



Ozone in Cooling Water Treatment

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When commercial ozone generators were first introduced for cooling water treatment, they were marketed as a stand-alone treatment, a cure-all or panacea. We now know this is not the case. Because there have been many misconceptions regarding ozone, this article is intended to review the basics of ozone, its true capabilities and limitations, and its potential benefits in cooling water treatment applications.

What is Ozone?

Ozone (O_3) is formed by combining three atoms of oxygen. The air we breathe contains two atoms of oxygen (O) in the molecular form of O_2 . When sufficient energy is applied to the molecular O_2 , such as the discharge of electricity during a thunderstorm or strong UV radiation from the sun, some of the molecular O_2 will split into two individual oxygen atoms. When the individual oxygen atoms merge with other oxygen molecules (O_2), they form O_3 . Ozone is a very unstable molecule and will readily revert O_2 .

Capabilities

Ozone is a very powerful oxidizing biocide, viricide, fungicide, sporicide, disinfectant and sterilizer. It kills microorganisms on contact by cellular lysis and cytoplasmic dispersion - it directly ruptures the cell walls of the microorganisms, which results in an instantaneous death. By comparison, chlorine kills bacteria by diffusing through the cell wall and then oxidizing the enzymes within the cell.

Ozone kills microorganisms including *E. Coli*, *Legionella*, *Pneumophila*, *Streptococcus Facalis Bacillus*, *Clostridium*, *amoebae cysts*, *Giardia*, *Cryptosporidium*, *Pseudomonas*, etc. It also eradicates fungi, mold and yeast. In addition, ozone:

- Oxidizes and mitigates pollutants from water and wastewater.
- Breaks down volatile organic compounds (VOC) such as, phenols, benzene, pesticides and other aromatic hydrocarbons.
- Breaks down inorganic compounds such as cyanides, sulfides, nitrites.
- Removes color.
- Bleaches.
- Removes taste and odor.
- Removes soluble iron and manganese indirectly by converting them to filterable insoluble solids.



Ozone is very friendly to the environment. The extra atom of oxygen makes ozone very unstable. While it has a half-life of about 20 minutes in clean water, its half-life in dirty water is even shorter as it is consumed by the microorganisms, VOCs and other compounds. Because ozone breaks down to oxygen, ozone does not leave any toxic or carcinogenic by-products. It does not impart any taste, odor, color or solids.

By comparison, chlorine forms carcinogenic by-products, such as trihalomethanes (THM) and other halogenated compounds. When added to water, chlorine hydrolyzes to hypochlorous acid, which further hydrolyzes to hypochlorite ion, both of which can linger and adversely affect our hydrological system.

Since ozone reverts rapidly to oxygen, it cannot be packaged and stored. Thus, it must be generated on-site. In turn, this on-site generation eliminates any hazards associated with transportation, storing and handling.

Oxidizing agent	Oxidation potential(volts)	Power relative to chlorine
Fluorine (F ₂)	3.6	2.25
Ozone (O ₃)	2.07	1.52
Hydrogen Peroxide (H ₂ O ₂)	1.77	1.30
Potassium Permanganate (KMnO ₄)	1.67	1.23
Chlorine (Cl ₂)	1.36	1.00
Chlorine Dioxide (ClO ₂)	1.27	0.93
Bromine (Br ₂)	1.09	0.80

Table is courtesy of CEC the Ozone Company

What is the Significance of Ozone?

Ozone is a very powerful oxidant, even more powerful than chlorine. Shown in Table 1 is a comparison of the oxidizing potential of ozone to other oxidizing agents.



Commercial Production

Ozone is produced commercially in the same way it is formed naturally by lightning or UV radiation from the sun. The commercial lightning method is called corona discharge. Dried air or oxygen is passed through an electrified field (corona) generated by a high voltage between positive and negative grids. The high voltage splits the molecular oxygen into atomic oxygen. Some of the atomic oxygen merges with molecular oxygen to form ozone, while other oxygen atoms simply recombine to form O_2 . A fraction of oxygen in the air is transformed into ozone.

