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**"Development of an On-Site Hypobromite Generator"**

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**Introduction**

Water, due to its low cost and physical properties, is the best material for transfer of heat and use as an evaporative cooler. Unfortunately, warm water, with dissolved and suspended solids, is also an excellent medium for growth of microorganisms. The uncontrolled growth of microorganisms in recirculating cooling water systems can create several severe problems:

- increased risk of Legionnaires' disease
- plugging due to physical blockage of cooling water passages
- accelerated corrosion under biological masses
- reduced heat exchanger efficiency due to biofouling of surfaces

Decreasing supplies of fresh water and environmental regulations have placed increased pressure on industry to minimize water usage and wastewater discharge by increasing the concentration (cycles) at which cooling towers are operated and encouraging use of reclaimed wastewater as cooling tower makeup water. Operating at higher cycles, or with reclaimed wastewater as makeup, increases the solids and nutrient content of the cooling water, making the cooling water environment even more conducive to microbiological growth.

Current microbiological control programs rely upon various oxidizing and non-oxidizing biocides, which while often effective, have numerous problems such as high costs, corrosivity issues, health and safety concerns, security issues, environmental problems, selective effectiveness on an organism basis, and incompatibility with other chemical additives needed to operate cooling towers at higher cycles. These problems are expected to become of even more concern in the future due to higher cycle operation, reduced quality feedwater, and increased regulatory control.

Given the existing and anticipated problems with current biocide technology, we wondered if a better method for biological control could be devised.

A literature review showed that bromine was an excellent biocide; it is effective at low dosages and high water pH values, not as chemically reactive as chlorine, is effective against legionella, and has a lower vapor pressure than chlorine, ozone, and chlorine dioxide.

Bromine is currently used as a biocide with three common technologies for delivery to cooling water uses; on-site generation by mixing solutions of sodium hypochlorite and bromide, provision as a controlled reactivity hypobromite (CRB) solution, and as a solid bromated organic.

On-site generation by mixing solutions of sodium hypochlorite and sodium bromide is low cost and efficient. Major problems with the process include use of a regulated hazardous material, sodium hypochlorite; the excess alkalinity introduced into the cooling water due to the sodium hydroxide content of the hypochlorite; sodium hypochlorite corrosion and handling problems; and the rapid degradation of sodium hypochlorite in storage.

The CRB products do an excellent job, but present some problems of their own. All three products on the market are hazardous materials, chemical feed problems are common due to product outgassing, excess alkalinity is introduced into the cooling water due to the sodium hydroxide content of the products, and the products are more costly on a unit bromine delivered basis.

Bromated organics were developed to provide bromine in a concentrated, easy to handle package. While solid products are not as susceptible to spills and subsequent environmental contamination issues as liquids, handling and feeding of solid materials present unique problems not common to the water management business. In addition, bromated organics are listed as hazardous materials, there have been several instances where solid bromine feeders have exploded due to gas evolution, and the cost on a unit of bromine delivered is quite high.

Given the advantages presented by use of bromine as a biocide, we believed there was a need for a cost effective, non-hazardous bromine biocide delivery system. An investigation into making bromine on-site by electrolysis of sodium bromide solution was started in 1995. The use of electrolysis was appealing as sodium bromide solutions are non-hazardous and low cost, while the electrolysis process is used for industrial production of chlorine and bromine, so substantial literature existed to research.

The literature search showed that the major problems for an on-site unit would be low conversion efficiency, about 35%; the highly corrosive environment of the electrolytic cell; and the high cost of the cell itself, due to both the materials of construction and fabrication.

### Efficiency

Addressing the efficiency issue first, based on our experience in manufacturing CRB, we wondered if a little "chemical trickery" could be used to increase the conversion of bromide to bromine.

