Demonstration of an On-site Electrolytic Hypobromite Generator at a Power Generation Station

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Abstract:
Gas chlorine has been economically used with acceptable results for control of microbiological growth in power station cooling towers for many years. Recent concerns related to security, designation of gas chlorine as an extremely hazardous substance under SARA Title III, and the pending proposal by the USEPA to make gas chlorine a restricted use pesticide; have generated considerable interest in gas chlorine replacements.

Following a review of possible alternatives, Indianapolis Power and Light Company (IPL), Petersburg, IN, an operating unit of AES, decided to undertake a full scale test of a recently developed, patent pending electrolytic process for on-site generation of hypobromite to replace chlorine gas used in the cooling towers serving 1100 MW of generation capacity. Prior to the trial being conducted, approximately thirty (30) days of baseline thermal and biological performance data was collected on the two cooling towers to be used in the test. Two electrolytic hypobromite units with a total generation capacity of 180 lb/day as bromine were subsequently installed and operated to totally replace the use of chlorine gas.

We will present details on IPL water quality and cooling tower specifications, hypobromite unit specifications, and review baseline and trial results to determine the efficacy and economics of the on-site hypobromite process as compared to gas chlorine.

Introduction

Indianapolis Power and Light Company (IPL), an operating unit of AES, operates a coal fired power generating station equipped with four boiler/generator units at Petersburg, IN. Units One and Two, 220 and 455 MW, utilize once through cooling water for condenser cooling. Units Three and Four, 531.5 and 565 MW, utilize two, separate cooling tower systems for condenser cooling.

IPL has historically used gas chlorine for control of biological fouling and growth in the two cooling tower systems, acceptable results were obtained with four, 30 minute doses/day per unit at a delivery of 84 lbs of gas chlorine per dose. Daily gas chlorine use for the two cooling towers thus averaged 672 lb/day, delivered via a vacuum eductor system drawing from one (1) ton cylinders.

Recent concerns with use of bulk gas chlorine related to security, designation of gas chlorine as an extremely hazardous substance under SARA Title III, and the proposal by the USEPA to make gas chlorine a restricted use pesticide; prompted IPL to evaluate other means for control of biological fouling and growth in the two cooling tower systems. Following review of several alternatives such as hypochlorite, hypochlorite and sodium bromide, stabilized bromine solution, and hydantoin; the decision was reached to test a full scale on-site hypobromite generation system, the "ElectroBrom Biocide System", developed by ProChemTech International, Inc.

The primary reasons for the decision to use the on-site hypobromite system were:

- no hazardous materials are used or produced by operation of the system

- projected operating costs, while about three (3) times higher than gas chlorine, were expected to equal hypochlorite and be lower than the other alternatives

- hypochlorite systems are generally known to be high maintenance items

Hypobromite Generator Theory and Practice

Bromine is generally accepted to be an effective oxidizing biocide, especially at cooling water pH levels above 7.0 where chlorine loses much of its efficacy. One means of obtaining bromine is via on-site electrolysis of an aqueous sodium bromide solution, which is non-hazardous and relatively low cost. The major problem with electrolysis of sodium bromide solution to produce a hypobromite solution is a low bromide to bromine conversion efficiency, about 35%, which makes operation of such a process quite costly in terms of delivered bromine.

The new on-site electrolytic process obtains lower cost operation due to a bromide to bromine conversion efficiency exceeding 95%. This increase in conversion to the desired end product is obtained by use of an equimolar aqueous solution of sodium bromide and chloride.

When such a solution is subjected to electrolysis at a direct current power input of one ampere per square inch of electrode area, an equal production of chlorine and bromine is obtained due to the equal probability that an electron will react with either a chloride or a bromide ion.

The produced chlorine, however, immediately reacts with any bromide present, converting it into bromine via a simple replacement reaction. This secondary replacement reaction taking place in the electrolysis solution drives the conversion rate of bromide to bromine to over 95%.

