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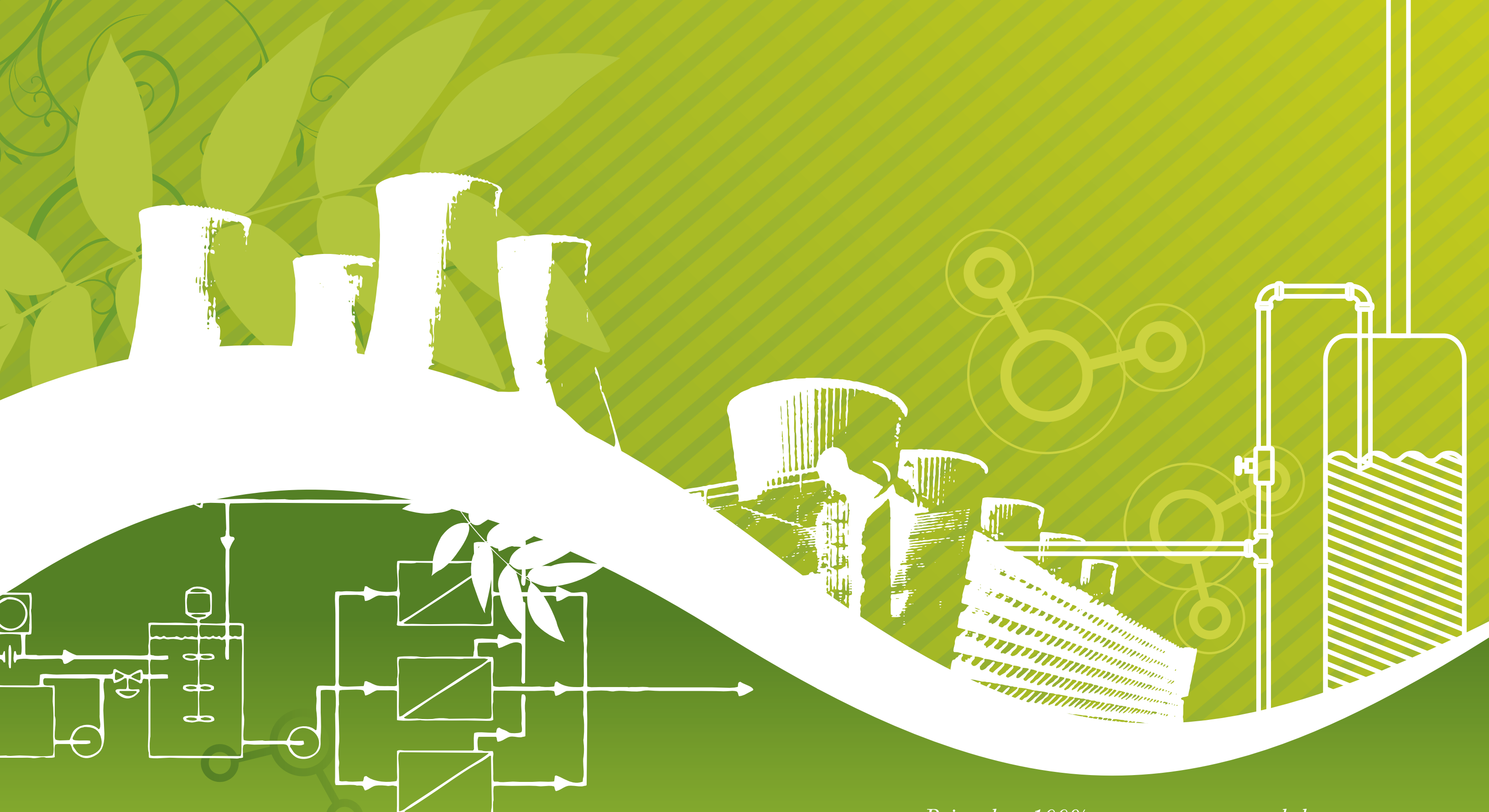

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# Peracetic Acid – A Green Cooling Water Biocide

