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Electrolytic Bromine: A Greener Biocide

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Green Introduction

The word “green” is today being applied to more and more products in commerce and generally indicates that the product so designated has superior attributes from the environmental standpoint. In the cooling water management business, we are seeing “green” applied to a number of different products; non-chemical devices claim to be green as their use eliminates discharge of “hazardous” chemicals to the environment, solid feed products claim to be green due to reduced potential for hazardous chemical spills, while at least one biocide is claimed to be “greener” than others due to reduced product toxicity.

Given the obvious commercial appeal of calling your product green in today’s marketplace, an independent definition of “green” is needed. Our friends at the USEPA have kindly provided their view point by using the definition in “The Twelve Principles of Green Chemistry”[1]. Review of this document shows that several of these principals can be applied to typical AWT member firms as follows:

- Design safer chemicals and products
- Use renewable feedstocks
- Design chemicals and products to degrade after use
- Minimize the potential for accidents

The other eight principals, involved with chemical manufacture, do not apply to the majority of AWT members as we generally do not make active product ingredients, such as polymers and phosphonates.

The USGBC LEED program also impacts the cooling water management business as LEED certification, a recognized green designation, considers water use reduction, innovative wastewater technologies, rapidly renewable materials, indoor chemical and pollutant source control, controllability of systems, and innovation in design[2] .

In addition to these recognized green definitions, green products are generally expected to address depletion of resources, pollution of the environment, and worker health and safety. In the cooling water management field, use of toxic chemicals, biocides, to control micro-organism growth in cooling towers presents the greatest opportunity to “go green”.

Current Technology

Cooling water management is concerned about control of corrosion, scale, deposition, and microorganism growth in cooling systems. When the typical actives[3] used in cooling water management programs are reviewed as to their conformance with the noted green criteria, we find that biocides, used for control of microorganism growth, are the least green product(s) used in treatment of cooling towers. Biocides used are hazardous, toxic chemicals such as chlorine, ozone, chlorine dioxide, dithiocarbamate,

HVAC Cooling Towers

isothiazolin, hydantoin, and glutaraldehyde; which are routinely added to cooling towers to control micro-organisms by killing them. While these biocides are often quite effective, their use represents substantial environmental, health and safety concerns given that there are over 300,000 cooling towers in the United States using an estimated 40 million pounds of such chemicals on an annual basis.

Due to different modes of toxicity, biocide products are generally classed as either oxidizing, which kill the target microorganisms by oxidation of the cellular structure, or non-oxidizing, which operate by various means to upset the internal metabolism and/or structure of microorganisms sufficiently to kill them.

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[4].

Biocide Product	CAS	LC 50 aquatic toxicity		Typical Dosage
glutaraldehyde 25%	111-30-8	rainbow trout daphnia	56.2 ppm 16.9 ppm	130 to 650 ppm
isothiazolin 1.5%	26172-55-4	rainbow trout daphnia	0.14 ppm 0.13 ppm	35 to 883 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 daphnia	1.6 ppm 0.47 ppm	5 to 315 ppm
tetrakishydroxymethyl phosphonium sulftate 20%	55566-30-8	rainbow trout daphnia	446 ppm 71 ppm	130 to 525 ppm

Cooling towers, being basically evaporative coolers, increase cooling water solids content rapidly with the result that routine blowdown is required to prevent scale formation. 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, if any, in use.

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

Health and Safety Problems

Use of toxic biocides is commonplace 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. This widespread use of toxic biocide chemicals represents a significant hazard in shipping, storage, and handling as to operating personnel health and safety.

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 explode when mixed with many organic materials, such as sawdust or even flour.

The non-oxidizing biocides in common use represent a substantial worker hazard due to toxicity, with several of the products being readily absorbed through the skin. The following table summarizes some relevant toxicity data on six chemicals commonly used as cooling water biocides[5].

