A Non-Hazardous Biocide for Cooling Water Treatment

Typical biocides are reactive and toxic, exposing workers to a variety of hazards caused by the nature of these chemicals.

by Timothy Keister

Because of purchase and operating economics, "wet" cooling towers are the technology of choice for commercial and industrial cooling systems. Water is the best material for both transfer of heat and evaporative cooling, but one drawback is that such use presents a biological control problem. Warm water, with dissolved and suspended solids present, is an excellent medium for growth of microorganisms.

Growth of microorganisms in cooling water is further encouraged by use of reclaimed wastewaters as makeup and increased cooling tower cycles of concentration, current trends that are being driven by freshwater shortages, increased water and sewer charges, and stricter environmental restrictions. The uncontrolled growth of microorganisms in cooling water causes severe problems related to increased risk of Legionnaires' Disease, plugging due to physical blockage of cooling water passages, accelerated corrosion under biological masses, and reduced heat exchanger efficiency due to biofouling of surfaces.

Present Practice

Current technology for biological control of cooling water depends upon various toxic, hazardous chemicals, such as chlorine, ozone, chlorine dioxide, dithiocarbamate, isothiazolin, hydantoin, and glutaraldehyde, that are commonly termed "biocides." While these biocides are often quite effective for biological control, their use represents a substantial health and safety concern. There are more than 300,000 cooling towers in the United States using an estimated 40 million pounds of such chemicals on an annual basis.

This toxic, hazardous chemical use is basically everywhere. Cooling towers are found throughout our country, in neighborhoods, towns, and cities. In addition to typical industrial installations, cooling towers are commonly found at hospitals, hotels, grocery stores, office buildings, warehouses, apartment buildings, and retirement homes—basically, anywhere air conditioning or process cooling is needed. Smaller users represent a special worker safety concern because cooling water treatment, and application of biocides, is often the responsibility of generally untrained workers. Replacement of hazardous biocides by a non-hazardous technology will provide a substantial improvement in health and safety.

During biocide application, workers can be exposed to a variety of hazards caused by the reactive and toxic nature of these hazardous chemicals. Oxidizing biocides, commonly used as a gas such as chlorine, chlorine dioxide, and ozone, present a serious safety issue because low gas water solubility, reagent spills, and leakage can result in workers' exposure to toxic levels of the gases. Liquid oxidizers, such as sodium hypochlorite, are corrosive and reactive, exposing workers to chemical burn, toxic gas evolution, and explosion hazards during handling.

Solid oxidizers, such as hydantoin, are quite reactive and can explode when mixed with many organic materials, such as sawdust or even flour. In addition, typical handling of these materials exposes workers to a very irritating, toxic dust. These concerns can manifest themselves in "incident" reports, especially if the root cause is that proper protective equipment is not worn, or if it is not readily at hand for "routine" operations.

Chlorine gas is commonly used in larger cooling water applications because of its low cost and ease of application. This chemical is extremely toxic in the gas form and, if released as such, presents a major risk for fatalities and serious injury within both the plant and surrounding community. Chlorine gas is generally provided in one-ton cylinders to larger users, so the security risk of such use is very high due to the ease with which a terrorist's intentional release could be accomplished and the potential for massive fatalities and serious injuries.

Many governmental agencies have recognized this security risk and have responded by requiring that the people involved with use of chlorine gas in the public sector, such as water and wastewater treatment operators, be given a security check prior to license renewal. Additional security measures are also being required for installations using chlorine gas, such as restricted access and better fencing. A non-hazardous biocide technology would completely eliminate these concerns.

The following table summarizes some relevant toxicity data on five commonly used hazardous chemical biocides:

Product	CAS	Acute oral toxicity, rat LD 50
glutaraldehyde	111-30-8	134 mg/kg
isothiazolin	26172-55-4	57.2 mg/kg
dithiocarbamate	142-59-6	395 mg/kg
bromochloro hydantoin	32718-18-6	877 mg/kg
dibromo propionamide	10222-10-2	308 mg/kg

Non-hazardous Biocide Technology

Bromine, in its various delivery forms, has been recognized as an effective biological control agent for many years. While effective, the existing delivery forms all suffer from various problems ranging from health and safety issues to simple high cost. Use of on-site electrolysis to make aqueous bromine is appealing because sodium bromide solutions are non-hazardous and relatively low in cost, while the electrolysis process is time proven, having been used for industrial production of both chlorine and bromine for more than 100 years.