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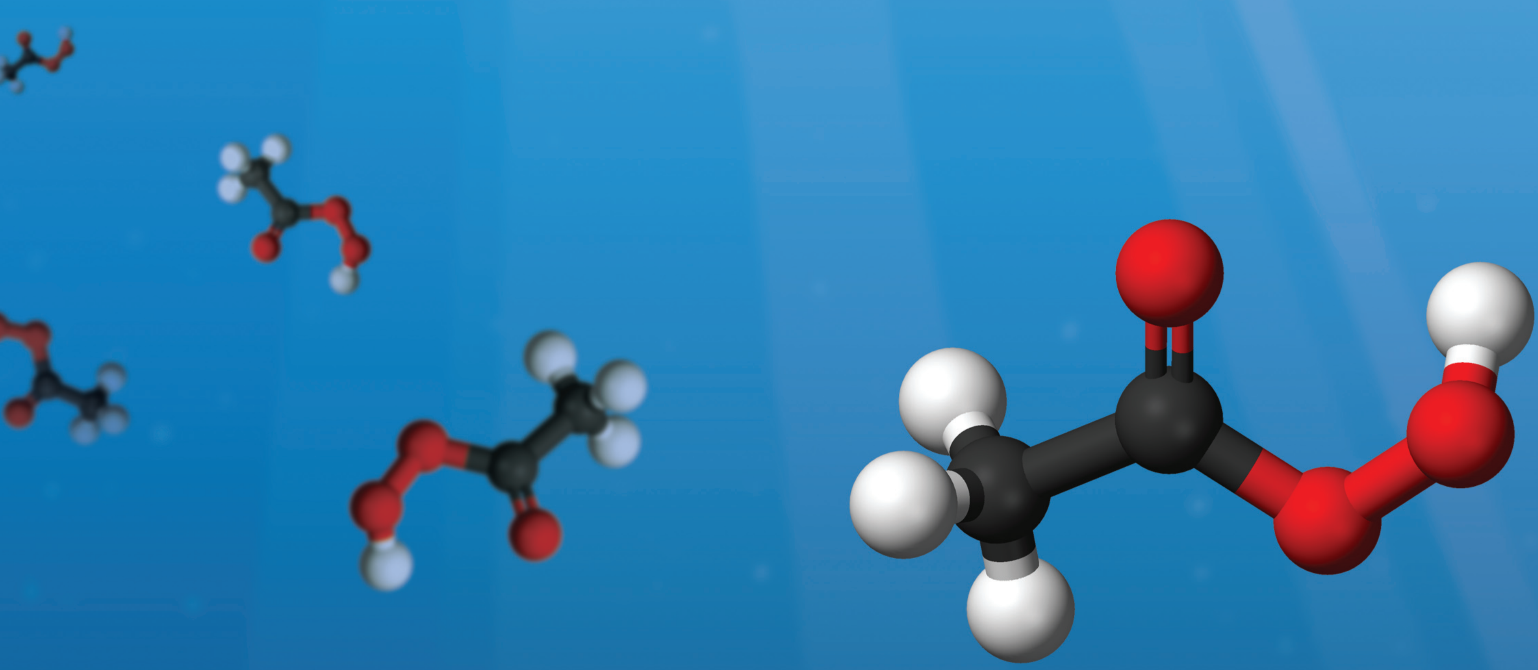


## Abstract

Peracetic acid (PAA) has been used for many years as an effective, non-halogen based biocide and disinfectant. Interest is growing for its use as a green alternative for cooling water treatment. PAA is commonly produced and sold as 5-30 wt% concentrates composed of equilibrium mixtures of PAA, with high levels of hydrogen peroxide (HP) and acetic acid (AA) in water with added stabilizers. Even with stabilizers, PAA has a much more limited shelf life than HP, and it must be shipped in vented containers due to its instability. PAA of this composition can be excessively oxidizing or corrosive for some applications.

Eltron Water Systems is completing testing of a fourth-generation, pilot-level system to produce

PAA on-site and on demand, which contains minimal HP and AA content. Green, cost effective and scalable, the proprietary technology integrates with treatment systems, delivering PAA that is ready to use. The system eliminates storage and handling issues, is safer for operators, and requires only water, air and a readily available generally regarded as safe (GRAS) feedstock.

## Introduction

Eltron Water Systems is completing testing of a pilot-level system to produce peracetic acid (PAA) on-site and on demand. PAA has been used for many years as an effective, non-halogen based biocide and disinfectant. Interest is growing for its use as a green biocide in cooling water systems. This article presents a high-level view of PAA's efficacy as a biocide and describes Eltron Water Systems LLC's green, emerging technology.

