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Title: Electrolytic Bromine: A Green Biocide for Cooling Towers

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Abstract

While water is the best material for transfer of heat and use as an evaporative cooler, its use in cooling towers presents a biological control problem as warm water is an excellent medium for growth of microorganisms. 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.

Current technology for biological control of cooling water uses an estimated 40 million lbs/yr of dangerous to handle, hazardous/toxic chemicals such as chlorine, ozone, chlorine dioxide, dithiocarbamate, isothiazolin, and glutaraldehyde in the estimated 300,000 cooling towers located throughout the country. While these chemicals are often quite effective for biological control use, they have numerous problems such as high cost, corrosivity issues, health and safety concerns, security concerns, environmental problems, selective effectiveness on an organism basis, accidental spill problems, and incompatibility with other cooling water additives.

Bromine has been recognized as an effective biological control agent for many years which, due to its rapid degradation to harmless bromide, is not a persistent pollutant. We have invented a novel, economic process for producing bromine at the point of use by electrolysis from a non-hazardous aqueous solution of sodium bromide and chloride. Produced electrolytic bromine is used to totally replace use of hazardous/toxic chemical biocides for control of microorganisms in cooling towers. The chemistry and equipment of this novel process as well as economics, environmental impact, and health & safety aspects will be discussed and compared to existing biocide technology.

Electrolytic Bromine: A Green Biocide for Cooling Towers

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Background

Cooling Towers at a Public School

Due to purchase and operating economics, "wet" cooling towers are the technology of choice for commercial and industrial cooling systems as water is the best material for both transfer of heat and evaporative cooling. One drawback is that such use presents a biological control problem as 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 driven by fresh water shortages, increased water and sewer charges, and stricter environmental regulation. 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 - Problems

Current cooling water biological control technology depends upon various toxic, hazardous chemicals such as chlorine, ozone, chlorine dioxide, dithiocarbamate, isothiazolin, hydantoin, and glutaraldehyde; commonly termed “biocides". While these biocides are often quite effective, their use represents substantial environmental, health, and safety concerns as there are over 300,000 cooling towers in the United States using an estimated 40 million pounds of such chemicals on an annual basis. Use of toxic biocides is basically everywhere as 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, schools, colleges, and retirement homes; basically, anywhere air conditioning or process cooling is needed.

Gas form oxidizing biocides such as chlorine, chlorine dioxide, and ozone; present a serious safety issue as low water solubility, reagent spills, and leakage can result in exposure of workers to toxic levels of the gas and explosion hazards. Liquid oxidizers, such as sodium hypochlorite and n,n,dibromosulfamate, are corrosive and reactive, exposing workers to chemical burns, toxic gas evolution, and explosion hazards. Solid oxidizers, such as hydantoin, are quite reactive and can self ignite when mixed with many organic materials, such as sawdust or even flour.

Chlorine gas is commonly used in larger cooling water applications due to its low cost and is thus present on site in large amounts. This chemical is extremely toxic and, if released in large amounts, represents a major risk for fatalities and serious injury within both the using facility and the surrounding community.

The non-oxidizing biocides in common use represent a substantial worker hazard due to high toxicity values, with several of the products being readily absorbed through the skin. The following table summarizes some relevant toxicity data on five chemicals commonly used as cooling water biocides.

Chemical Product	CAS Number	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
bromochlorohydantoin	32718-18-6	877 mg/kg
dibromo propionamide	10222-10-2	308 mg/kg

Smaller users, the vast majority of cooling tower operators, represent a special worker safety concern since cooling water treatment, and application of biocides, is often the responsibility of workers not trained in handling of toxic chemicals.

Environmental Considerations

The widespread transport, storage, and use of biocides presents many opportunities for accidents which would result in release of these products into the environment with generally severe results. Both oxidizers and non-oxidizers are extremely toxic to most aquatic life and even small product spills and leaks can product catastrophic effects. The following table summarizes some aquatic toxicity data for several commercial cooling water biocides along with the typical cooling water dosage range.

Biocide Product	CAS	LC 50 aquatic toxicity		Typical Dosage
glutaraldehyde 25%	111-30-8	rainbow trout	56.2 ppm	130 to 650 ppm
		daphnia	16.9 ppm	
isothiazolin 1.5%	26172-55-4	rainbow trout	0.14 ppm	35 to 883 ppm
		daphnia	0.13 ppm	
dithiocarbamate 30%	142-59-6	rainbow trout	0.10 ppm	40 to 120 ppm
bromochlorohydantoin 98%	32719-18-6	rainbow trout	0.42 ppm	12 to 72 ppm
dibromo propionamide 20%	10222-10-2	rainbow trout	2.3 ppm	25 to 100 ppm
polyquat 20%	7173-51-5	bluegill sunfish	1.6 ppm	5 to 315 ppm
		daphnia	0.47 ppm	

Cooling towers, being basically evaporative coolers with about 80% of the input heat load being removed by evaporation, increase cooling water solids content rapidly with the result that routine blowdown is required to prevent scale formation. Typically, operating at four cycles of concentration, a cooling tower will evaporate 2,655 gpd and blowdown 885 gpd per 100 tons of thermal load. This blowdown has been recognized as a substantial source of highly toxic chemical input to the environment dependent upon the biocide(s) and discharge treatment in use.