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 equations summarize the process:

1. $4\ H_2O + 4\ e^- = 4\ OH^- + 2H_2$

2. $2\ Cl^- = 2Cl + 2\ e^-$

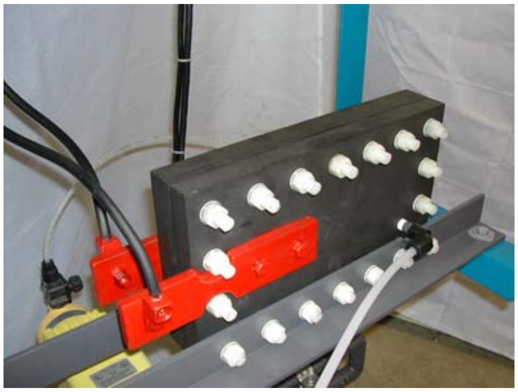
3. $2\ Br^- = 2Br + 2\ e^-$

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 only byproduct from 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. The 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.



The design of the electrolysis cell is unique in that it is constructed of impregnated graphite blocks, which form both the electrodes and the cell itself. A complete cell consists of two graphite blocks, which are drilled and assembled with a 0.25 inch Viton gasket between them to form the container for the electrolysis solution. Drilled and tapped holes on the diagonal in the blocks provide entry and exit for the electrolysis solution. Power is delivered by copper bars bolted to the side of each block, the power cables are then attached to the bars. The picture shows an 11.25 lb/day as bromine output electrolysis cell.

Direct current power to drive the electrolysis reaction is provided by use of a step down transformer, bridge rectifier, and power control circuit.

The power control circuit is of the "constant current" design, maintaining a set current so as to compensate for reasonable changes in electrolysis solution temperature and conductivity produced by variations in sodium bromide and chloride brines, dilution water, and ambient temperature. Automatic polarity reversal and use of an antiscalant in the electrolysis solution prevents scale formation in the electrolysis cell and product piping.

Larger output cells are constructed using a "bipolar" design, with a third electrode in the center of the assembly. This effectively makes two cells in one assembly, doubling the output over the two electrode design. Typical operating parameters for the on-site electrolytic hypobromite generators are:

cell voltage	3 to 12 volts DC
cell amperage	1 ampere/sq in of electrode surface
electrode separation distance	0.25 inch
ionic strength of electrolysis solution	0.24 equivalents/l (20,500 mmhos)
bromine production	2.25 grams/amp-hr

Petersburg Station Installation

The coal fired Units 3 and 4 of the IPL Petersburg, IN, station are rated 531.5 MW and 565 MW respectively. Makeup water for the two cross flow, mechanical draft cooling towers used for condenser cooling is drawn directly from the White River with no pretreatment. The following is an annual average analysis, with min/max range, of the makeup water used:

Parameter	Value	Min	Max
pH, su	7.98	7.54	8.38
conductivity, mmhos	318	156	520
suspended solids, mg/l	118	7	1048
calcium, mg/l as $CaCO_3$	145	76	241
total hardness, mg/l as $CaCO_3$	206	111	362
total alkalinity, mg/l as $CaCO_3$	128	71	233

Specifications for the Unit 3 and 4 condensers and cooling towers are as follows:

Parameter	Unit 3	Unit 4
Power Rating, MW	531.5	565
Recirculation pump capacity, gpm	171,560	194,000
Condenser design	single pass	single pass
Condenser area, sq ft	309,000	297,034
Tubes	7/8" OD	7/8" OD
Tube material	304 SS	304 SS
Water velocity , fps low pressure	8.0	8.7
fps high pressure	6.9	7.4

	Unit 3	Unit 4
Auxiliary cooling flow, gpm	13,000	12,900
Cooling tower (CT) design	cross flow mechanical draft 14 cells	cross flow mechanical draft 13 cells
CT recirculation rate, gpm	171,560	190,330
CT water volume, gallons	1,870,000	1,650,000
CT water makeup, gpm	7,533	7,133
CT delta T, degrees F	33.0	28.0
CT cycles	4.0	4.0

Sulfuric acid is added to the cooling tower basins to maintain the cooling water pH at a target level of 8.2 su. HEDPA phosphonate is maintained at a level of 0.75 mg/l in both cooling towers as a scale inhibitor.

