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"Use of Electrolytic Bromine as a Cooling Water Biocide"

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Abstract:
Use of traditional oxidizing and non-oxidizing biocides in treatment of cooling towers presents substantial problems to both the water treater and end user in the areas of health&safety, efficacy, cost, and environmental impact. On-site generation of electrolytic bromine can solve these problems, but general use of the technology has been stopped, to date, by the cost of the electrolytic generator unit and low bromide to bromine conversion efficiency.

With commercialization of the patent pending ElectroBrom Biocide System tm, a low cost electrolytic generator with a conversion efficiency greater than 95% is now available for cost effective use on cooling towers as small as 100 tons. We will discuss the theory behind the technology, method of unit sizing, chemical use calculations, and determination of system operating costs. Case history reports on four separate installations will be presented.

Introduction

While water is the best material for transfer of heat and use as an evaporative cooler, its use presents a biological control problem as warm water, with dissolved and suspended solids present, 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 an estimated 300,000 cooling towers located throughout the country. While these chemicals are often quite effective for biological control use, they have numerous health & safety, efficacy, cost, and environmental impact problems.

Health & Safety Problems

Transport, storage, and use of biocides significantly increases the risk of worker, and bystander, injury. Looking at some common oxidizers; chlorine forms an extremely toxic gas if accidentally released, sodium hypochlorite is a corrosive material which can release chlorine gas if mixed with acid, while mixture of sodium chlorite with any organic compound represents a significant risk of fire and explosion. As shown by the following table, many commonly used non-oxidizing biocides are quite toxic.

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

Efficacy

Due to economic and environmental reasons, cooling towers are today being operated at higher cycles than in the past which increases cooling water pH. Operation at high pH substantially reduces the efficacy of chlorine based biocides as the chlorine available to "react" with microorganisms decreases to 24% at a pH of 8.0, further decreasing to just 9% at a pH of 8.5. Current research has also shown that many heavily used non-oxidizing biocides are marginally effective against hazards such as Legionnaires' Disease.

In addition to these problems, the detention time of many cooling tower systems, especially the evaporative condensers favored for small HVAC systems, is insufficient for many common non-oxidizing biocides to obtain a good microorganism kill. A study in our own laboratory gave the following times required to obtain an acceptable decrease in initial ATP readings:

20% polyquat - 29 hours	1.5% isothiazolin - 29 hours
30% carbamate - 5 hours	15% glutaraldehyde - 5 hours

Cost

Some biocides, such as isothiazolin and glutaraldehyde, are supplied to the market by just one manufacturer, with the result that pricing is higher than products with multiple suppliers. In addition, increased USEPA regulatory activity has increased the cost for all biocide products.

Biocide use cost can be readily compared by construction of a table with average USEPA label usage rates and calculating the resultant use cost of each product. The following table compares some popular biocides via this method:

Product	Dose mg/l	lb/1000 gal	$/lb	$/1000 gal
20% polyquat	170	1.42	1.60	2.27
10% quat	200	1.67	1.10	1.84
30% carbamate	50	0.42	1.60	0.67
98% hydantoin	26	0.22	3.10	0.68
20% DBNPA	37.5	0.31	2.55	0.79
1.5% isothiazolin	127	1.06	1.95	2.07
15% glutaraldehyde	227.5	1.90	1.35	2.57
"stabilized bromine"	37.5	0.31	1.85	0.57
"electrolytic bromine"	14.4	0.12	1.60	0.19

Environmental Impact

Strong oxidizers such as chlorine, sodium hypochlorite, and sodium chlorite represent substantial risks due to accidents during transportation. Due to their high toxicity, spill of strong oxidizers into waterways during an accident can result in substantial environmental damage due to immediate fish kills and destruction of aquatic biota. In addition to being toxic to the user, most biocides are dangerous to aquatic life when either spilled or discharged in cooling tower blowdown. This problem is particularly significant with some slow to degrade non-oxidizing biocides such as those in the following table:

