Cooling Tower
Water Conservation &
Chemical Treatment Elimination
12/28/11

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H-O-H Water Technology's "Green Machine", has Generated Significant Resource Savings, Eliminated Traditional Chemistry, Reduced Chemical Hazards & Pollution, & Is Poised to Significantly Reduce National Use of Energy. New Complimentary Technology Now Permits Broader Efficacy & Efficiency

1 *2011 - <u>H-O-H Water Technology, Inc. Milestones</u>:*

a. Incorporation of boron doped, ultrananocrystalline diamond (BD-UNCD) technology to carryout electrochemical reactions at substantially higher overpotential to produce much higher yields of hydroxide free radical and other reactive oxygen species. This innovation permits more efficient oxidation of native chloride to free-chlorine/hypochlorite, and substantially greater in-situ oxidation of organic contaminants, thus removing nutrients that support microbiological activity thus extending the capabilities of H-O-H's Green Machine (GM) cooling water treatment process.

b. Academic study conducted to show the effectiveness of H-O-H's Electrochemical Precipitation Technology (*Green Machine, GM*) in controlling cooling water microbiology. Testing conducted at the Special Pathogens Laboratory (SPL), University of Pittsburg.

2 H-O-H Water Technology, Inc. *Status*:

H-O-H Water Technology is a small business with 78 employees and annual sales of less than 40 million dollars.

3 *Focus Areas*, *Use of greener reaction conditions:*

a. *Primary*: - Greener Reaction Conditions – in-situ electrochemistry used to eliminate hazardous & polluting chemicals to significantly improve cooling tower resource & operating efficiency.

b. *Secondary*: - Much less toxic than current cooling water treatment strategies; inherently safer regarding accident and spill potential, safer and less burdensome for atmosphere and aquatic discharge.

4 Current design and product development of Electrochemical Precipitation Technology for treating cooling tower water is the sole product of work conducted by H-O-H Water Technology, Inc. Application of BD-UNCD technology is the result of collaboration with Advanced Diamond Technologies, Inc, Romeoville, IL. Primary research to develop BD-UNCD vapor deposition was carried out at Argonne National Laboratory, Lamont, IL.

Over 3,000 cooling tower systems use electrochemical precipitation technology world-wide to control scaling due to calcium carbonate formation. Approximately 500 cooling systems in the United States use electrolytic treatment to prevent mineral deposition, scaling of heat exchangers and problematic sludge formation.

H-O-H Water Technology has previously presented on the electrochemical mechanisms that control troublesome calcium carbonate deposits throughout cooling water systems. This work was presented at the ASHRAE 2009 Winter Conference; Palmer House Hilton, Chicago, Illinois, January 27, 2009. Presentations before ASHRAE, FEW, Cooling Technology Institute (CTI), Electrochemical Society, and others have endeavored to establish this technology using clearly delineated physical-chemical and engineering principles mimicking municipal & industrial calcium removal by traditional "*Cold Lime Softening*".

5 *Abstract*:

Properly engineered electrolytic extraction of calcium carbonate from recirculating cooling water has successfully controlled deposit formation on heat exchange and other surfaces in practical systems such as industrial and HVAC cooling tower systems. Electrolysis of ionic-rich water produces exploitable in-situ chemistry requiring no external chemical reagent other than electricity. A *Green Machine* consists of a series of steel tubes that are made the cathodic element of an electrolytic cell where water is reduced to form molecular hydrogen and hydroxide ion, and calcium carbonate is subsequently made to accumulate. Centered in each tube typically is a titanium rod coated with a mixture of ruthenium and iridium oxides, and made the anode of the electrolytic cell. The common name for an anode of this type is "dimensionally stable anode", or DSA. It is the coating of the anode that is critical in driving the oxidation of water to produce molecular oxygen, hydrogen ion and higher oxygen species such as hydroxyl free radical & ozone. DSA technology allows for the efficient splitting of water at a low practical voltage potential above that theoretically required, the difference being termed overpotential. DSA's have been responsible for past Green Machine success. Supplementing DSA's with anodes coated with boron doped, ultrananocrystalline diamond (BD-UNCD) now allows not only control over troublesome calcium carbonate deposition, but more efficient in-situ chlorine formation and degradation of organic contaminants. Microbiological control in cooling water is significantly more efficient.