If an equimolar solution of sodium chloride and sodium bromide is subjected to electrolysis, we will have equal production of chlorine and bromine due to the equal probability that an electron would react with either a chloride or a bromide ion. The produced chlorine, however, would immediately react with any bromide present, converting it into bromine via a simple replacement reaction. This secondary replacement reaction taking place in the electrolysis solution can drive the conversion of bromide to bromine to almost 100% efficiency. While the non-converted sodium chloride does add cost to the process, chloride ion is about 1/6 the cost of bromide ion, so the increase in efficiency is obtained at a relatively low cost. The following chemical reactions summarize this process:

1.  $4 \text{ H}_2\text{O} + 4 \text{ e}^- = 4 \text{ OH}^- + 2\text{H}_2$
2.  $2 \text{ Cl}^- = 2\text{Cl} + 2 \text{ e}^-$
3.  $2 \text{ Br}^- = 2\text{Br} + 2 \text{ e}^-$
4.  $2 \text{ OH}^- + 2\text{Br} = \text{BrO}^- + \text{Br}^-$  (Br<sup>-</sup> recycles to 3.)
5.  $2 \text{ OH}^- + 2\text{Cl} = \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$  (Cl<sup>-</sup> recycles to 2.)
6.  $\text{ClO}^- + \text{Br}^- = \text{BrO}^- + \text{Cl}^-$  (Cl<sup>-</sup> recycles to 2.)

The only byproduct of this series of reactions is hydrogen gas, which is of some concern given its flammability. However, the actual amount produced is quite small at 0.05 lb hydrogen per pound of bromine produced. Our preferred method to dispose of produced hydrogen is to simply pipe the produced hypobromite solution from the electrolysis cell directly to the cooling tower basin, or to a hot cooling water return pipe, with the hydrogen subsequently being disposed of by evolution and simple dilution in the air flow through the cooling tower. An alternative method is to accumulate the produced hypobromite solution in a top vented holding tank, with the vent being to the atmosphere.

## Laboratory Experiments

We then moved to the laboratory to attack the many questions on design and construction of a cost effective unit. Specific major questions we needed to resolve were:

- electrode material
- electrode area and separation distance
- amperage per electrode area needed for a given bromine output
- voltage needed for electrolysis cell operation
- composition and concentration of the electrolysis solution

Our literature research had found a substantial amount of information on production of chlorine by electrolysis. This information suggested some reasonable starting points for our experiments: cell operation in the range of 3 to 4 volts, 1.3 amperes/square inch of electrode, and an electrolysis solution salt concentration of 2.8%.

For laboratory determination of these questions, we fashioned experimental cells, using various electrode materials, designed for easy variation of the distance between electrodes, with an electrode area of 1 sq inch when suspended in a 250 ml glass beaker with 200 ml of solution in it. Solution mixing during experiments was provided by a magnetic stirrer, with power for the electrodes supplied by a laboratory DC power unit with adjustable voltage and ampere settings.



## Laboratory Experimental Setup

Our first tests involved electrode material selection. Electrodes were fashioned of various resistant materials, such as Hastalloy G, titanium, and nickel. Most of these materials were found to corrode at high rates during operation of the cell. Platinum plated titanium (PtTi) was found to be suitable for continued research work, while electrode material evaluation continued.

Using the PtTi electrodes, one of our summer interns was employed for three months to determine the relationships between voltage, amperage, solution ionic strength, time, and produced bromine. This work resulted in experimental determination of many design variables such as the relationship between electrode separation and voltage at a constant amperage and solution composition.

Since the OSHA Hazard Communication Standard (HCS) program classifies oxidizer solutions above 1% active concentration as hazardous, we decided to design our unit to produce an electrolyzed bromine solution with 0.8% active as Br to avoid any HCS hazardous classification. With this key criteria in place, the results obtained by our summer intern can be summarized in the following design standards:

electrode power level = 1 ampere/sq in

bromine production = 2.25 gram/amp-hr

electrode distance = 0.25 inch

ionic strength of solution = 0.24 equivalents/l  
(20,500 mmhos)

average operating DC voltage = 6.0

The continued research on electrode materials during this time period resulted in the determination that electrolytic graphite was suitable, and much more cost effective, than the PtTi for construction of electrodes.