Product	CAS	LC 50 aquatic toxicity	
glutaraldehyde 25%	111-30-8	rainbow trout	56.2 ppm
		daphnia	16.9 ppm
isothiazolin 1.5%	26172-55-4 and 2682-20-4	rainbow trout	0.14 ppm
		daphnia	0.13 ppm
dithiocarbamate 30%	142-59-6 and 128-04-1	rainbow trout	0.10 ppm

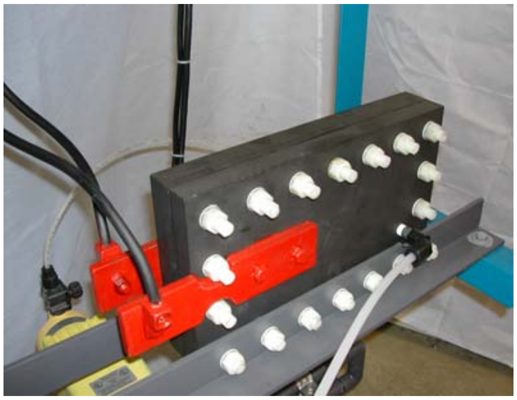
Electrolytic Bromine

Bromine, in its various delivery forms, has been recognized as an effective biological control agent in high pH cooling waters for many years. While effective, the existing delivery forms all suffer from various problems ranging from health and safety issues to simple high cost.

Given the advantages of bromine for biological control, we began to investigate making bromine on-site in 1995. Use of electrolysis was 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.

A major problem was that current electrolysis technology has a conversion efficiency of around 35%. While sodium bromide is not extremely costly, 35% conversion to active product was not economically viable. Our solution to this problem was to use a solution equimolar in bromide and chloride ions for electrolysis, chloride converted to chlorine in the electrolysis cell undergoes an immediate replacement reaction with any bromide present, forming bromine and returning to chloride. By means of this mixed salt solution, the bromide conversion efficiency was increased to a minimum of 95% at the cost of unused chloride, which is 1/6 the cost of bromide, in the produced biocidal solution. The following equations are the basis of our process:

1. $4\ H_2O + 4\ e^- = 4\ OH^- + 2H_2\ \hat{}$
2. $2\ Cl^- = 2\ Cl + 2\ e^-$
3. $2\ Br^- = 2\ Br + 2\ e^-$
4. $2\ OH^- + 2Br = BrO^- + Br^- + H_2O$ (Br^- recycles to 3.)
5. $2\ OH^- + 2Cl = ClO^- + Cl^- + H_2O$ (Cl^- recycles to 2.)
6. $ClO^- + Br^- = BrO^- + Cl^-$ (Cl^- recycles to 2.)



The cost of the electrolysis cell was another challenge as current cell construction technology, using precious metals, was much too expensive. After substantial experimentation, use of impregnated electrolytic graphite in a novel design electrolysis cell was discovered to provide the desired qualities of low cost with an acceptable cell life. A final patent application, dated May 30, 2003, has been filed for both the apparatus and process. USEPA primary registration of the precursor mixed salt solution as a pesticide was obtained in September, 2002.

Our studies show that generation of one (1) gram of bromine requires approximately one (1) amp-hr of direct current power input and that our impregnated graphite electrodes function well at a power density of one (1) amp per square inch and separation distance of 0.25 inch. These design specifications have been used to design a product line of electrolytic bromine generators with rated outputs from 1.3 to 90 lb/day as bromine. The units consist of a DC power supply, salt solution dilution/delivery, and the electrolysis cell. Produced bromine solution, actually a mixture of hypobomite and hypobromous acid at 0.8% total bromine content, is normally delivered as made directly to the system being treated.

Units are manufactured in two basic layouts, small units, less than 4.5 lb/day output, use a "day" tank where the mixed salt precursor, powder or liquid, is diluted with city water prior to being pumped through the electrolysis cell.

Large units have an automatic dilution system where either concentrated mixed salt liquid, or concentrate from brine tanks, is diluted with city water prior to passage through the electrolysis cell.