6 Executive Summary:

Industrial and HVAC cooling towers evaporate water to move heat to the atmosphere. These systems use roughly 5 trillion gallons of water annually in the US by EPA estimate. The energetic aqueous environment created presents four significant challenges to sustained efficient operation; mineral scaling, corrosion, biological activity and water conservation. Control measures rely on chemicals specific to each problem. Organic, phosphorous-containing scale inhibitors and polymeric dispersants dramatically slow calcium carbonate formation (kinetics modification) and minimize crystal adhesion. Acid or salt based ion-exchange remove individual constituent of calcium carbonate. Various inorganic and organic compounds are used to minimize corrosion and oxidizing and non-oxidizing biocides control algae, slime and organisms supportive of corrosion. Additionally, biocides are used in certain cases to control organisms representing public health issues such as Legionella.

Cooling tower bleedoff transports organics captured from the atmosphere along with organic chemical treatment additives to waste streams and eventually to the environment in the form of BOD & COD; some of which is easily decomposed biochemically, and some of which is not (refractory).

Treatment of refractory organic contaminants using green chemistry: *Electrochemical advanced oxidation based on boron-doped BD-UNCD electrodes*

Water containing refractory organic contaminants requires the use of oxidants with higher oxidizing potential than provided by commonly used disinfectants such as chlorine, bromine or ozone to effect breakdown. Additionally, some reaction mechanism, environment or system is needed to provide efficient contact between the oxidizing agent and the refractory organic. The common characteristic of the specific treatment methods to date, known as Advanced Oxidation Processes (AOPs), is the production hydroxyl radicals, which oxidize efficiently these organic species [1]. Most AOPs in use today rely on the use of hydrogen peroxide combined with UV, other chemicals (Ozone), or catalysts (Fentons) to generate hydroxyls in situ. All of these approaches suffer from high costs or the extensive use of reagents that give rise to problems associated with hazardous waste handling and disposal. Over the past few years the electrochemical (reagent free) production of hydroxyls using boron-doped diamond (BDD) anodes has gained a great deal of attention and has shown superior performance in the oxidative destruction of a broad range of refractory wastes and is set to emerge as an alternative AOP technology for a number of applications [2]. In addition, the production of hydroxyls on the BDD surface can in turn be used to generate a number of other oxidants suitable for water remediation, including hydrogen peroxide, ozone, and peroxodisulfate.

Boron-doped diamond has a high overpotential for oxygen evolution, in contrast to traditional DSA anodes. This high overpotential can allow substantially greater formation of the active hydroxyl radical (OH°) directly from water, according to the following reaction

$$H_2O \rightarrow HO° + H^+ + e- \qquad (1)$$

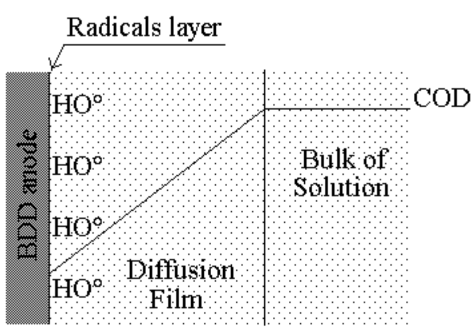


Fig. 1. Heterogeneous advanced oxidation process on the BDD anode.

As Fig. 1 indicates, organic species that reach the anodic surface can be oxidized by electro-generated hydroxyl radicals. The degradation rate of organics by these hydroxyl radicals is very fast, and the reaction take place in a thin film close to the anode surface. This process is heterogeneous in nature, and consequently it is subject to mass transfer limitations. As the oxidation of the organic species on the BDD anode surface involves hydroxyl radicals, the treatment can be considered as an electrochemical AOP.