We are aware of several cases where environmental agencies have either banned the use of, or required treatment for, various biocides prior to direct stream discharge of blowdown. In the case of a smaller POTW and a large blowdown discharge, the POTW mixed liquor bio mass could be easily wiped out by the biocide content of the blowdown.

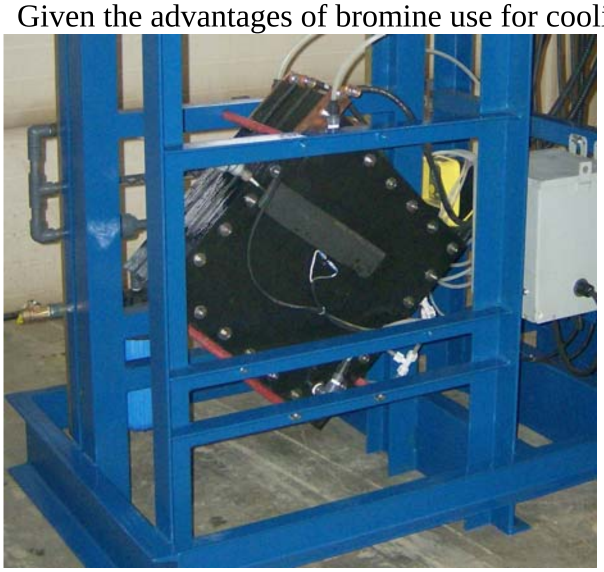
In addition to the intentional blowdown discharged from cooling towers, spillage of concentrated biocide products are a substantial threat to operation of POTW. For instance, a spill of 55 gallons of a biocide product like 30% carbamate could totally wipe out an activated sludge plant with a mixed liquor volume of up to 1.3 million gallons. We are aware of several such accidents in the past five years.

Since most non-oxidizing biocides are both long lived and/or difficult to destroy, oxidizing biocides, which can be easily destroyed by addition of a reducing reagent to the blowdown stream, are preferred from the standpoint of minimizing the environmental impact of cooling tower blowdown or spills. Oxidizing biocides, however, still present significant hazards during transport, storage, and use.

Bromine, an oxidizing biocide, in its various delivery methods has been recognized as a superior cooling water biocide for many years. Unfortunately the delivery methods all suffer from the same environmental, health, and safety issues as other oxidizers as well as being somewhat costly. Use of on-site electrolysis to make aqueous electrolytic bromine is appealing as sodium bromide solutions are non-hazardous and relatively low cost, while the electrolysis process is time proven, having been used for industrial production of both chlorine and bromine for over a hundred years. The problem with existing electrolysis technology for manufacture of aqueous electrolytic bromine is mainly economic in that platinum plated titanium is used in construction of electrolysis cells which operate with a typical bromide to bromine conversion efficiency of just 35%.

Green Biocide Delivery System

Given the advantages of bromine use for cooling water biological control, a project was started in 2001 to devise a cost effective electrolysis based delivery technology to make aqueous electrolytic bromine on-site, an initial patent application was filed in May, 2002.



Containerless Graphite Electrolysis Cell

The project resulted in development of a new delivery technology to produce aqueous electrolytic bromine on-site from a non-hazardous precursor bromide salt solution. The process is based on a unique containerless electrolytic cell constructed of impregnated electrolytic graphite, which is much lower cost than existing design electrolysis cells. A second innovation is use of a mixed solution of sodium bromide and chloride salts to obtain a high conversion rate from bromide ion to electrolytic bromine.

Both liquid and solid separate and mixed precursor salt products have been registered with the USEPA as biocides and the electrolytic units are manufactured in a USEPA registered facility.

Electrolytic bromine produced by the new cell design has been determined to be an aqueous mixture of bromine, hypobromous acid, and hypobromite produced by electrolysis of a minimum 1:2 molar ratio of sodium bromide and sodium chloride according to the following equations:

1. $2\ H_2O + 2\ e^- = 2\ OH^- + H_2$
2. $2\ Cl^- = Cl_2 + 2\ e^-$
3. Cl2 + 2Br - = **2Br** + 2Cl- (bromine)
4. $2\ H_2O + Cl_2 = HClO^- + HCl + H_2O$
5. HClO- + Br- = **HBrO-** + Cl- (hypobromous acid)
6. 2 Br- = **Br_2** + 2 e- (bromine)
7. 2 OH- + Br2 = **BrO-** + Br- (hypobromite)
8. $2HCl + 2\ e^- = H_2 + 2Cl^-$

Note that the Cl- and Br- recycle back to equations 2, 3, 5, and 6, increasing the reaction efficiency for bromide conversion to oxidizing species to about 85% at a 1:2 molar ratio of bromide to chloride, increasing to almost 100% at a 1:3 ratio. Hydrogen gas is the primary byproduct.