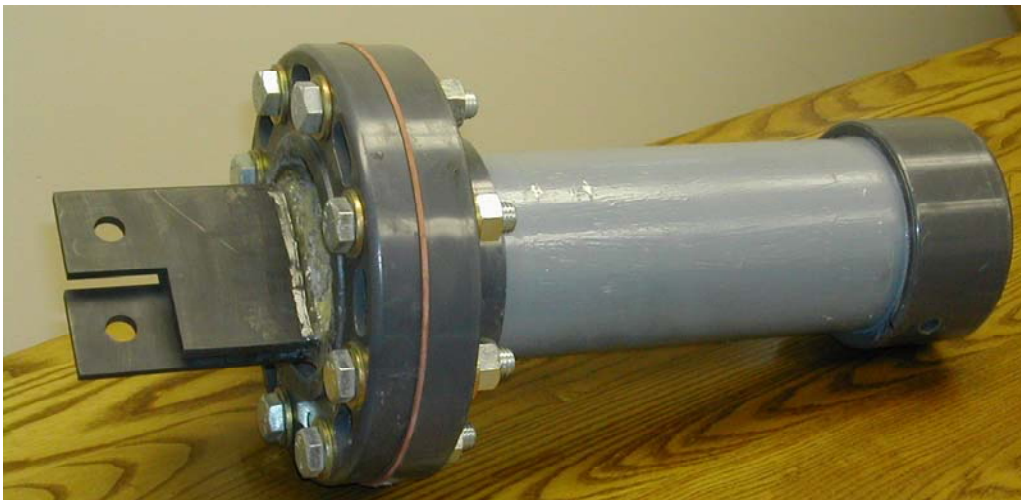
Since many cooling towers are less than 1000 tons capacity, we also decided to devise a "one drum" product for production of electrolysis solution on site by dilution. Starting with the requirement that the solution be equimolar in sodium chloride and sodium bromide, we found that the most concentrated solution that was stable consisted of 12.7% sodium chloride, 22.3% sodium bromide, and the balance water by weight. This solution, assigned our product number 3024, has since been registered as a primary biocide by the USEPA.

To obtain the desired ionic strength for the electrolysis solution of 0.24 equivalents/l, 3024 is typically diluted 1:24 with water.

### **Unit Design**

With the above design criteria and information in hand, we proceeded with design of the first full scale experimental electrolysis unit, target 5 lb/day output as chlorine. Power supply design was simple; we contracted with a power supply vender to build a 110 volt ac powered unit with an output of 0-100 amps at 0-12 volts DC. The amperage output was adjustable with the set current maintained ("constant current") and meters were provided for monitoring of both output voltage and amperage.

The first attempt at building a full size graphite electrolysis cell involved placing two electrolytic graphite electrodes, 18 inches long X 4 inches wide X 0.25 inch thick inside a section of 4 inch diameter PVC pipe. These electrodes were spaced 0.25 inch apart and exited the cell at one end through a modified blank flange. The other end of the pipe was closed with a pipe cap, and electrolysis solution was introduced and removed from the cell via 0.25 inch diameter holes placed at opposite diagonals of the electrodes.



First Design Electrolysis Cell

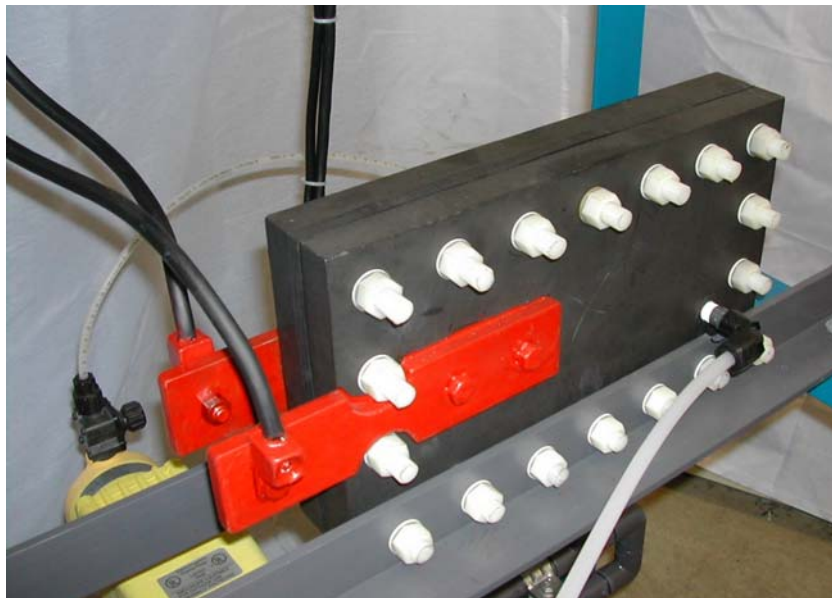
With the above electrolysis cell construction, the effective plate area was 68 sq inches giving a target power input of 68 amperes. Testing started at lower power levels, 20 amperes, with halogen obtained in line with the power input.

