloride	Stabilized solution	BrCl
Chlorine Dioxide	Aqueous solution of gas	ClO ₂
Hydrogen Peroxide	Aqueous solution	H ₂ O ₂
Peracetic Acid	Aqueous solution	
Ozone	Gas	O ₃

Figure 2
Chlorine Dioxide Free Radical Oxidizing Agent

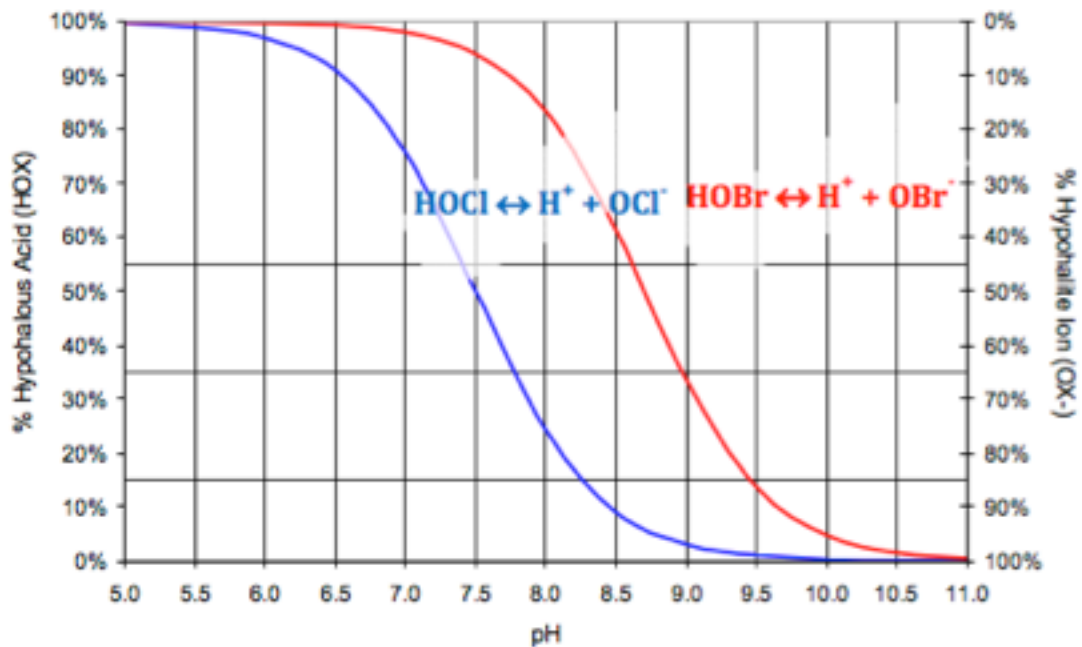


unpaired electron, considered to be a free radical
high reactivity for oxidation and disinfection



$$E^0 = 0.95 \text{ V}$$

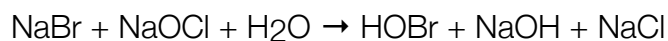
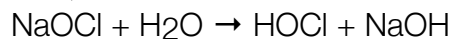
Figure 1
Dissociation Curves for Chlorine and Bromine



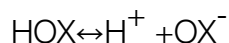
HALOGENATION

The most commonly used are the halogens chlorine and bromine. Sodium hypochlorite and bromide activated with sodium hypochlorite are probably the most popular approaches for halogenation programs. Sodium hypochlorite is obviously a lot easier and safer to handle than chlorine gas, but it does have the disadvantage that it decomposes with time, losing its active chlorine strength. Therefore fresh supplies are desirable or progressive increased volumes are required to obtain the target free halogen concentration.

The main biocidal compound in these approaches is hypochlorous acid or hypobromous acid,



However, in water the hypohalous acid, HOX, undergoes a reversible reaction, being in equilibrium with its corresponding hypohalite anion.



This reaction moves to the right with increasing pH, the pKa values being in the order of 7.5 for chlorine and 8.6 for bromine. Relative proportion of the acid and anion are shown in Figure 1. This dissociation graph is often wrongly interpreted and people believe that “chlorine is not effective at high pH” or “bromine is required in Alkaline Cooling Water Treatment Programs”. These comments are not true and the effect of pH on the efficacy of chlorine needs to be defined. At higher pH the speed of kill with chlorine is longer than at lower pH, but overall chlorine is still effective at alkaline pH.