The electrolytic hypobromite generator installation at the Petersburg station was designed to replace 672 lb/day of gas chlorine. The design calculations considered the loss of 50% of the chlorine to the chlorine-water hydrolysis reaction and the relative biological availability of bromine to chlorine at higher pH values. For the calculations, a pH of 8.0 was utilized with availability of bromine at 83% and chlorine at 24%. These calculations indicated that an electrolytic system capable of providing about 180 lb/day as bromine would be sufficient to replace the gas chlorine.

For operation at a bromine generation rate of 180 lb/day, 580 lb/day of 40% sodium bromide solution, 132 lb/day of sodium chloride, 2,426 gallons of dilution water, and 438 kwh of power; would be used. Please note that use of an on-site sodium chloride brine maker was included to reduce the chemical operating cost for the electrolytic system.

The actual system supplied consisted of two Model EBG-40 units, total combined output of 180 lb/day, feeding into a 1000 gallon capacity accumulation tank. Sodium bromide solution, 40%, was supplied via tote delivery while a saturated sodium chloride solution was made on-site using a supplied brine maker to take advantage of the low cost salt, $0.048/lb, at the station. Sodium bromide and chloride solutions are delivered to the dilution water stream by two separate chemical feed pumps, allowing adjustment in the ratio of the two salts to optimize unit operation. The eight daily "doses", an initial total of 2,696 gallons per day, were delivered to the cooling towers from the accumulation tank using a pump and the existing gas chlorine piping system.

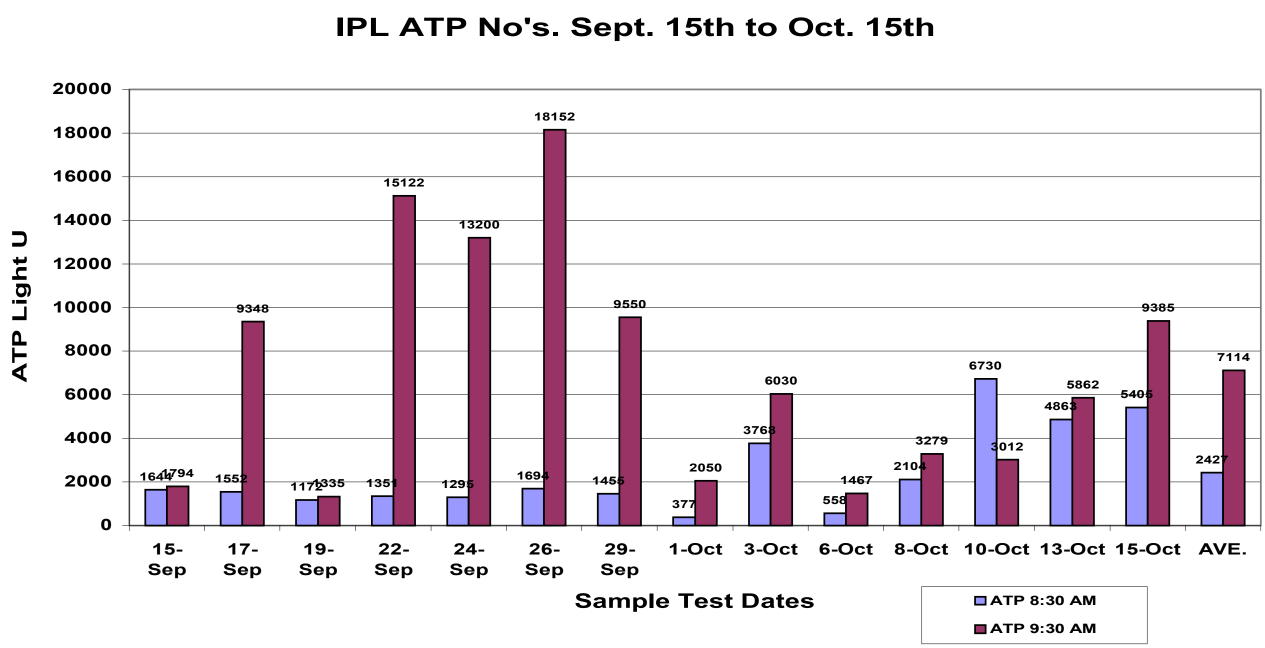
The accumulation tank was equipped with level controls to cycle the two electrolytic generators so as to maintain sufficient electrolysis product for the dosing cycle.