## PAA – Green Cooling Tower Water Treatment

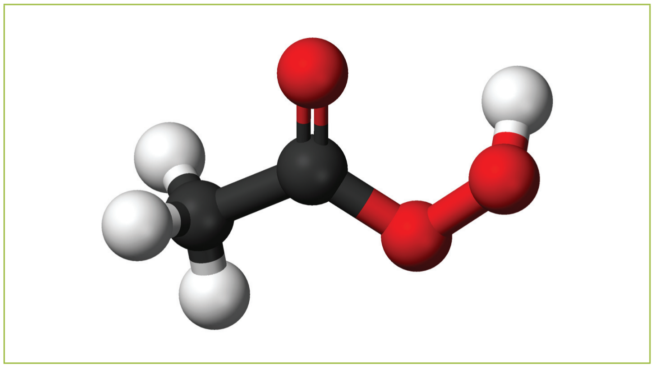
Controlling the growth of bacteria, mineral deposits and corrosion is essential to cooling tower operation, performance and return on asset investment, regardless of its size and location. Microbiological fouling reduces system cooling efficiency. Mineral deposits, corrosion and fouling also shorten the lifetime of the cooling process equipment and ancillary water treatment filtration membranes, forcing unnecessary capital investment and compounding the increased costs driven by inefficient operation.

Of course, it is not just what is inside the cooling tower that is important. Regulations on blowdown water dictate chemical treatment options, and fees associated with treatment facility acceptance of this wastewater can account for significant cooling tower operating costs. Continually heightened sensitivity to the environmental effects of chemical treatment processes, as well as safety and security issues, are shaping the future of these regulations.

Traditional oxidizing and non-oxidizing chemical biocide treatment methodologies, while effective at varying degrees, are either costly or pose environmental hazard and safe handling challenges. Even using $H_2O_2$, one green alternative, is problematic in that it is shipped and stored at high concentration (50-70 wt %), making it dangerous to transport and handle.

PAA is a biocide and disinfectant that decomposes to only oxygen and acetic acid, which is readily broken down in the environment. It is commonly produced and sold as 5-30 wt % concentrates composed of equilibrium mixtures of PAA, with somewhat high levels of hydrogen peroxide (HP) and/or acetic acid (AA) in water with added stabilizers. Even with stabilizers, PAA has a much more limited shelf life than HP, and it must be shipped in vented containers due to its instability. In most applications, PAA is used at concentrations of 100 mg/L or less. Depending on the composition, PAA can be excessively oxidizing (due to the excess HP) or result in excessive organic loading (from increased AA concentration), which, for some applications including cooling tower maintenance, can be problematic. Figure 1 shows the chemical structure of peracetic acid.

Figure 1. Molecular representation of peracetic acid. Carbon, oxygen and hydrogen are represented as black, red and white, respectively. *Source: Wikipedia*



Eltron Water Systems LLC is developing an on-site PAA generation system that enables cooling tower operators to take advantage of PAA's green oxidizing capabilities. The PAA delivered by Eltron Water's prototype has lower concentrations of HP and AA than merchant-produced equilibrium PAA, and on-site generation eliminates the shipping and handling logistics issues at point-of-use concentrations. PAA's environmentally benign composition and breakdown products makes it an attractive biofilm control chemical.

## PAA Background

PAA has been used for many years as a biocide and disinfectant. A broad spectrum, non-halogen based biocide, it is capable of killing fungus and bacteria such as *Candida albicans*, *Aspergillus niger*, *Legionella*, and *Bacillus cereus*. It has been shown to eradicate algae at low concentrations of 5 mg/L. In October 2001, PAA was one of the chemicals used to neutralize the anthrax in letters sent in the bioterrorism attacks that resulted in the deaths of five people.

Table 1: Relative oxidizing capacities of common oxidizing agents

| **Oxidizer** | **eV*** |
|---|---|
| Ozone | 2.07 |
| **Peracetic Acid** | **1.81** |
| Chlorine Dioxide | 1.57 |
| Sodium Hypochlorite | 1.36 |
| Hydrogen Peroxide | 1.33 |

*electron volts

PAA is a very strong oxidizer, second only to ozone among common oxidizing agents, as shown in Table 1. It is lipid soluble, does not contain halogens nor produce harmful disinfection by-products. It is active at low temperature and from low to high pH.