Problems with existing electrolysis technology for manufacture of aqueous bromine were mainly economic, in that platinum-plated titanium is used in construction of the electrolysis cells, which operate with a typical bromide to bromine conversion efficiency of just 35 percent. Given the advantages of bromine use for biological control, a project to devise a new electrolysis-based technology to economically make an aqueous bromine solution on site was initiated several years ago.

This work resulted in development of a new electrolytic technology to produce an aqueous bromine solution on site from a non-hazardous precursor bromide salt solution. The process uses a novel, low-cost electrolytic cell based upon impregnated electrolytic graphite to produce an aqueous bromine solution economically as needed, from an equimolar aqueous solution of sodium bromide and chloride.

Electrolysis of this bromide-chloride solution in the new cell obtains a 95 percent conversion of bromide ion to the desired aqueous bromine, which has a high biocidal efficiency in the alkaline cooling waters commonly encountered today. The U.S. Environmental Protection Agency has registered the new electrolysis process as a cooling tower biocide.

The following table notes the toxicities of the two salts used in the electrolysis process:

Product	CAS	Acute oral toxicity, rat LD 50
sodium bromide	7647-15-6	3,500 mg/kg
sodium chloride (table salt)	7647-14-5	3,000 mg/kg

As can be seen, both of the salt components used in the electrolysis process are substantially less toxic than any of the commonly used biocides. Worker exposure to the salt solution thus presents a minimal hazard due to toxicity. Because the bromine solution produced by the electrolysis process is made "as needed" and immediately fed into the cooling tower water, there is essentially no worker exposure to the material. To put the potential toxicity hazard of the produced bromine solution into a common perspective, household bleach is a highly alkaline, pH > 12.5, 5 percent hypochlorite solution. The active product produced by the electrolysis process is a mildly alkaline, pH < 10.0, 0.8 percent aqueous bromine solution.

Public Safety

While both OSHA and the Cooling Technology Institute recommend continuous halogenation for control of legionella bacteria in cooling waters so as to minimize the transmission of Legionnaires' Disease via cooling tower waters, few cooling tower operators have implemented the recommendation because of the issues of worker safety, complexity, and cost.

The electrolysis process is a simple, cost-effective means to provide continuous halogenation of cooling waters, thus providing optimal protection against spread of Legionnaires' Disease via cooling tower windage or drift. Using either time-based dosing or oxidation reduction potential controls to automate dosage, the electrolysis process makes continuous halogenation economical and practical for even small cooling tower installations.

Comparing the cost to operate the new electrolysis process, as shown in the following table for a cooling tower in terms of dollars per 1,000 gallons of cooling water treated, it is less than present technology based on toxic, hazardous biocides:

Product	Dose mg/l	lbs/1,000 gals	$/lb	$/1,000 gals
30% carbamate	50	0.42	2.30	0.97
98% hydantoin	24	0.20	3.90	0.78
20% dibromo propionamide	37.5	0.31	3.30	1.02
1.5% isothiazolin	127	1.06	3.25	3.44
15% glutaraldehyde	227.5	1.90	2.45	4.66
electrolysis process	6.0	0.29	0.75	0.22

Proven Technology

Following six months of field trials, the first commercial electrolysis process units were installed in June 2003 and have proven to be a cost-effective, reliable means of controlling the growth of microorganisms in cooling waters. Looking at a typical, 1,000 ton cooling tower, we have compared the cost of a traditional two-biocide program (hydantoin and glutaraldehyde, alternated dosing twice a week) with an electrolysis process installation. For the traditional program, our calculations show a total cost of $326.40 per month, while the electrolysis process has a cost of just $136.40 per month.

Two papers have been presented to date on the technology, the first at the Cooling Technology Institute in February 2004, the second at the International Water Conference in October 2004. In particular, the International Water Conference paper reports on the successful replacement of chlorine gas use as a biocide by the electrolysis process at an 1100 MW power station. Of great interest was that the operating cost for the electrolysis process was determined to be the same as chlorine gas, making the electrolysis process a very economical alternative technology.

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PROCHEMTECH INTERNATIONAL, INC.

This cooling tower installation is operating at a public school in Arizona.

PROCHEMTECH INTERNATIONAL, INC.

This graphite block electrolytic cell is the "heart" of the ElectroBrom unit.

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