

The TREND

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Oxidizing Biocides

Technical Note

If you are using the biocide APS-35 and performing the UV digestion for phosphonate, you will get positive interference from the biocide. You should time your service calls to these accounts to avoid interference.

\$\$ Fuel Saver \$\$

The cost of fuel affects everyone these days. Look for details on an upcoming new Chemtex program to help you save fuel and reduce your carbon footprint.

Coming up next in *The Trend*

The next issue of The Trend will highlight our line up of coil cleaners and how to pick the right one for the job!

Oxidizing biocides are a common term in the water treatment vocabulary. The words used to explain the chemical reactions behind these biocides are not so common, making it difficult to express treatment choices to your customers. Understanding the concepts of oxidizing biocides will provide you with the knowledge to properly and cost-effectively treat your systems, consequently keeping them free of microbiological fouling.

An oxidizing biocide attacks microorganisms by oxidizing (an electron transfer reaction) the cell structure, disrupting nutrients from passing across the cell wall. Chlorine, bromine and chlorine dioxide are very effective oxidizing biocides. They are all relatively easy to disperse, measure and control. Each has distinct benefits and disadvantages that will help you decide which one will be the most effective in a particular system. Temperature, pH, pre-treatment conditions and other specifics of the water systems are factors

in choosing the proper biocide.

Chlorine

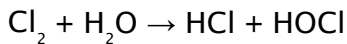
Chlorine has been used as a disinfectant since 1846 and is the most widely used control method for microorganisms



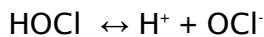
in industrial cooling systems. Despite EPA regulations to limit chlorine discharge due to toxicity and carcinogen concerns, chlorine continues

to be a popular choice of biocide as it is both effective and economical.

When chlorine is added to water, the initial chemical reaction creates a mixture of hypochlorous acid (HOCl) and hydrochloric acid (HCl):



HOCl is the actual oxidant that attacks the microorganism. As pH increases, HOCl starts to dissociate into hypochlorite (OCl⁻):



OCl⁻ is also an oxidant, but a much weaker one than HOCl. Together these chlorine species are known as free chlorine. At a pH of 5.5, the HOCl concentration in the solution is near 100% (Figure I). As the pH of the solution increases to 8.5, the HOCl concentration drops to near 10% and the OCl⁻ concentration is now 90%. Since most cooling towers operate at a pH greater than 7.5, the tower water will never have more than 50% of the desired HOCl.

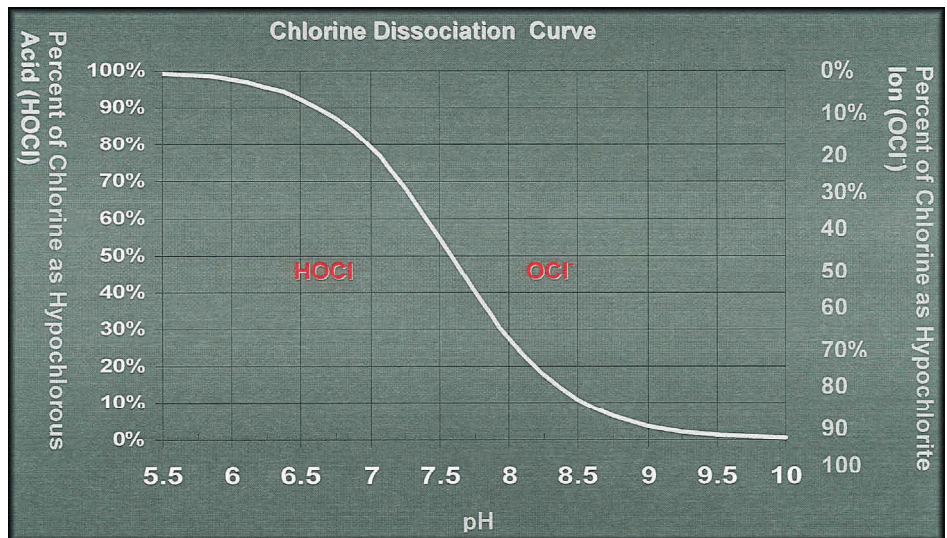
There are several other reactions chlorine undergoes when introduced to water. These reactions use up the chlorine, so less is available