Chemically, PAA is produced by reacting HP with acetic acid, as shown below:

$$H_2O_2 + CH_3C(O)OH \leftrightarrow CH_3C(O)O\text{-}OH + H_2O$$

hydrogen peroxide + acetic acid ↔ peracetic acid + water

Much like chlorine, PAA can be used in many applications. It is well established as an effective, safe chemical for clean-in-place applications and food processing. Wineries, vineyards and beverage plants, as well as dairy products production facilities, use PAA to sanitize the inside and outside of machinery. Pulp and paper mills making the move to totally chlorine free (TCF) production have turned to PAA for its bleaching power. Hospitals can use it to control infection and in place of bleach for cleaning linens; the PAA is both easier on the fabric and doesn't result in phosphate and fluoride discharge. It can help keep swimming pools safe for public use and to improve the quality of the water.

In 1998, the EPA granted an "Exemption From the Requirement of a Tolerance" based on test data that showed PAA was safe to use in low concentrations.[1] According to the EPA, PAA at low concentration is non-toxic, non-carcinogenic, and degrades into water, oxygen and acetic acid, which is GRAS. In 2000, PAA was approved for use in organic food production under 7 CFR 205.601 (a).[2] What is significant about these studies and approvals is that PAA is effective and safe for cooling water and wastewater treatments at levels as low as 0.25 mg/L. Even though PAA is considered to be a pesticide, FIFRA compliance is not required for non-food applications.[3]

PAA has been used, albeit not widely, in industrial recirculating cooling water treatment, wastewater treatment, and to clean UF and RO membranes. As PAA is consumed at a biofouled surface, the oxygen gas bubbles released can provide additional turbulence that enhances removal of biofilms and scale. It does not react with ammonia, is compatible with many anticorrosives and antiscalants and does not produce residuals such as free chlorine or sodium bromide in the blowdown discharge. And, unlike chlorine, PAA does not lose oxidizing activity at elevated pH.

Its outstanding oxidizing and biocidal characteristics, along with its green chemistry, make PAA an ideal choice for these applications. So, why isn't it the cooling tower water and membrane treatment chemical of choice? Cost, safety and the logistics of handling bulk PAA have discouraged adoption. Merchant PAA is classified as a hazardous material and is subject to stringent shipping and storage requirements.

## On-Site PAA Delivery System

Eltron Water Systems LLC is in the pilot-scale development phase of a system that produces PAA on-site via a proprietary process that uses water, air and a readily available GRAS feedstock. This green, emerging technology for water treatment and membrane cleaning enables point-of-use delivery of PAA. The system integrates with existing water treatment infrastructure and can operate continuously or in batch mode. Furthermore, the system is scalable, both up and down, and the concentration of the PAA can be varied, which allows PAA production at a volume and concentration to compensate for changing conditions within the cooling tower. Because the PAA is delivered at point-of-use concentrations, dilution may be unnecessary and operator safety improved. Table 2 shows a comparison between commercially delivered PAA and Eltron's process.

Table 2: Pound for pound comparison for HP, AA and TOC

| Generation method | PAA | HP | AA | TOC | pH range |
|---|---|---|---|---|---|
| Equilibrium, 15% | 1 | 1.53 | 1.13 | 0.77 | 1-1.5 |
| Eltron's PAA | 1 | 0.08 | 0.26 | 0.63 | 2-3 |

PAA generated by Eltron Water's system differs from merchant-produced, equilibrium PAA. In addition to being delivered at low concentration, the ratio of PAA to HP is much higher. Eltron Water's PAA has about 20 (and as high as 70) times less HP per pound of PAA than equilibrium PAA. It also has about 4 times less AA. Typically, merchant produced PAA has a PAA:HP ratio of 1:1.53 (for 15% PAA equilibrium solutions commonly available). PAA produced with Eltron's system has a ratio of 1:0.08. It also has lower total organic carbon (TOC) content. One pound of PAA produced by this system contains 0.63 lb TOC, as opposed to 0.77 lb for other commercially produced PAA as shown in Table 2. Consequently, on-site produced PAA does not present the potential for over-oxidizing or corroding the cooling water system and the wastewater requires less treatment.