BDD anodes can also oxidize compounds via direct electron transfer at the electrode surface and by hydroxyl radicals produced via water oxidation, such as perflorinated oxisulfinates (PFOS) [3]. Additionally, BDD cathodes have demonstrated structurally selective reduction of organic compounds thought to occur by charge transfer on the electrode surface [4]. The combination of target compound destruction at both the anode and cathode during electrochemical treatment provides an additional mechanism for compound removal over traditional AOPs. BDD electrodes are also resistant to fouling by redox active metals and do not need pre-conditioning prior to use.

In the diamond research community it is well known that using diamond as an electrode material has several advantages over other electrode materials for this application but the cost and poor lifetimes exhibited by incumbent technologies have greatly inhibited the adoption of this technology. Interest in the use of UNCD for organic destruction resides in whether its unique materials properties will provide longer lasting, better performing electrodes that can offer a significant cost/performance advantage over incumbent technologies. Advanced Diamond Technologies, Inc. executed a Phase I NSF SBIR project that addressed both these issues and the results were particularly encouraging. In particular, operational current densities were achieved that open up the possibility of replacing DSA (dimensionally stable electrodes) with UNCD electrodes for OSG (on-site generation) of concentrated solutions of advanced oxidants (hydrogen peroxide, persulfate, ozone)--a much more cost-effect means of water treatment compared to in-line processing of water for disinfection and remediation applications. This opens up the possibility of addressing numerous applications from disinfection of cooling-tower waters to remediation of recalcitrant waste waters generated during oil refining.

Destruction of low concentration refractory organics using EAOP based on diamond electrodes is challenging due to mass transport limitations. However, the unique capabilities of UNCD technology to support high current density operation results in an alternative approach, the electro-synthesis of green oxidants in high concentrations suitable for direct treatment of refractory waste waters. For instance, hydroxyl radicals produced on BD-UNCD surface can react with sulfate to form the corresponding peroxide (eq. 2):

$$2HO^\circ + 2HSO_4^- \rightarrow S_2O_8^{2-} + H_2O \qquad (2)$$

These peroxides are relatively stable and can be produced at high concentration in an appropriate electrolyte without any problem of mass transport limitation. The treatment of the wastewater would occur in a separate chemical reactor.

In the reactor, the peroxide is activated thermally, catalytically (e.g. iron for persulfate) or with UV radiation to produce hydroxyl radicals that oxidize the organic pollutants. This is similar to existing AOP except that the peroxide is generated on site using EAOP. The combination of local production of the peroxide and the subsequent AOP step avoids the mass transfer limitation of the direct electrochemical wastewater treatment.
Peroxides like hydrogen peroxide, ozone, percarbonate and peroxodisulfate can be produced efficiently with the use of the BDD anode. The first two oxidants are normally used in AOPs,

while peroxodisulfate, despite its superior characteristics, has not been sufficiently considered for this kind of process. Via the use of a non-electro-active supporting electrolyte ($HClO_4$), hydrogen peroxide [6], ozone [7,8] and oxygen are easily produced on the BDD anode. The hydrogen peroxide production is due to the recombination of two hydroxyl radicals (eq. 21.8) that are just formed by water discharge, according to eq. 3:

$$2HO° \rightarrow H_2O_2 \qquad (3)$$

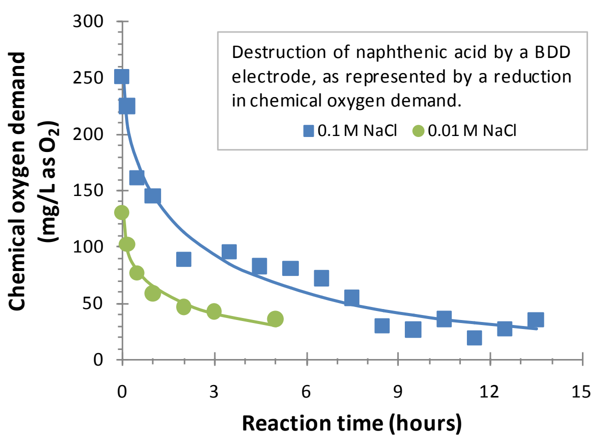
while the ozone production is due to the following reactions:

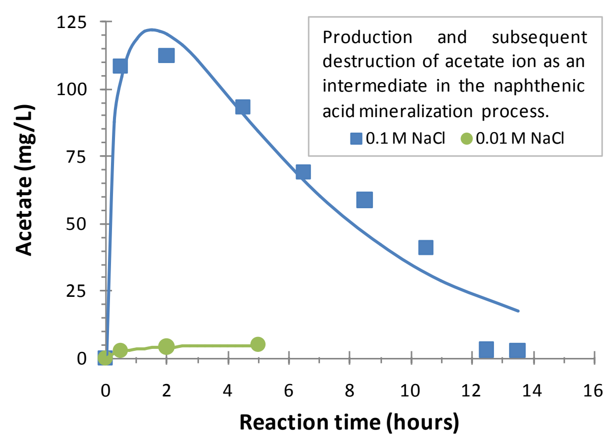
$$HO° \rightarrow O° + H^+ + e- \qquad (4)$$
$$2O° \rightarrow O_2 \qquad (5)$$
$$O° + O_2 \rightarrow O_3 \qquad (6)$$

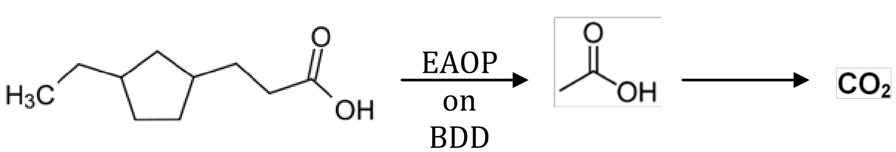
Ozone and hydrogen peroxide in the electrolyte increase linearly with the applied current density. Using concentrated sulfuric acid peroxodisulfate is efficiently produced on BDD anodes (current efficiency > 90%):

$$2HO° + 2HSO_4^- \rightarrow S_2O_8^{2-} + H_2O \qquad (7)$$

In summary BDD anodes can be used for both in-line processing of waste water and the direct oxidation of contaminants via hydroxyl radicals on the surface of the diamond anodes, or the *in situ* production of strong oxidants, which can be activated in a separate chemical reactor in order to produce active hydroxyl radicals for the oxidation of organic pollutants. UNCD technology enables both these approaches by supporting the high current density & electrode lifetimes needed to make these approaches economically viable.







naphthenic acid acetate & others carbon dioxide

Cooling Tower Study Shows First "Green" Nonchemical Device to Control Bacteria in Water

(Edited – follow link for full text)

Cooling tower operators wanting to rely less on chemicals to treat water-based air conditioning systems may have an environmentally friendly alternative. A "green" nonchemical device (NCD) reduced bacterial growth, including Legionella (the bacterium that causes Legionnaires' disease) according to a recent study by Special Pathogens Laboratory and the University of Pittsburgh. PITTSBURGH Pa., August 7—Cooling tower operators wanting to rely less on chemicals to treat water-based air conditioning systems may have an environmentally friendly alternative. A "green" nonchemical device (NCD) reduced bacterial growth, including Legionella (the bacterium that causes Legionnaires' disease), according to a recent study by Special Pathogens Laboratory and the University of Pittsburgh. The positive results come on the heels of a previous NCD study funded by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE). Researchers, Janet E. Stout, PhD, Director of Special Pathogens Laboratory, and Radisav D. Vidic, PhD, the William Kepler Whiteford Professor and chair of Civil and Environmental Engineering at Pitt's Swanson's School of Engineering, tested five different types of NCDs from different manufacturers in model cooling towers.