The "footprint" of the system as designed was approximately 19' 6" by 8' 6", please note attached drawings CP 644 and 645 for the equipment layout and process schematic.

Prior to installation of the electrolytic hypobromite system, a Bridger Scientific DATS II Fouling Monitor (DATS) was installed to monitor thermal performance data on the condenser cooling water. This fouling monitor consists of a heat source installed on a small section of heat exchanger tube with temperature probes to measure cooling water and heat source temperatures, and a flow rate meter to monitor cooling water flow through the heat exchanger tube. The unit automatically calculates resistance to heat flow in terms of (hr-sq-ft F)/btu. System setup variables are heat input and flow rate through the test heat exchanger.

In addition to the fouling monitor data, biological dip slides and ATP testing of the condenser water, both prior and post, dose events were undertaken.

Baseline Chlorine Results
Baseline fouling data, dip slides, and ATP biological testing of the condenser discharge water from Unit 3 were undertaken from September 15 to October 15, 2003, on the "morning" chlorine dose. The following chart summarizes the ATP results obtained



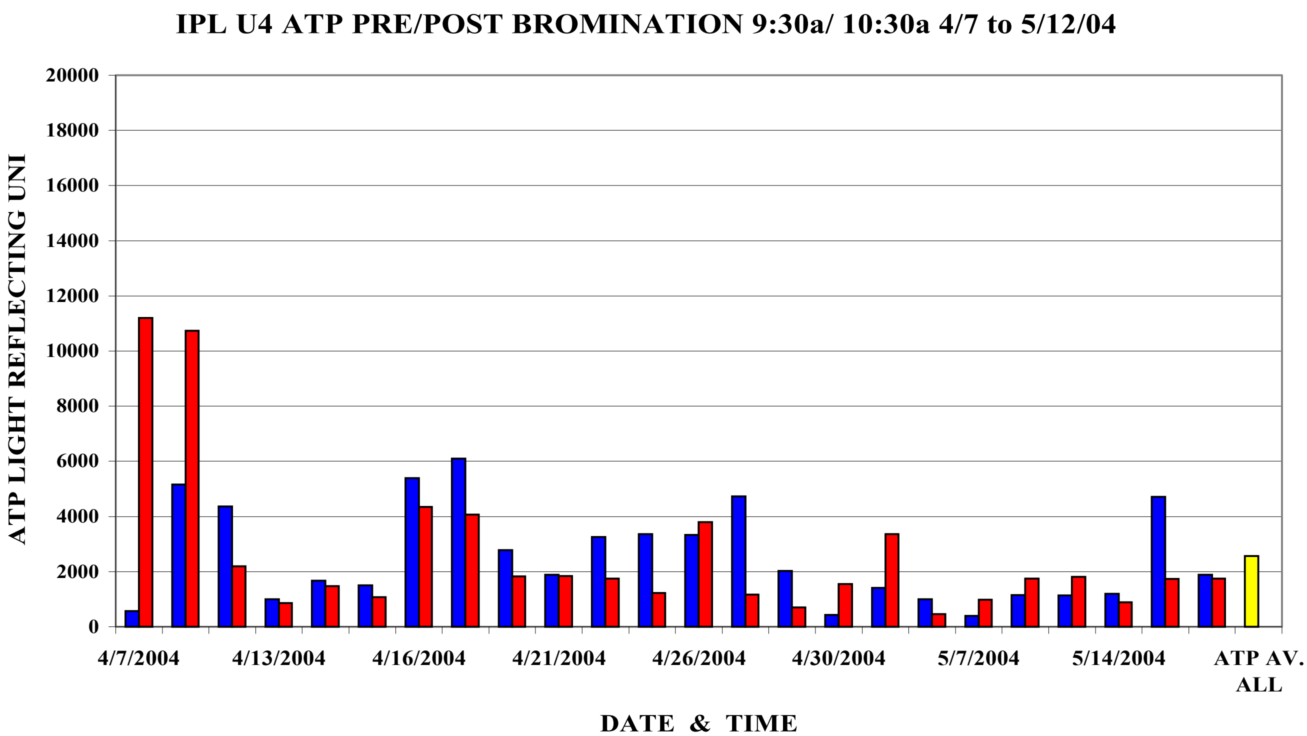
before (8:30 am - blue) and after (9:30 am - red) the dose.