Health and Safety

The oral toxicities of the two salts used in the electrolysis process, sodium bromide at 3500 mg/kg and sodium chloride (table salt) at 3000 mg/kg, are far higher than any other biocides, making them for practical purposes nontoxic as to worker and public exposure. Aqueous salt solutions are, of course, even less toxic due to dilution.

As the electrolytic bromine solution produced by the process is made "as needed" and immediately fed into the cooling tower water, there is essentially no worker exposure to the oxidizing product, minimizing health and safety risks. To put the potential toxicity hazard of the produced electrolytic bromine solution into a common prospective, household bleach is a highly alkaline, pH > 13.5, 5% sodium hypochlorite solution, the active product produced by the electrolysis process is a mildly alkaline, pH < 10.0, 0.8% aqueous electrolytic bromine solution. At the design 0.8% oxidizer content, the output of the electrolysis cell is below the OSHA hazardous designation level of 1.0% for oxidizers.

Environmental

First considering precursor spills, solid sodium bromide and chloride salts and their aqueous solutions, these materials have very high aquatic toxicity values and present very little danger of environmental damage due to accidental discharges as compared to other biocides. For instance, a 40% sodium bromide solution has a 96 hr LC 50 of > 1000 ppm for rainbow trout as compared to 1.5% isothiazolin at 0.14 ppm.

The recommended dose of electrolytic bromine for typical cooling waters is 0.5 to 1.0 ppm measured as total bromine. Following a dose, the electrolytic bromine normally degrades to harmless bromide ion, present in sea water at 65 ppm, in one to two hours.
Many cooling tower controllers can be programmed to “lock out” blowdown during, and for a set time after, a biocide feed event. By proper programming of the cooling tower controller, any discharge of electrolytic bromine in cooling water blowdown can oftentimes be avoided.

In some cooling systems, due to makeup water characteristics or specific thermal requirements, it may be impossible to lock out blowdown for the required time to degrade the electrolytic bromine, in which case an appropriate feed of a reducing agent, such as sodium sulfite, into the blowdown can be used to destroy the residual biocide. However, considering that typical sanitary wastewater is highly reducing, discharge of electrolytic bromine treated cooling water blowdown to sanitary sewers will not present a problem unless the blowdown flow is a very significant portion of the total flow to the receiving POTW.

Economics
Capital cost for the new electrolytic bromine units is generally about 30% of the cost of equal capacity units based upon containerized, platinum plated titanium electrode technology. For cooling water biocide use, we have commercialized units in outputs ranging from 1 to 30 lb/day as bromine. A one (1) pound a day unit would usually be suitable for cooling towers with a thermal capacity up to 500 tons and cost about $1300. A thirty (30) pound a day unit is currently in service at a 90 MW power station, approximately 37,700 tons thermal load, with a selling price of $22,000.

Comparison of the cost to operate the new electrolysis process, as shown in the following table for a cooling tower in terms of $/1000 gallons of cooling water treated, shows that it provides a substantial operating cost reduction over many commonly used biocides.

Product	Dose – mg/l	lb/1000 gallons	$/lb product	$/1000 gallon
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
electrolytic bromine	28 *	0.23	1.05	0.24

* as liquid precursor, 12.7% Br
Power cost to operate the electrolytic process is minor, at $0.10/kwh the power cost calculates as $0.17/lb bromine, or $0.04/1000 gallons cooling water treated, jumping the total cost to $0.28.

Proven Technology
Following six (6) 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. The first three units installed, two in Pennsylvania and one in Indiana, are still operating. A paper at the 2004 International Water Conference in Pittsburgh reports upon a one year demonstration where chlorine gas use as a biocide was totally replaced by electrolytic bromine at an 1100 MW power station.

Of great interest was that the operating cost for this installation, using separate salt solution feeds, was determined to be the same as chlorine gas, making the electrolytic bromine process a very economical alternative technology.

Given the environmental, health, and safety hazards presented by current biocide technology and the proven advantages of the new electrolysis process, we expect that electrolytic bromine will eventually become the biocide of choice.

Shown at left is a 30 lb/day bromine output unit, note the separate power supply, electrolysis cell, and salt solution delivery pump.

Case history reports and other referenced material, can be downloaded from the ProChemTech web site – www.prochemtech.com

The electrolytic bromine process discussed is patent pending and has been commercialized under the trademark names ElectroBrom and MiniBrom by ProChemTech International, Inc.

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Speaker Biography: Timothy Keister, CWT, FAIC, has a B.Sc. in Ceramic Science, Pennsylvania State University, and was employed by Brockway Glass Company 1973 to 1986 as Section Head, Water/Wastewater. In 1987 founded ProChemTech International as a water management firm to provide innovative chemistry, equipment, and systems for the many economic, environmental, and technical problems resulting from process, boiler, and cooling use of water. Presently Chief Chemist/President of ProChemTech; Chairman, Brockway Area Sewerage Authority; AWT Certified Water Technologist; Technical Director, Little Toby Creek Watershed Association; Fellow of the American Institute of Chemists; senior member of the American Institute of Chemical Engineers; and member of Association of Water Technologists, Water Environment Federation, American Chemical Society, and American Society of Heating, Refrigerating, and Air Conditioning Engineers.