Table 3: Calculations for PAA requirements in a medium-size cooling tower

| | | |
|---|---|---|
| Cooling Tower Volume | gal | 77,500 |
| Water Circulation Rate | gpm | 5,000 |
| **Residence Time per Cycle** | **minutes** | **15.5** |
| **PAA Residual Required** | **mg/L** | **0.25** |
| PAA Half Life in CT | minutes | 25* |
| Evaporation Rate | % of Circ. | 1.5 |
| PAA in Evaporate | mg/L | 0.06* |
| Drift Rate | % of Circ. | 0.05 |
| Blowdown Rate | % of Circ. | 0.2 |
| Makeup Water Rate | % of Circ. | 1.75 |
| Makeup Water Rate | gpm | 87.5 |
| PAA Loss to Drift and BD | lbs/day | 0.04 |
| PAA Loss to Evaporate | lbs/day | 0.05 |
| PAA Loss to Consumption | lbs/day | 7.9 |
| PAA Injection Concentration | mg/L | 0.38 |
| **PAA Makeup Rate** | **lbs/day** | **8.0** |

*estimates

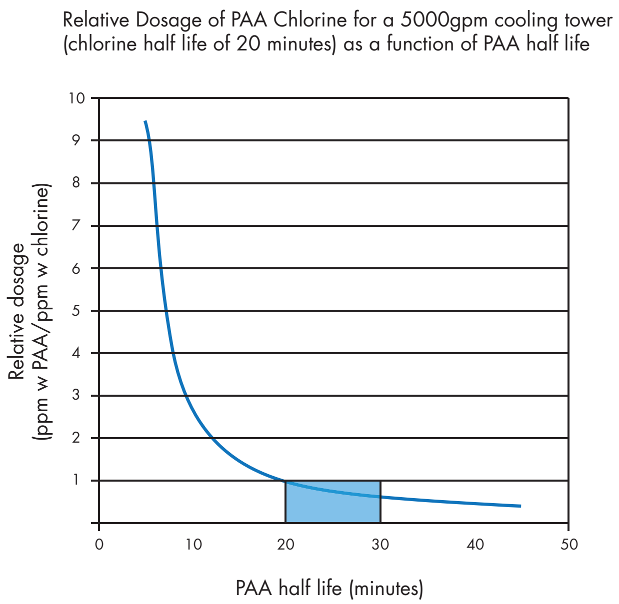
The present process delivers PAA without high levels of AA and the residuals that are inherent in merchant-produced PAA. Since no stabilizers are included in the composition, they also are not present in blowdown.

## Examples

The required volume of PAA that needs to be produced to maintain cooling tower water can be determined using data collected during our development. Table 3 is an example describing a 5,000 gpm recirculating cooling water system on a manufacturing facility. In this scenario, we assumed that the half life of the PAA is 25 minutes, that the system would be operating in continuous production mode, and that the PAA residual in the water is 0.25 mg/L. Eight pounds of PAA/day is required to achieve good microbiological control.

The relative required dosage of PAA compared to chlorine can be estimated for this example as well, as shown in Figure 2. Based on information in the literature, we calculated the dosage requirements of PAA and chlorine for a medium-size cooling tower. According to the calculations, the volume of PAA required will be equal to the amount of chlorine required, given that the half-life of the PAA is 20 minutes in the tower. If the half-life is longer, then less PAA would be required than chlorine. Just like other treatment paradigms, the dose required will vary from tower to tower and in response to changes in the environment. With Eltron Water's system, you simply adjust production to meet changing conditions.

Figure 2: Relative dosage of PAA to chlorine and formula how results were obtained.




$$\frac{c_r}{c_i} = \left(\frac{1}{2}\right)^{t_r / t_{1/2}}$$

$$m_{ox} = M \cdot (c_i - c_r)$$

$c_i$ – *initial oxidizer concentration*

$c_r$ – *residential oxidizer concentration*

$t_r$ – *residence time between dosage*

$t_{1/2}$ – *oxidizer half life*

$m_{ox}$ – *oxidizer mass flowrate in makeup*

$M$ – *mass recirculation rate in tower*

## Conclusion

This PAA delivery system is an emerging, green water treatment technology that promises a cost-effective solution for controlling biofilm in recirculating cooling water systems and maintaining filtration membranes. The overall system cost, environmental advantages, simplified operational logistics and less costly regulatory compliance add up to a compelling argument for adopting this green alternative. The prototype, on-site PAA delivery system will integrate seamlessly with existing cooling tower infrastructure and is easy to operate.

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