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
tetrakishydroxymethyl phosphonium sulftate	55566-30-8	431 mg/kg

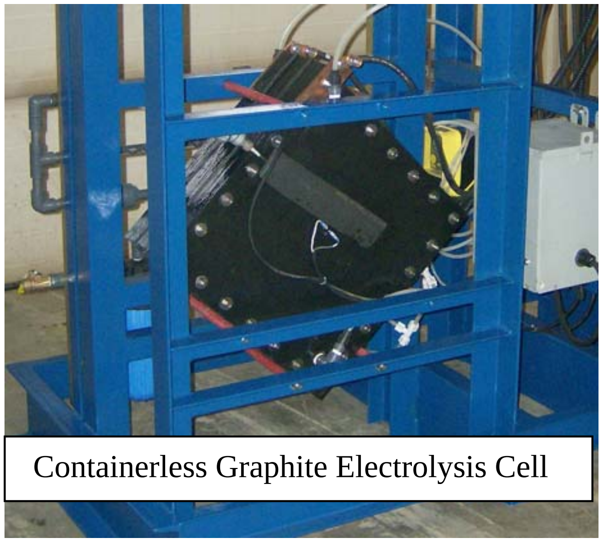
Smaller users, which represent the majority of cooling tower operators, represent a special worker safety concern since cooling water treatment, and application of biocides, is often the responsibility of workers not trained in handling of toxic chemicals. A non-hazardous biocide technology would constitute a green technology by reducing this concern.

"Green" Biocide Delivery System

Bromine, an oxidizing biocide, in its various delivery methods has been recognized as a superior cooling water biocide for many years. As bromine can be easily recovered from sea water, its use presents no issues as to depletion of the resource, unlike many other biocides which are based upon petrochemicals for their manufacture.

Unfortunately, the generally used delivery methods for bromine all suffer from the same environmental, health, and safety issues as other oxidizers. 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[6].

The problem with existing electrolysis technology for production of aqueous electrolytic bromine is 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%.


Containerless Graphite Electrolysis Cell

Given the advantages using bromine for cooling water microorganism control, a project was started in 2001 to devise a cost effective electrolysis based delivery technology to make aqueous electrolytic bromine on-site. This project resulted in development of a new delivery technology [7] 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[8], **which is much lower cost than existing electrolysis cells.** A second innovation is use of a mixed solution of sodium bromide and chloride salts to obtain an 85+% conversion of bromide ion to bromine. Both liquid and solid mixed precursor salt products have been registered with the USEPA as biocides and the electrolytic units are manufactured in a USEPA registered facility.

The "electrolytic bromine" produced by the new cell design has been determined to be an aqueous mixture of bromine, hypobromous acid, and hypobromite which is produced by electrolysis of a minimum 1:2 molar ratio of sodium bromide and sodium chloride with the following reactions taking place in the electrolysis cell:

1. $2\ H_2O + 2\ e^- = 2\ OH^- + H_2$
2. $2\ Cl^- = Cl_2 + 2\ e^-$
3. $Cl2 + 2Br^- = \mathbf{2Br} + 2Cl^-$ (bromine)
4. $H_2O + Cl_2 = HClO + HCl$
5. $HClO + Br^- = HBrO + Cl^-$ (hypobromous acid)
6. $2\ Br^- = \mathbf{Br_2} + 2\ e^-$ (bromine)
7. $H_2O + Br_2 = \mathbf{HBrO} + HBr$ (hypobromous acid)
8. $HBrOr \leftrightarrow \mathbf{OBr^-} + H^+$ (hypobromite) pH dependent

Note that the Cl and Br ions 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, along with some increase in alkalinity, and at the levels produced is safely disposed of via dilution by discharge of the electrolytic bromine solution into the cooling tower.

Environmental Impact

The recommended dose of electrolytic bromine for typical cooling waters is 0.5 to 1.0 mg/l measured as total bromine. Following a dose, the bromine degrades to harmless bromide ion, as found in sea water at 65 mg/l, in a short time period. A recent experiment in an operating cooling tower equipped with an electrolytic bromine unit showed that 45 minutes of unit operation were required to reach the control level of 0.5 mg/l bromine. Following shutdown of the unit, bromine level in the cooling water was monitored and returned to non-detectable within one hour. As many cooling tower controllers can be programmed to “lock out” blowdown during, and for a set time after, a biocide feed event, any discharge of electrolytic bromine in cooling water blowdown can be totally avoided by simple controller programming.