1.3 lb/day Br Output

4.5 lb/day Br Output

90 lb/day Br Output

Sizing of Electrolytic Bromine Units

For most cooling tower applications, electrolytic bromine units should be sized to provide a "slug" biocide dose resulting in a residual of 0.5 to 1.0 mg/l total bromine following unit operation for a maximum daily period of four (4) hours. For example, using an assumed bromine demand of 2 mg/l with a typical 1000 ton HVAC cooling tower the calculations are as follows:

system volume = 1000 tons x 5 gal/ton = 5000 gallons/1,000,000 = 0.005 mg
bromine dose = (1 mg/l + 2 mg/l) x 0.005 mg x 8.345 = 0.125 lb Br per dose
0.125 lb Br /4 hr = 0.03 lb Br/hr x 24 hr/day = 0.75 lb/day Br, = minimum generator size

Thus our 1.3 lb/day unit would be suitable with a run time of :

0.125 lb/dose/1.3 lb/day x 24 hr/day = 2.3 hours

Chemical Use Calculation

For the small units, we normally use a "day" tank installation diluting either the concentrated liquid, or dry, mixed salts. Continuing our above example and using the liquid product, which is 17.3 % bromine:

product needed/dose = 0.125 lb Br/0.173 = 0.72 lb product/dose
as the mix ratio of liquid product to water is 1 gallon to twenty five gallons, our day tank usage can be calculated as:

volume product use = 0.72 lb product/10.9 lb/gallon = 0.07 gal/dose
0.07 gal/dose x 25/1 dilution = 1.75 gal diluted product/dose

Using a standard two doses/week we find that our diluted product usage is:

1.75 gal x 2 dose/week x 4 weeks/month = 14 gallons/month, thus a 30 gallon day tank would give about two months between product makedowns

Determination of Operating Costs

Again using our 1000 ton HVAC cooling tower, monthly chemical use is:

0.72 lb product/dose x 2 dose/week x 4 weeks/month = 5.76 lb product/month

at our list price of $1.60/lb, in 50 lb containers, this gives a monthly chemical cost of:
5.76 lb/month x $1.60/lb = $9.22

We sell the 1.3 lb/day electrolytic bromine units for $1300.00, so assuming an amortization period of three (3) years, the monthly equipment cost calculates as $36.11.

Power, which is a very minor cost, is provided "free" by the customer, so the operating cost of the example installation is $45.33/month.

For comparison purposes, we have assumed the above cooling tower treated with a classic alternating oxidizing/non-oxidizing biocide program using bromo hydantoin and glutaraldehyde with two doses/week. Using our previous cost table to minimize calculations, we find that the chemical cost of this program is:

hydantoin = 5000 gal x $0.68/1000 gal = $3.40/dose
glutaraldehyde = 5000 gal x $2.57/1000 gal = $12.85/dose

monthly chemical cost = ($3.40 + $12.85) x 4 = $65.00/month

The equipment for such a program would normally consist of one chemical pump and one tablet feeder. Using our internal pricing for such units, we obtain an equipment cost of $700.00 which when amortized over three (3) years gives a monthly cost of $19.44. Again, with the customer providing "free" power, our total operating cost comes to $84.44/month, in comparison to the electrolytic bromine unit at $45.33/month.

Case Histories

Our first electrolytic bromine system was installed in November, 2002, and there are currently more than 40 active installations across the country. The following case history studies are intended to provide a cross section of these installations, from very large to small, and uses of the technology to solve some specific problems.

Power Plant

A large coal fired electrical power station in southern Indiana historically used chlorine gas for control of biological growth in two cooling tower systems serving 531.5 MW and 565 MW steam turbine generators. Due to the increasing restrictions on use of chlorine gas by the USEPA, DHS, and OSHA; the station desired to convert to an alternative, "non-hazardous" biocide program.