Chlorine is used in a number of diverse processes, 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 for antifreeze and synthetic fibers.

for microbiological control. One of the most important reactions is with ammonia to form chloramines, which are very weak biocides. Some municipal water treatment facilities use chloramines as a disinfectant instead of chlorine due to EPA recommendations to reduce the carcinogenic byproducts of chlorine. Depending on the pH of the solution and the hypochlorous to ammonia ratio, the reactions may form mono, di, and trichloramine. These chloramines are referred to as combined chlorine.

tion and stripping due to volatility must be considered when correctly dosing cooling water systems.

To measure free and total chlorine, the DPD (N,N'-diethyl-p-phenylene-diamine) colorimetric method is fast and relatively easy to perform in the field. Chlorine testing should be done at the time of sampling due to volatility. The intensity of the pink color formed in the reaction is proportionate to the chlorine level in the solution. Interferences with the DPD test



Total chlorine is the sum of free chlorine (HOCl and OCl⁻) and combined chlorine. Since free chlorine is the most effective in microbiological control, it is good practice to monitor free chlorine residuals as well as total chlorine in the water system.

Chlorine also reacts with iron, manganese, sulfur and organic matter. Oil, grease, leaves, tannin and lignin present in a fouled system can significantly decrease the biocidal effectiveness of chlorine. Chlorine consumption, or chlorine demand, along with heat, sunlight degrada-

tion include high calcium and alkalinity, which can be overcome by lowering the pH of the test sample between 6 and 7 with 1 N sulfuric acid.

Bromine

Similar to chlorine, bromine hydrolyzes in water to form hypobromous acid (HOBr), which has the same oxidizing power as HOCl. HOBr dissociates to form H⁺ and OBr⁻, but the reaction happens at a higher pH than chlorine. A bromine solution with a pH of 8.5 will contain close to 60%

HOBr, whereas a chlorine solution at the same pH would yield 10% HOCl. In many cases, a smaller dose of bromine will obtain the same microbiological control as using chlorine in a cooling tower system.

Another advantage of bromine is that it reacts with ammonia and other nitrogen compounds to form bromamines which, unlike chloramines, are effective biocides. Bromine is also less corrosive than chlorine to copper alloys.

The name Bromine originates from the Greek word Bromos meaning "stench".

Bromine reacts with iron, manganese, sulfur and organic matter. Heat and sunlight contribute to bromine demand, but stripping is less due to lower volatility than chlorine. Its toxicity to aquatic life and possible formation of carcinogens is similar to chlorine and has therefore led to EPA discharge regulations.

Bromine residual can be analyzed using the same DPD colorimetric method and reagents as chlorine testing as long as other oxidants are absent. Like chlorine, bromine testing should be done at the time of sampling. If a spectrophotometer does not have a bromine program, the result given on the chlorine program can be multiplied by 2.25 to obtain a bromine concentration. It is usually unnecessary to test for free bromine residuals since most combined forms of bromine, such as bromamines, are just as effective as free bromine. If testing for free bromine is required, it should be noted that full color development by the DPD method will take 2-3 minutes for stabilized bromine products instead of the directed 30 seconds.

Chlorine Dioxide

Chlorine dioxide (ClO₂) is a powerful oxidizer that is soluble in water, but remains in a gaseous state until it reacts with a microorganism. ClO₂ has more than double the oxidizing capability of chlorine and is not affected by system pH. It does not react

with nitrogen compounds or organics, eliminating possible carcinogen formation. ClO₂ does react to form chlorite, which can be toxic to aquatic life, and is very volatile. Chlorine dioxide is an expensive oxidizing biocide, but its advantages and effectiveness over chlorine and bromine may offset the cost in certain situations.