At about 40 amperes power input, a severe overheating problem on the electrodes became evident. The electrode area outside of the cell, a section 2 inches X 2 inches X 0.25 inches, was used for attachment of the power cables. When the power input exceeded 40 amperes, this section heated up, rapidly approaching boiling. This was clearly not acceptable.

We discussed the problem with our graphite plate supplier, who was pleased to inform us that exceeding 40 amperes per cubic inch converted the graphite into a resistance heater. Our electrode connection area had exactly one cubic inch of volume !

Another major problem with this electrolytic cell design was manufacturing related. It was very difficult to obtain a good, water tight seal in the area between the electrodes where they exited through the blank flange.

Given these problems, a new design was invented. We decided to use the graphite for both the electrodes and to form the cell itself! The design was simple, two graphite blocks, functioning as the electrodes, were drilled and assembled with a 0.25 inch Viton gasket between them to form the electrolysis cell. Drilled and tapped holes on the diagonal in the two blocks provided entry and exit for the electrolysis solution. Power was delivered by simply bolting copper bars to the side of each block, the power cables then being attached to the bars.



Second Design, "Block", Electrolysis Cell



Following assembly of the first "block" electrolysis cell, using 16" X 12" X 2" thickness graphite blocks giving a cell surface area of 96 square inches, we proceeded to testing. An immediate problem was evident in that the cell "wept"; electrolysis solution was passing right through the graphite !

We again contacted the graphite supplier and, after some discussion, it was decided to vacuum/pressure impregnate our two carbon blocks with a heat cured phenolic resin. This was accomplished and the reassembled cell subjected to testing again. At 80 psi pressure, no weeping or leakage of any kind was noted on the impregnated graphite block electrode assembly.

### **Results**

The first full scale experimental unit, designed to produce up to 5 lb/day bromine reported as chlorine, was finished August 23, 2002.



Full Scale Experimental Unit

We proceeded with operational testing, at various current levels, for a total on-line time of 236 hours through November 11, 2002.



The following data table is typical of the information collected during this time period.

Date: 11/08/02

Time	Power Input		Flow l/d	Effluent			
	Amps	Volts		Temp. C	pH	Cl mg/l	Cl lb/day
9:02 am	40	4.8	541	27.0	10.2	1,014	2.3
11:00 am	60	5.3	524	34.0	10.1	2,729	3.2
1:05 pm	80	6.0	536	40.0	10.3	3,191	3.8
3:00 pm	90	6.0	513	45.0	10.2	3,758	4.3

Comparison with the experimental design data for bromine production reported as chlorine, 1 gram/amp-hr, shows that production of the first full scale experimental unit was 80.3 gr/hr vers an experimental design value of 90 gr/hr running at 90 amp current input on 11/08/02.

Looking at bromide to bromine conversion efficiency on a typical day when unit operation was stabilized for several hours at one current input, 12/19/02, we recorded operating parameters of:

Current - 80 amps      Flow - 501 l/d      T. Cl - 3,545 mg/l  
 Voltage - 5.8      Temperature - 44 C      pH - 10.1  
 3024 feed rate - 4.9 gpd

The effluent bromine level calculates as 0.80% as Br, giving an output of 8.81 lb/day as Br. With an 3024 input of 4.9 gpd, the input of bromide as bromine was 9.24 lb/day, which when compared to the measured output, gives a conversion efficiency of 95.3%.

We then proceeded to operate the experimental 5 lb/day unit for a total of 617 hrs at the 80 amp current level to determine the amount of wear on the electrodes. On disassembly, we found that one electrode showed no appreciable wear, while the other was eroded, with an average material loss of 0.156 inch. It was noted that the area of the wear electrode adjacent to the inlet showed substantially less material loss.