Control of biological growth in both cooling systems with chlorine gas was judged to be acceptable using four slug doses per day. System specifications are:

	Unit 3	Unit 4
flow rate, gpm	171,560	190,330
system volume, gal	1,870,000	1,650,000
makeup rate, gpm	7,533	7,133
delta T, deg F	33	33

condenser tube metallurgy 304 stainless steel

makeup water quality	average	minimum	maximum
pH	7.98	7.54	8.38
conductivity	318	156	520
suspended solids	118	7	1048
total hardness	206	111	362
total alkalinity	128	71	233

Unit 4 Cooling Tower

The two cooling tower systems are normally operated at 4 cycles with addition of 0.75 mg/l HEDPA phosphonate and sulfuric acid addition to control cycled cooling water pH to 8.2 su.

Makeup water is taken directly from the White River with no pretreatment.

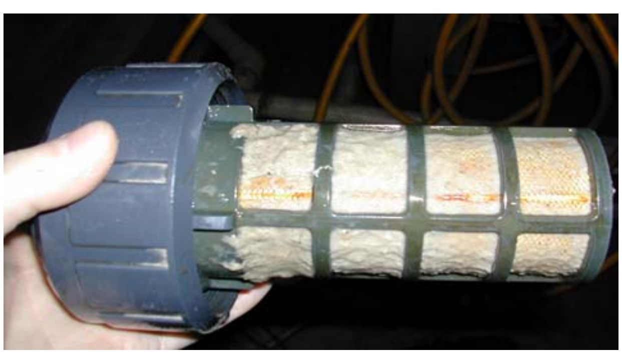
We proposed replacement of the gas chlorine system with an electrolytic bromine system consisting of a 90 lb/day unit equipped with a brine tank for sodium chloride supply, tote feed of stabilized sodium bromide, and a product accumulation tank to supply their existing dose system. This large electrolytic bromine system was installed and started up in March, 2004, and was the subject of an IWC paper in October, 2004.

Comparison of baseline chlorine and electrolytic bromine results using a fouling monitor, dip slides, and ATP testing; showed that the electrolytic bromine process produced biological control results equal to, or better, than the previous use of chlorine gas. Use of on site produced sodium chloride solution also resulted in a total operating cost equal to that obtained with gas chlorine.

Problem System

A northwest Pennsylvania lumber mill installed an advanced vacuum kiln drying system to decrease the time needed to process dimensional hardwood from months to weeks. The system exposes the hardwood to a vacuum while heating it to 50 C using hot water coils within the wood stacks. Water seal vacuum pumps, drawing through a water cooled condenser, are used to evacuate the kilns. Cooling water, recirculated from a 75 ton counterflow cooling tower, supplies the condenser and vacuum pump water.

Following start-up, an extreme biofouling problem developed. Another water management firm attempted to treat the problem by continuous feed of DETA II biodispersant and large multiple weekly slug doses of polyquat, DBNPA, and stabilized bromine. In spite of this treatment program; in-line filters, condensers, and the cooling tower fill would become plugged with bio slime in as little as one week.



This plugging caused major problems as the equipment had to be disassembled and manually cleaned. The rapid biofouling is due to the low vapor point organics, good bionutrients, drawn from the drying wood and introduced into the cooling water via the vacuum pump.

Following review of the system, we recommended that the four biological control chemicals be replaced by a 4.5 lb/day capacity electrolytic bromine unit using our mixed salt solution as the precursor. This was accomplished in August, 2003.

Typical makeup and cooling water data at start-up for this system were:

Parameter	Makeup	Cooling Tower
pH	8.3	8.2
total alkalinity	130	370
conductivity	569	1713
calcium as Ca	29.8	59.0
magnesium as Mg	9.7	21.6
silicon as Si	4.0	10.0
chloride as Cl	110	322
sulfate as SO4	22	100
total phosphate as PO4	0.75	26.2
suspended solids		32
total hardness CaCO3	114	236

Biological control, with the electrolytic bromine unit replacing the four noted products, has been excellent. ATP test data from monthly service calls shows high levels, up to 17,718 rlu immediately after start-up, dropping to a long term mean of 1070 rlu.