Dip slide testing produced daily readings which averaged 1,000 cfu/ml.

DATS results showed thermal resistance readings which varied from 0.00083 to 0.00097 hr-sq-ft-F/btu.

Hypobromite Results

Following system installation and a short test run of the electrolytic hypobromite generators in February, 2004; continuous operations were started in April, 2004. Fouling data, dip slides, and ATP biological testing of the condenser discharge water from Unit 4 were undertaken from April 7 to May 14 , 2004, on the "morning" hypobromite dose. The following chart summarizes the ATP results obtained before (8:30 am - blue) and after (9:30 am - red) the dose.



Dip slide testing again produced daily readings which averaged 1,000 cfu/ml.

DATS results showed thermal resistance readings which varied from 0.00085 to 0.00089 hr-sq-ft-F/btu.

Optimization work during continued hypobromite generator use has since reduced the amount of electrolysis product dosed from the start-up amount of 2,696 gal/day to the present level, as of August 10, 2004, of just 320 gal/day. This reduction in use has been accomplished with no appreciable increase in ATP levels, dip slide results, or thermal resistance readings, as compared to the values obtained during the initial 30 day start-up period. At this level of electrolysis product usage, a single on-site hypobromite generator is sufficient to produce the entire daily requirement.

Discussion of Data

Two items are immediately evident on comparison of the chlorine and hypobromite data:

- The average ATP values while using chlorine were considerably higher, both before and after dosing, than with use of hypobromite.

We believe that this difference is a good indication that the on-site produced hypobromite is much more effective than chlorine as a biocide in the IPL cooling towers. The initial high ATP readings obtained during the first few hypobromite doses, followed by a significant decrease and continued low readings, clearly demonstrates the superior efficacy of a bromine based biocide in a high pH system.

- The average difference between the ATP before and after dose values while using chlorine, 4687, is much higher than the average difference found, 86 , when the hypobromite was in use. Of note is that the hypobromite difference is low enough to be considered to be within the error range of the test method and thus no difference is present.

As an increase in ATP results immediately following a biocide dose is generally taken to indicate removal of biofilm, the large average difference obtained with chlorine indicates that substantial biofilm was accumulating between dose events and then being removed. The lack of any difference when using hypobromite, coupled with the initial large difference changing to no difference and lack of any increase in heat transfer resistance, is a good indication that little, or no, biofilm was forming between doses when using hypobromite. It is believed that this effect is due to a residual biocidal effect present with use of hypobromite but lacking with chlorine.

The biological dip slide results from the chlorine and hypobromite evaluation periods are virtually identical.

As with the biological dip slide results, the thermal resistance readings do not show any significant average difference between use of chlorine and hypobromite during the evaluation periods. We would note that loss of biocide feed, with either chlorine or hypobromite, appeared to cause an increase in the thermal resistance reading within 24 hours.

Economics

Looking at economics, we find that the chemical cost for gas chlorine use was about $134/day, with chlorine at $0.20/lb. The cost to operate the hypobromite generator in the initial test period calculates to $473/day, including the $63/day rental of the on-site hypobromite generator system. The substantial decrease in hypobomite feed obtained during continued operations has reduced this cost to $136/day, making the hypobromite process economically cost competitive with gas chlorine.

Conclusion

The on-site electrolytic generation of hypobromite has been shown to provide biological control results equal to, or better than, gas chlorine. At this specific installation, optimization of the hypobromite application has resulted in an operating cost very close to that previously obtained with gas chlorine.