By reaction with organic matter or organic compounds, chlorine and bromine can form Trihalomethanes (THM) which are environmental pollutants and many are suspected to be carcinogenic (Alavanja et al., 1980). They can also form Adsorbable Organic Halides (AOX) which are also regarded as environmental pollutants and some Water Authorities stipulate a maximum AOX concentration in plant effluent consents. In a programs utilizing halogenation, particularly chlorine, other chemical components commonly applied in treatment programs may be susceptible to degradation or decomposition through reaction with the halogen. Alternative halogen resistant treatment chemicals are available but these may be more expensive than the traditional chemicals.

These issues tend to make halogenation, particularly chlorination, becoming less favorable in certain countries. Although chlorine dioxide contains a halogen, its properties and mode of action is entirely different to halogenation, basically the chlorine dioxide free radical (Figure 2) as opposed to a hypohalous acid. As an alternative to halogenation chlorine dioxide is a viable approach since it does not produce THMs or AOX and has several other benefits compared to halogenation.

CHLORINE DIOXIDE

Chlorine dioxide is an unstable gas and is typically generated at point of use and applied as an aqueous solution of the gas. It is applicable over a wide range of water pH between 4 and 11 (Lykins and Griese, 1986). Studies have shown that microbial disinfection with chlorine dioxide is as effective or superior to disinfection with free chlorine, particularly in regard to inactivation of viruses (Narkis and Kott, 1992; Junli et al., 1997).

BRIEF HISTORY OF CHLORINE DIOXIDE

The discovery of chlorine dioxide is accredited to the British chemist Sir Humphrey Davy in 1811, using sulfuric acid (H₂SO₄) to synthesize chlorine dioxide from the acidification of potassium chlorate (KClO₃). Over the passage of time, the original sulfuric acid (H₂SO₄) was replaced by hydrochloric acid (HCl), and potassium chlorate (KClO₃) was replaced by sodium chlorate (NaClO₃) for large- scale production (White 1999).



The ability of chlorine dioxide to control phenol related tastes and odor by oxidizing causal compounds led to its first use in treating drinking water in the United States in the 1940s, when it was utilized in treatment plants along the Niagara River in New York State (Gates 1998 citing Aston 1947). The success of this application quickly led civic leaders and scientists to rely on it for resolving related odor problems in other municipal potable water treatment facilities (McCarthy 1945; Synan 1945; Vincent 1946). However, despite its proven value in this area of application, during the 1960s-70s, chlorine dioxide was increasingly abandoned because of a variety of problems related to its implementation. Some of the reasons for this abandonment were equipment and installation design problems, and the increasing cost of chemicals related to its use. Other factors involved the destructive damage to facilities due to the corrosive nature of the precursor, the poor chlorine dioxide yield obtained with the earlier generation methods and inadequate control of dosing (Gates 1998).

Despite a series of setbacks over two decades, in the 1980s chlorine dioxide again captured the interest in the potential of again using it to treat drinking water. Currently in Northern America, chlorine dioxide is used continuously in as many as 500 water utilities and on an intermittent or seasonal basis in up to 900 plants (Hoehn 1993).

METHODS OF GENERATING CHLORINE DIOXIDE

There are several basic ways by which chlorine dioxide can be generated. One main difference is the number of chemicals or precursors required. Apart from chemicals used the main difference is the efficiency of the reaction or chlorine dioxide yield, and/or weight of chlorine dioxide that the method can practically accomplish. Using photometric or electrolytic methods only one chemical, sodium chlorite (NaClO₂) is required.

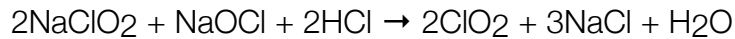
Other methods use two precursors, sodium chlorite (NaClO₂) plus chlorine gas (Cl₂)

$$2\text{NaClO}_2 + \text{Cl}_2 \rightarrow 2\text{ClO}_2 + 2\text{NaCl}$$

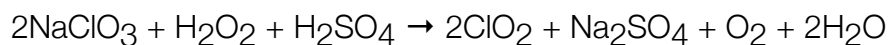
or sodium chlorite (NaClO₂) plus hydrochloric acid (HCl)

$$5\text{NaClO}_2 + 4\text{HCl} \rightarrow 4\text{ClO}_2 + 5\text{NaCl} + 2\text{H}_2\text{O}$$

The last basic method involves three precursors, sodium chlorite (NaClO₂) plus sodium hypochlorite (NaOCl) plus hydrochloric acid (HCl)



or using sodium chlorate (NaClO₃) plus hydrogen peroxide (H₂O₂) plus sulfuric acid (H₂SO₄)



The majority of chlorine dioxide used in industry is for bleaching wood pulp within the Pulp and Paper Industry, where high yields and large production volumes are required. A three chemical method is used reducing sodium chlorate (NaClO₃) with methanol (CH₃OH) or sulfur dioxide (SO₂) and acidifying with sulfuric acid (H₂SO₄). It has been reported that the inclusion of hydrogen peroxide in this methanol based approach increases the rate of chlorine dioxide generation (Yin and Ni, 1999), although hydrogen peroxide can be used to “neutralize”, degrade or destroy chlorine dioxide.