Industrial Installation

A large sintered metal parts plant in northwest Pennsylvania has historically suffered oil contamination of the 2000 ton capacity plant cooling tower system due to leakage from shell and tube heat exchangers used to cool hydraulic forming presses. In an effort to control microbiological growth resulting from this oil contamination, we installed a chlorine dioxide generator system in 1996.

While the chlorine dioxide was successful in controlling the microbiological problem, it created new problems due to the hazards of safely handling and using chlorite and chlorine dioxide solutions. In one accident, a plant employee was hospitalized for a week due to respiratory problems resulting from inhalation of chlorine dioxide fumes.

Following development of the electrolytic bromine system, we recommended that the chlorine dioxide system be replaced with a 4.5 lb/day capacity unit as a health and safety upgrade. A unit was subsequently installed and started up on August 18, 2003.

Biological control, with electrolytic bromine replacing chlorine dioxide, has been judged to be visually the same, or better. This observational data has been verified by routine ATP test data from monthly service calls. A mean ATP of 362 rlu, std. dev. of 238, was obtained when operating with chlorine dioxide. The data when operating with the electrolytic bromine unit shows a mean of 298 rlu, std. dev. of 114.

The following corrosion coupon results were obtained during operation with the two different biocide programs;

	chlorine dioxide	electrolytic bromine
mild steel	1.24 mil/yr	0.94
copper	0.01 mil/yr	0.01
brass	0.06 mil/yr	0.07

This corrosion coupon data shows that the excellent corrosion control at this plant, soft water makeup, when operating with chlorine dioxide has been maintained after conversion to electrolytic bromine.

HVAC Installation

A Phoenix, AZ, primary school became concerned about use of toxic chemical biocides (carbamate and polyquat) in their 400 ton cross flow HVAC cooling tower system due to the potential for student exposure. Our proposal for a demonstration electrolytic bromine system was accepted and the unit was installed in September, 2004.

Typical analytical data two months following start-up for this system were:

Parameter	Makeup	Cooling Tower
pH	7.9	8.8
total alkalinity	135	715
conductivity	611	4810
calcium as Ca	22.1	220
magnesium as Mg	23.8	171
silicon as Si	10	35.8
chloride as Cl	98	758
sulfate as SO4	39	662
total phosphate as PO4	0.36	14.4
suspended solids		< 1
total hardness CaCO3	153	1254

This being our first electrolytic bromine system in a high sunlight area with "open" cross flow cooling towers, we were surprised that control of algae, even at high bromine doses, was a problem. On examination, the problem appears to be that the produced bromine is rapidly inactivated, converted back to bromide, by action of sunlight, and thus is not available for a sufficient time in the cooling tower to destroy all the algae.

Given that an almost identical installation at a neighboring school using our stabilized liquid bromine product was getting good results, we modified the electrolytic bromine process to produce a stabilized end product. In the case of this installation, the change simply involved addition of a stabilized sulfamate solution to the day tank whenever the mixed salt solution is madedown. While the additional product adds about 20% onto the chemical operating cost of the process, it is still less costly than use of a stabilized liquid bromine product.

Based on our routine visual inspections, modification of the electrolytic bromine process by addition of a stabilizer to the bromine as produced has solved the algae problem presented by cooling towers receiving intense sunlight.

Conclusions

Based on our experience over the past three years, we have reached the following conclusions concerning use of electrolytic bromine as a cooling water biocide:

- it is an inherently safe technology, no hazardous chemicals are used

- it has good efficacy in contaminated, high pH, and short detention time systems

- lower cost than most other biocide technology

- little or no adverse environmental impact

- now field proven technology

Bio: Timothy Keister, CWT, holds a B.Sc. in Ceramic Science from PSU and is a Fellow of the American Institute of Chemists, senior member of the American Institute of Chemical Engineers, member of the American Chemical Society, Water Environment Federation, and American Society of Heating, Refrigerating, and Air Conditioning Engineers. He is presently the President and Chief Chemist at ProChemTech International and has over thirty years experience in the water management field.