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.

In addition, considering that typical sanitary wastewater is highly reducing, discharge of electrolytic bromine, an oxidizer, treated cooling water blowdown to sanitary sewers is not expected to present any problem unless the blowdown flow is a very significant portion of the total flow to the receiving POTW.

Health and Safety

As the electrolytic bromine solution produced by the process is made "as needed" and immediately fed into the cooling tower water, there is no potential for spills of highly toxic chemicals during transport, storage, and use; and essentially no worker exposure to any hazardous material, minimizing health and safety risks. At the design 0.8% oxidizer content, the output of the electrolysis cell is below the hazardous designation level of 1.0% for oxidizers as established by OSHA. Note that the maximum voltage used on the electrolysis cell is 12 volts DC, minimizing electrical safety concerns.

Green Economics

While it is great to have a green replacement for hazardous biocides, green is generally better if it is also cost effective. We have compared the cost for containerless graphite cell electrolytic bromine units to equal capacity platinum plated titanium units, generally the graphite units are 30% of the cost of equal capacity units. At the present time, we have commercialized this technology under the trademarks “ElectroBrom” and “MiniBrom”, with outputs ranging from 2.5 to 60 lb/day as bromine. A 2.5 pound a day unit would usually be suitable for cooling towers with a thermal capacity up to 1500 tons with a cost in the $3000 range. A thirty (30) pound a day unit suitable for about 15,000 tons thermal load costs in the range of $25,000.

Comparison of the cost to operate the containerless graphite cell 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[9]	\$/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 *	0.24	1.05	0.25

* 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 \$0.29.

Is It Green?

Considering electrolytic bromine as a biocide against the four USEPA green principals which generally apply to the water management field we find:

- **Design safer chemicals and products**: The precursor chemicals used to produce electrolytic bromine, sodium bromide and chloride, are substantially safer than any biocide in current use. Electrolytic bromine solution, while a potent biocide, is much safer to handle than other products as it is a low strength, aqueous solution and is only made on demand and immediately dosed, so there is little product subject to accidental spillage.

- **Use renewable feedstocks**: Ultimately, the sodium bromide and chloride used in the process return to the sea, which is a source of both compounds. For the ultimate “green” process, renewable power such as wind or solar, could be used to power the electrolytic reactions.

- **Design chemicals and products to degrade after use**: Electrolytic bromine rapidly degrades back to harmless salts after use.

- **Minimize potential for accidents:** As the precursor chemicals are non-hazardous and the electrolytic bromine is manufactured on demand and immediately dosed, the potential environmental and health and safety hazards associated with any type of accidental discharge is minimized.

Considering the USGBC LEED program, certification credits could awarded for use of electrolytic bromine as a cooling water biocide in the areas of renewable materials, indoor chemical and pollutant source control, controllability of systems, and innovative design.

Proven Technology

The first commercial containerless graphite electrolysis units were installed in June, 2003, and have proven to be a cost effective[10], reliable means of controlling the growth of microorganisms in cooling waters. Units are currently in operation on a variety of process and HVAC cooling towers in Pennsylvania, Ohio, Arizona, New Jersey, Florida, California, Maryland, Australia[11], and Indiana.

Case History #1
A large zinc and aluminum die casting plant in Western Pennsylvania was using over $300 per week worth of proprietary isothiazolin and glutaraldehyde based organic biocides to control biological growth in one 16,000 gallon volume cooling tower system, the “ZDCW” system. Even at this high biocide dosage, control was borderline; the cooling water was very turbid with a strong septic odor. Controlling biological growth in this system was difficult due to significant contamination from entry of die lube, which contains various surfactants and emulsified oils, into the cooling water. The following table summarizes typical analytical results obtained on makeup and cooling water samples from this system as operated with organic biocides.