The ASHRAE study found that none of the NCDs (pulsed electric-field, ultrasonic, hydrodynamic cavitation, magnetic) prevented bacteria from growing in the water-cooling systems. In fact, most produced the same or more bacteria as found in untreated water. In this recent study, Stout and Vidic tested a "green machine," a mechanical water treatment device that relies on an electrolytic process to improve cooling tower performance (H-O-H Water Technology). This NCD was evaluated using the same methodology as the ASHRAE study. The results showed that the device removed hardness and alkalinity from the cooling water, and was 100 times more effective in reducing bacteria in the model cooling tower compared to control, and more effective than all previously tested NCDs.

"The H-O-H device is the first device among the NCDs we've tested that showed a bactericidal effect," says Stout, who is also a research associate professor in civil and environmental engineering at the Swanson school. "The results also support our scientific method of using model cooling towers to evaluate water treatment devices." According to Stout, "We observed a 1.9 log greater reduction in the total bacteria (HPC) counts in bulk water, and a 2.3 log reduction in Legionella. This data suggests that the H-O-H device may achieve bacterial control that could meet industry standards set by organizations like the Cooling Technology Institute and the Association of Water Technologies. This is a promising sign for cooling tower operators who are environmentally conscious. However, similar experiments on full-sized cooling systems are needed to validate our findings in the model system."

While chemicals are most effective in controlling biofilm, corrosion, and deadly bacteria in evaporative air-conditioning systems, the results of this study suggest that a greener solution could become a reality.

During 2011, H-O-H Water Technology *Green Machine* installations produced the following: Statistics include a total of 127 cooling water systems totaling 86,660 tons of cooling capacity:

Additive or Resource	Total Saved	2010/11 Added Savings	Additive or Resource	Total Saved	2010/11 Added Savings
Make-up Water	248,502,410 gals.	44,747,510 gals.	Sodium Hypochlorite, 12.5%	199,184 lbs.	35,861 lbs
Sulfuric Acid, 66^{o} Baume'	121,230 lbs.	21,830 lbs	Stabilized Bromine/Chloride	26,557 lbs.	4,782 lbs
Salt, NaCl	347,590 lbs.	62,590 lbs	Isothiazolin, Biocide	71,938 lbs.	12,954 lbs
Phosphorous, as P	4,332 lbs.	780 lbs	Transported Materials	819,705 lbs.	147,603 lbs
Polymer	49,797 lbs.	8,967 lbs	Diesel Fuel in Transportation	1,421 gals.	256 gals
Organic Carbon, as COD	29,715 lbs.	5,351 lbs			

The ultimate National potential of this technology may then be viewed against projected cooling tower statistics assuming average bleedoff reduced nationally by roughly 50%:

1. *Approximate Number of Cooling Towers Systems* — *500,000*
2. *Approximate Annual Make-up* — *5.0 trillion gals*
3. *Average cycles-of-Concentration (CC), H-O-H database* — *4.94*
4. *Annual Bleedoff @ 4.94 CC* — *1.01×10^9 gals*
5. *Annual Bleedoff @ 10.0 CC* — *0.20×10^9 gals*
6. Potential Water Savings @ 10.0 CC — 812×10^6 gals
7. Potential Sulfuric Acid Eliminated — 1.7×10^6 tons
8. Potential Salt Eliminated — 0.61×10^6 tons
9. Bromine/Chlorine Eliminated — 0.27×10^6 tons
10. Phosphorous Eliminated — 6.4×10^3 tons
11. Phosphonate Eliminated — 32×10^3 tons
12. Polymers Eliminated — 66×10^3 tons
13. Organic Carbon, as COD Eliminated — 7.77×10^3 tons
14. Chloramines & Trihalomethanes Traditionally Formed — 50 to 75% Reduction

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