### **Experimental Field Operations**

After resurfacing the eroded electrode, the experimental unit was reassembled and shipped to a customer plant for field evaluation on a glass plant recirculating cullet quench system, replacing a chlorine dioxide generator used for biological control. Plant personnel monitor this system twice a week using "bio-tab" paddles for total bacteria. With the chlorine dioxide generator, the cullet quench system had averaged 65,000,000 cfu/ml for the 17 samples taken just prior to the experimental unit installation. The average for the next 36 samples, running the experimental unit, was 65,000 cfu/ml, showing a substantial improvement in biological control.

One major problem became evident during this trial, scale formation within the electrolytic cell. The dilution water had an average hardness of 225 mg/l as calcium carbonate and formed scale due to the pH elevation resultant from the electrolysis reactions. This scale formation was so severe that the cell had to be taken apart and cleaned three times, due to complete plugging, during the five months it was operated on the cullet quench system. Use of either soft dilution water, or regular polarity reversal, was advanced as a "cure" for this problem.

While our initial thinking was to supply the electrolysis cells with softened dilution water, discussions with potential customers showed substantial resistance to the idea of having another unit process, water softening, involved. Polarity reversal was thus adopted as the preferred solution to hardness scale buildup within the electrolysis cell. A side benefit was that routine polarity reversal would also reduce electrode wear by splitting it across two surfaces instead of one.

Another problem was also shown by the scale caused plugging, overheating of the electrolysis cell due to loss of dilution water. Without the cooling provided by dilution water, the temperature of the electrolysis cell increased into the area of 80 to 90 C, warping the plastic angle structure supporting it and causing failure of input and output plastic plumbing. Since loss of dilution water could be expected on units in the future, this problem was addressed by addition of a temperature sensor to the cell assembly, which shuts down the unit at a set temperature.

With this information, and a history of safety problems with the chlorine dioxide generator, the customer elected to permanently replace the chlorine dioxide generator with the second commercial unit we produced.

### Commercial Units

Based on the results obtained by laboratory and field testing of the experimental unit, we have proceeded to develop commercial units in sizes from 2 to 40 lb/day output as chlorine. As shown in the following photo, these units are much smaller than the experimental unit.



Commercial Unit

Specifications for the commercial units are summarized as follows:

Model	Output Chlorine lb/day	Bromine lb/day	Power Use kwh	3024 Use lb/day	Water Use gal/day
EBG-2	2	4.5	7.6	26.8	61
EBG-5	5	11.25	19	64.6	152
EBG-10	10	22.5	38	130	303
EBG-20	20	45	76.4	260	606
EBG-40	40	90	153	520	1212

Using the USEPA label average dosages, we have calculated the following table to demonstrate the operating economics of a typical commercial unit installation compared to some common biocides on a \$/1000 water volume treated.

Biocide	Dose ppm	lb/1000 gal	\$/lb	\$/1000 gal
20% polyquat	170	1.42	2.30	3.27
30% carbamate	50	0.42	2.30	0.97
98% hydantoin	24	0.20	3.90	0.78
20% DBNPA	37.5	0.31	3.30	1.02
1.5% iso	127	1.06	3.25	3.44
15% glut	227.5	1.90	2.45	4.66
electro unit	6.0	0.29	0.75	0.22

note: Unit dosage shown as ppm bromine, allowance made for bromine demand of 5 ppm, 3024 price for 55 gallon drum.

As of the end of October, 2003, three commercial units have been in service for about three months each. Six additional units are under construction with shipping dates prior to the end of 2003.

Unit one, a 2 lb/day output unit, replaced a chlorine dioxide generator, due to safety concerns, on a 2000 ton cooling tower system at a sintered metal components plant. The system provides cooling for metal sintering furnaces, compressors, and hydraulic presses. The unit was set up to operate on a three days a week schedule with each operation event to obtain a final bromine residual in the cooling water of 0.5 mg/l. To date, biological control, based on ATP testing and visual observation, is deemed equal, or better, than that obtained with chlorine dioxide.

Unit two is the 5 lb/day output unit already noted as being installed on a glass plant recirculating cullet quench system to replace a chlorine dioxide unit. The commercial unit has continued to provide the superior biological control demonstrated in this application during the experimental unit field trial.