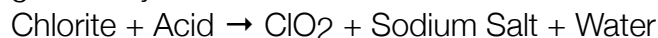
POTENTIAL HAZARDS ASSOCIATED WITH CHLORINE DIOXIDE GENERATION

Traditionally chlorine dioxide was made with liquid precursors, which means that the entire process from initial delivery, though generation and local storage, to dispensing or dosing the chlorine dioxide product relies on fluid solutions. There are several safety concerns with respect to the nature and characteristics of the precursor, their mixture and generated chlorine dioxide solution, which many consider to be “dangerous”. The “dangers” are the potential for spillage of precursors which include strongly acidic solutions and acidic fumes, leading to potential corrosion, and, if the spilt precursors mix, premature uncontrolled generation of chlorine dioxide in an open area. There are also potential fire and explosion hazards with some precursors, their mixture and generated chlorine dioxide solution. The gas phase of the generated chlorine dioxide solution is explosive at solution concentrations above 8 grams ClO₂ per liter or 8000 ppm ClO₂. Chlorine dioxide gas detectors and alarms should be fitted in enclosed spaces containing the generator. Bunds and even storage of precursors in separate rooms minimizes risks of spillage of precursors. Generator design and operation addresses the potential of explosion from concentrated chlorine dioxide solutions. There are two basic approaches commonly used to address this issue, the use of dilute precursor solutions or dilution of concentrated precursors en route to the generator, or, sending the concentrated precursors, unmixed, to a mixing chamber or generator situated underwater, such as submerged in a cooling tower basin, or in a water distribution line. Obviously, the many safe applications of chlorine dioxide practiced today prove that modern day design and operation of chlorine dioxide generators is a safe process.

The one area where there still is, or may be, a potential safety concern is the initial precursor solutions. Particularly in the case of the two precursor approach there is a potential for leakage in the lines carrying the precursor to the generator, but, the greater potential safety hazard is human error where the wrong precursor is fitted to the wrong section of the generation system, or the wrong precursor is dispensed into the wrong tank or container. Unfortunately there have been incidents of this nature resulting in violent and destructive explosions.

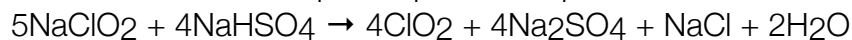
SOLID PRECURSORS

A potential route to minimize risks associated with precursors and chlorine dioxide generation would be the use of solid precursors, as opposed to a concentrated liquid or gas precursor. If one reviews the methods of generating chlorine dioxide from liquid precursors, one will soon notice that sodium chlorite and sodium chlorate can be in a solid form but many of the precursors required to “activate” the chlorite or chlorate are only existing as a liquid or gas. In order to consider the sole use of material in a solid form one needs to initially look at the reaction of sodium chlorite with hydrochloric acid more generically.



Now there is a choice of using an acid which is available in a stable solid form to “activate” sodium chlorite. This could be an organic acid among which be citric acid, ascorbic acid, erythorbic acid, succinic acid, malic acid, oxalic acid or acetylsalicylic acid could be contenders. Alternatively it could be an inorganic salt that produced an acidic solution when dissolved in water, for which sodium hexametaphosphate, sodium dihydrogen phosphate or sodium bisulfate could be considered. Another approach would be to use a strong solid oxidizing agent like a persulfate ($\text{S}_2\text{O}_8^{2-}$) although this route can take a long time, up to 2 days’ to produce the chlorine dioxide. Obviously there are properties such as solubility and deliquescence which have a large or limiting influence on the choice of acid, and then efficacy or chlorine dioxide yield and costs become a consideration.

There are two basic approaches. A stabilized solid “chlorine dioxide release” tablet which is activated by dissolving in water. These are typically used for sterilizing of water for drinking when on outdoor activities such as sailing, hiking or camping where water supply of potable quality cannot be guaranteed. The other approach is the use of two powdered precursors which lends itself to the production of up to 1000 liters (264 gallons) of stable chlorine dioxide solution, which can be used as the basis of a cooling water treatment biocide program. This approach is commercially available using sodium chlorite and sodium bisulfate as separate powdered precursors.