Chlorine dioxide is also used as a bleaching agent in the recycling of paper products.

Chlorine dioxide can also be tested by using a variation of the DPD colorimetric method in the absence of other oxidants.

Oxidizing biocides are key players in the control of microbiological fouling of industrial water systems. Understanding the chemistry behind these biocides and their basic features will help you make treatment decisions that are both effective and economical.

PRODUCT	MAINTAINENCE DOSAGE MID RANGE	LBS/1000 GALLONS OF WATER	RELATIVE COST TO TREAT 1000 GALLONS (5 GALLON PAILS)
AA-1112	4 PPM BROMINE	0.03 LBS	\$\$\$
AAV-08	132 PPM	1.1 LBS	\$\$\$\$
AA-5010	12 PPM	0.1 LBS	\$\$
AA-6070T	5 PPM BROMINE	0.04 LBS	\$\$
AA-6090M	1 PPM CHLORINE	0.06 LBS	\$\$
25% SODIUM CHLORITE	1 PPM ClO ₂ ClO ₂ generator required	0.009 LBS	\$
BROMEX 11	4 OZ/1000 GALS	0.36 LBS	\$\$\$
SBR-40	3 PPM Must be combined with chlorine	0.17 LBS	\$\$

Test Kits

Bromine

Color Cube

Bromine is an oxidizer used as a biocide in cooling water systems. Bromine is more effective at a higher pH than chlorine.

Part Number	Description
21940-00	Hach Bromine Test Kit

Colorimeter

The Pocket Colorimeter II for Bromine is an accurate means of measurement. Includes reagents for 50-100 tests. Range is 0.05-4.50/0.2-10 ppm as Br₂.

Part Number	Description
58700-01	Hach Bromine Pocket Colorimeter II

Powder Pillow

Bromine and chlorine are tested using the same reagents. The instruments and cube are calibrated for bromine measurement. If chlorine is present in the system, it will add positive interference to the bromine result.

Part Number	Description
14064-99	Hach DPD Total Chlorine, for Bromine Color Cube
21056-69	Hach DPD Total Chlorine, 10 ml sample size, for DR/890 and PCII

Chlorine

Colorimeter

Chlorine is an oxidizing biocide frequently used in the water treatment industry. Both free and total chlorine can be measured with these reagents. The Pocket Colorimeter II for Chlorine is an accurate means of measurement. Includes reagents for 100 tests. Range is 0.02-2.00/0.1-8.0 ppm as Cl₂.

Part Number	Description
58700-00	Hach Free & Total Chlorine Pocket Colorimeter II

Powder Pillow

Part Number	Description
14064-99	Hach DPD Total Chlorine, 25 ml sample size
14070-99	Hach DPD Free Chlorine, 25 ml sample size
21055-69	Hach DPD Free Chlorine, 10 ml sample size, for DR/890 and PCII
21056-69	Hach DPD Total Chlorine, 10 ml sample size, for DR/890 and PCII

Chlorine Dioxide

Colorimeter

Chlorine dioxide (ClO₂) is a powerful oxidizing biocide. It is effective at controlling all types of microbiological growth in cooling tower and process water systems, as well as in domestic potable water systems. It is a more powerful oxidant than either chlorine or bromine and is more effective than either at high pH. The test for chlorine dioxide is a variation of the DPD test for chlorine. The Pocket Colorimeter for Chlorine Dioxide is an accurate means of measurement. Includes reagents for 100 tests. Range is 0.05-5.00 ppm as ClO₂.

Part Number	Description
58700-51	Hach Chlorine Dioxide Pocket Colorimeter II

Reagent Set

Part Number	Description
27709-00	Hach Chlorine Dioxide Reagent Set, for DR/890 and PCII