Unit three, a 2 lb/day output unit, was installed on a competitor treated 70 ton vacuum wood drying kiln cooling tower. Vacuum wood drying kilns, due to use of the cooling water in liquid seal vacuum pumps, have a very high loading of readily degraded organics from the drying wood. Biological control is extremely difficult to maintain on these systems and complete plugging of cooling tower fill with biological mass is common.

The competitive biological control program utilized continuous addition of DTEA II, a cationic material sold as a biodispersant; once a week addition of a 15% polyquat biocide; twice a week addition of a 5% DBNPA biocide; and three times a week addition of a CRB biocide. With this program, the customer had to routinely clean out heat exchangers and had plugged the tower

fill at least twice in the proceeding year.

With the unit set up to dose the system on a five day a week basis to a target of 0.5 mg/l bromine at the end of the dose, a substantial improvement in the system has been noted over the previous program.

### **Discussion**

The difference between expected bromine production and that actually obtained in the experimental and commercial units can be explained by noting that the full size electrode assemblies are not completely mixed due to the cell geometry and the probability that unknown side reactions are consuming some of the supplied current. Future work will examine the produced solution for other potential products of electrolysis, such as bromites and bromates.

Conversion efficiency has been found to range between 95 and 97% when operating the electrolysis cell at design current values. We consider this conversion efficiency range to be acceptable from a commercial standpoint.

Erosion of the electrode plates was not expected and results in decreased cell life. While the decrease in cell life is not prohibitive from a commercial application standpoint, maximum cell life is desired to minimize operation cost. We are investigating this problem from several points.

Our selection of a phenolic impregnating resin was likely not the best choice from the standpoint of chemical resistance since phenolic compounds are readily oxidized. We have since impregnated electrode blocks with both furan and epoxy polymers and are currently evaluating the performance of these resins for decreased erosion rate.

Plating of the active electrode surface, with a halogen resistant metal, such as silver, or a ceramic, such as ferrite, will also be investigated as a means of improving electrode life.

Operation of the electrolysis cell at a lower temperature, provided by increased dilution water flow, has been incorporated into the commercial design. The effect of this change on electrode life is presently being evaluated.

### **Conclusion**

An on-site hypobromite generator based on electrolysis of a mixed aqueous sodium bromide-chloride solution has been developed with a bromide-bromine conversion efficiency exceeding 95%. The major

design innovation is the use of impregnated graphite blocks to provide the electrode surfaces and form the electrolysis cell; which produces a low material cost, easy to manufacture electrolysis cell.

To date, limited operation of one experimental and three commercial units has demonstrated acceptable performance in actual plant systems.

An economic analysis shows that the units are quite competitive with common biocide technology in terms of \$/1000 gallons of water treated on an operational basis. The total economics for each installation will vary due to the cost of the electrolysis unit vers that of equipment needed for competing technologies. Limited comparison to date shows that the electrolysis technology is quite competitive on a total economic basis. To date, two commercial installations were approved based on safety considerations, while the third was on a combination of performance and cost.

The specific technology discussed is presently patent pending, preliminary application dated June 4, 2002, and final filing dated May 30, 2003. ProChemTech International, Inc., has commercialized this technology under the trade names "**ElectroBrom**" and "**MiniBrom**".

#### Biographic Information

Timothy Keister is presently the Chief Chemist/President of ProChemTech International, Inc. Prior to founding the company in 1987, he held the position of Section Head, Water/Wastewater Control, at the former Brockway Glass Company. A graduate of the Pennsylvania Sate University with a B.Sc. in Ceramic Science, he is an AWT Certified Water Technologist, elected Fellow of the American Institute of Chemists, senior member of both the American Institute of Chemical Engineers and American Chemical Society, and has presented papers at the Association of Water Technologies, International Water Conference, Water Environment Association, Association of Energy Engineers, New Mexico Environmental Health Association, and Metal Powder Industries Association.

Patrick H. Gill is presently the General Manager of the Performance Chemical Division of ProChemTech International, Inc. Prior to joining the company, he held several positions of

increasing responsibility at the former Calgon Corporation. A graduate of the Pennsylvania State University with a B.Sc. in Environmental Resource Management, he holds three patents and has presented papers at the Electric Power Research Institute, National Association of Corrosion Engineers, Cooling Technology Institute, and International Water Conference.