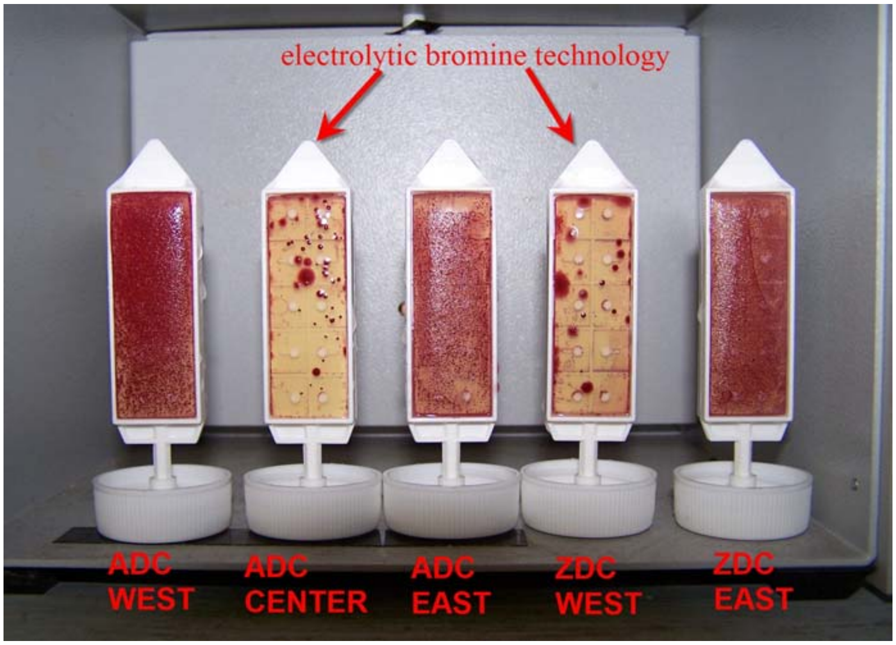
Parameter	Makeup Water	Cooling Water
pH	7.6	8.6
total alkalinity mg/l	245	590
conductivity mmhos	904	3000
calcium mg/l	0.05	38.9
magnesium mg/l	0.11	16.8
iron mg/l	<0.03	7.25
copper mg/l	<0.02	0.71
zinc mg/l	0.062	1.22
total phosphate mg/l	<0.15	15.8
ortho phosphate mg/l		3.12
chemical oxygen demand mg/l		5,416
suspended solids mg/l		400
ATP rlu		2,461
total oil/grease mg/l		266

The plant operators and management were not pleased with either the results or the cost of the biological control program on this, or any of the other four cooling towers in the plant.

It was suggested in March, 2007, that the organic biocides could be totally replaced by electrolytic bromine generated on-site. Based on sample results, a trial installation of a 4 lb/day as bromine capacity unit was proposed. The plant agreed to the proposal and a unit was delivered and installed with start-up around July 1, 2007. Use of organic biocides was totally discontinued and after some experimentation, the system was deemed to be in excellent biological control with a daily three hour dose of electrolytic bromine.

Results were deemed so good that a second electrolytic bromine unit was ordered for another 8,000 gallon volume cooling tower system, “ADCC”. This second unit, capable of generating 2.5 lb/day as bromine, was delivered and installed in early October, 2007.

Results
The cooling tower system operators run a weekly biological dip slide on each of the five installed cooling towers, the following picture was taken of the December 3, 2007, dip slides, which provide a good results comparison between the electrolytic bromine and organic biocide treated cooling tower systems. – photo provided by customer-



Concern has been expressed about increased corrosion rates from use of electrolytic bromine. To determine if there was any corrosion problem related to the first electrolytic bromine installation in the ZDCW system, a 95 day corrosion coupon study was carried out by the plant cooling system operators with the following results obtained:

steel C1010 – 0.23 mil/yr copper CDA 110 – 0.02 mil/yr brass CDA 260 – 0.01 mil/yr

These corrosion rates are considered to be excellent, showing that routine operation of the electrolytic bromine unit has not caused a high corrosion rate on common materials of construction.