Although the yield using these powdered precursors may be less than that obtained with liquids, smaller volumes of precursor are required since the precursor is not an aqueous solution but a solid active component. Therefore transportation and storage on an active component basis is less with these powdered precursors than their liquid equivalents. Inherent safety in handling is less and spillage unlikely to yield any chlorine dioxide gas or other toxic material unless water comes in contact with a mixture of the two powdered precursors. Nevertheless the powdered precursors have to be mixed into an aqueous reaction mixture which then becomes a stable solution of chlorine dioxide, and this involves some manual labor and handling. Therefore appropriate Personal Protective Equipment, such as protective clothing and safety shoes or boots, goggles and gloves or gauntlets, are required. Since the components are powdered, a dust mask is also required.

Even though dusting should not present a great potential hazard, appropriate precautions must be taken.

The two powdered precursors are mixed together to product a 0.3% solution of chlorine dioxide (3000 ppm ClO₂) in water. The precursors have a shelf life of at least 5 years and the 0.3% solution of chlorine dioxide has a kinetic half-life greater than 30 days. A representation of the preparation of a 0.3% chlorine dioxide solution is illustrated in Figure 3.

Using instructions

1 Always read the material safety data sheet (MSDS) and follow the safety instructions.

2 Fill the container with the exact amount of (tap) water.
 1 – 5 –
 10 – 25 liter

3 First, shake the jars of powder, and add component B to the container with water.

4 Afterwards add component A to the container.

5 Securely close the container.

6 Do not shake or stir.

7 Wait according to the timetable.

25 °C (77 °F)	≥ 3 H
20 °C (68 °F)	≥ 4 H
15 °C (64 °F)	≥ 5 H

8 Shake or stir the solution gently – Beware of ClO₂ gas release.

9 TwinOxide solution is ready for use for approx. 30 days – write the date of preparation on the label of the container.

10 Store in a cool and dark place.

For bigger volumes see separate using instructions.

50 – 100 liter

500 – 1000 liter

This “manual procedure may be suitable for preparing up to 10 liters, possibly 25 liters, of solution, a more convenient method and the method required to produce large quantities, up to 1000 liter, of the solution is to use a specially designed mixing or dissolution vessel. The chlorine dioxide solution can then be dosed directly from this vessel, using normal metering dosing pumps, directly to the system or area to be disinfected. Although the resultant solution of chlorine dioxide is stable some chlorine dioxide can exist in gas or vapor phases above the solution. The dosing unit vents back into the vessel so as to avoid exposure to chlorine dioxide gas or vapor.

Depending upon proximity of applications and volumes of solution required, each application can be served by its own individual dosing unit, or several applications can be served for one dosing unit. For intermittent dosing, dosing pumps would typically be fitted with timers.

LIMITATIONS

However good or innovative an idea or approach may be, there are always limitations or areas of application that may be more practical than others. The main limitation of the use of solid precursors is the volumes of chlorine dioxide solution that can be practically and conveniently prepared, which in turn limits application in cooling systems to those with comparatively small volumes. The target chlorine dioxide residual, chlorine dioxide demand and frequency of addition also need to be taken into account in deciding on volumes of solution required.

Such constraints in terms of practicality apply to many solid treatment product compositions that can be used for cooling water applications. This was not the case when solid sodium dichromate was the basis of cooling water treatments but these days chromate cannot be used for environments reasons. The use of solid treatment chemicals and dispensing into cooling systems is not new and post the chromate era there have been units that have been designed to dose treatment chemicals from bottles solid components. These have been available for over a decade. There seems to be a resurgence in the interest of solid treatment chemicals or “controlled release” solid formulations or mixtures (Emery 2013 and Hunter 2014) for use in cooling water treatment. The volume that can be practically treated is again a limitation. However, where practical the use of solid chemical products for the treatment of cooling water and in other applications undoubtedly can offer benefits in terms of safety, storage and handling.

Another limitation is the strength of chlorine dioxide solution that can be considered stable and “transportable”. An ideal situation would be to have a “Stable” chlorine dioxide solution at high concentration available commercially, whereby the supplier does the preparation of the chlorine dioxide solution. Unfortunately here again there is a limitation on the “stability” of such solutions and in practice solutions available as supposedly “stabilized chlorine dioxide” are not chlorine dioxide but are in fact sodium chlorite or sodium hypochlorite solutions.