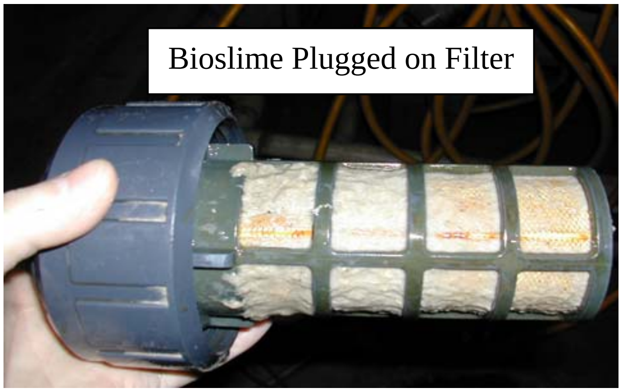
Total use of the electrolytic bromine precursor, from start-up through December, 31, 2007, totaled 1150 lbs. At a list price of $1.05/lb, the maximum cost for treating two systems for over three months was $1,207.50. In comparison, just the ZDCW cooling system would have consumed over $3,600 worth of organic biocides in the same time period, with poorer results.

Case History #2

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. A water seal vacuum pump, drawing through a water cooled condenser, is 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 use of a continuous feed of DETA II biodispersant and large multiple weekly slug doses of polyquat, DBNPA, and n,n,dibromosulfamate. 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, primarily easily biodegraded organic acids, which are drawn from the drying wood and introduced into the cooling water via the water seal vacuum pump.



Following our development of electrolytic bromine in 2003, it was recommended that the four biocide chemicals in use be replaced with a unit to produce 4.5 lb/day as bromine. On August 27, 2003, the use of the four biocide chemicals was discontinued and use of electrolytic bromine as the sole biocide started.

Results

Biological control, with electrolytic bromine replacing the four noted products, has been excellent. No downtime due to biofouling caused plugging problems has been reported through June, 2008.

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.

The following table summarizes analytical results from makeup (well water supply) and cooling water samples taken before and after use of electrolytic bromine as the sole biocide was started:

Parameter	Well 05/18/03	Tower 05/18/03	Well 02/01/05	Tower 02/01/05
pH	8.3	8.2	7.3	7.8
total alkalinity	130	370	105	145
conductivity	569	1713	502	1228
calcium	29.8	59.0	23.9	27.4
magnesium	9.7	21.6	8.88	10.2
iron	0.05	5.2	<0.03	1.2
copper	<0.02	0.15	<0.02	0.11
chloride	110	322	103	304
sulfate	22	100	18	25
molybdenum	-	14.1	-	12.5
total phosphate	0.75	26.2	<0.15	10.5
suspended solids	-	32	-	4

Given that this particular cooling water is considered to be highly corrosive due to the organic acids discharged into the cooling water via the drying kilns, corrosion coupon studies have been run on a routine 90 day cycle since start-up of the electrolytic bromine unit. The following results are the average of the latest six studies:

steel C1010 – 3.29 mil/yr copper CDA 110 – 0.17 mil/yr brass CDA 260 – 0.34 mil/yr

Conclusion

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 "green" biocide of choice[12].

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[1] Anastas and Warner, "Green Chemistry: Theory and Practice", Oxford University Press, New York, NY, 1998

[2] USGBC LEED for New Construction Version 2.2, June 26, 2007, USGBC

[3] Frayne, "Cooling Water Treatment Principals and Practice", Chemical Publishing Company, New York, NY, 1999

[4] Data obtained from USEPA required pesticide product labels for each product

[5] Data obtained from manufacturers' MSDS and/or product data sheets

[6] Mantel, "Industrial Electrochemistry", 3 rd edition, McGraw-Hill Book Company, New York, NY, 1950

[7] Keister and Gill, "Development of an On-site Hypobromite Generator", TP 04-15, Cooling Technology Institute, 2004

[8] "Flow Through Resin Impregnated Monolithic Graphite Electrode and Containerless Electrolytic Cell Comprising Same", US Patent Application 11/807,402, US Patent and Trademark Office, 10/25/07

[9] ProChemTech product list prices as of 06/15/08

[10] Lawler, Keister, and Teague, "Demonstration of an On-site Electrolytic Hypobromite Generator at a Power Station", IWC 04-19, International Water Conference, 2004

[11] Brooker and O'Rourke, "Development of a Cooling Treatment Program at Loy Yang B Power Station, API PowerChem, 05/08

[12] Keister, "Electrolytic Bromine: A Green Biocide for Cooling Towers", Water Environment Federation, 7/07

About the Author

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