When ambient air is used as a feed gas, the amount of ozone generated is between 1 and 2 percent by weight in air. When oxygen is used as a feed gas, the ozone generated is between 6 and 12 percent by weight.

Natural UV radiation is simulated commercially by UV lamps. Air is passed through a chamber between the UV lamp and a shield. UV light can create or destroy ozone depending on the UV wavelength. Wavelengths of 185 nanometers (nm) are required for the generation of ozone and 254 nm for the destruction of ozone. This method produces a very low level of ozone and is usually suitable for small applications. In addition to these methods, ozone may also be made through electrolytic and chemical reactions.

How is Ozone Injected?

Ozone is typically injected into water via a venturi. A side stream water pump is typically used to create the vacuum on the venturi with a static mixer installed after it to ensure adequate mixing, distribution and proper contact between the ozone and water. Another less popular alternative is the diffuser method, where ozone is injected under pressure through diffusers creating bubble columns - much like air diffusers in aquariums.

Destroying Ozone

Ozone can be destroyed by catalytic conversion units, activated carbon filters, thermal destructors or by ultraviolet radiation. Catalytic conversion is the most popular method of ozone destruction. Activated carbon filtration decomposes ozone but carbon is also consumed in the process. There is also a risk of fire as carbon could ignite under high exothermic condition. In thermal destruction, ozone is destroyed by heating it in excess of 300 degrees Celsius. Ultraviolet radiation decomposes ozone at the wavelength of 254 nanometers.



Early Misconceptions

In cooling water applications the most common problems encountered are scale, deposition, corrosion, fouling and microbiological (bacteria, algae, or fungi) growth. Today, there is an even greater threat – the emergence of pathogenic bacteria like *Legionella Pneumophilia*. Microbiological growth is a concern because it contributes to and amplifies deposition, corrosion and fouling by acting as a nucleation point or catalyst for these problems. The effect of microbiological growth on scale, deposition and fouling is one of the early misconceptions of ozone.

Early applications showed that ozone also removed mineral deposits. Later, it was found that this removal was only true where the deposits were held in a bio-matrix. It is like the steel structure of a building that holds up all the bricks. By destroying the steel structure at strategic points, the whole building implodes.

Comparing this analogy to the bio-induced deposits, the bio-matrix held the deposits together, acting like glue. When the ozone destroyed the bio-matrix, the attached crystals became dispersed. Not understanding this phenomenon fully, some ozone manufacturers began marketing their equipment as a scale inhibitor. Needless to say, ozone failed to prevent mineral deposits under other conditions, such as supersaturation, excessive hardness, and alkalinity.

Because microorganism also induces other problems such as corrosion and fouling, ozone was also marketed early on as a corrosion and fouling inhibitor, under similar biological pretext. Likewise, ozone failed to prevent these problems under non-biological conditions.

Traditionally, non-oxidizing biocides and oxidizing biocides are used to control microbiological growth. Typical non-oxidizing biocides are organo-sulfur compounds (carbamate based, thiocyanate), organotin, isothiazolone, organobromine (dibromonitrilopropionamide), organic thiocyno-azole (benzothiazole), glutaraldehyde and quaternary ammonia.

Typical oxidizing biocides are chlorine, bromine and chlorine dioxide. Most of the biocides have a long-term negative impact on the environment. As such, there is a growing pressure to reduce or restrict these biocides in the blowdown water, especially if the water is being discharged to a waterway.



In addition to the discharge burden, these biocides have to be stored, transported and handled, which increases potential health and injury risks to personnel.

Limitations

Because of its short half-life, ozone levels drop off rapidly as time progresses, and as the ozone moves away from the injection point, its disinfecting efficacy decreases. In systems with long piping runs, ozone may not travel far enough, leaving the farthest areas vulnerable to microbiological growth. This situation may be remedied by injecting ozone at various strategic points throughout the water system. A bio-dispersant can be added to penetrate and disperse the sessile bacteria (growing on surfaces) so that they can become planktonic (floating in water), thus enabling the bacteria to be transported to the ozone injection point for destruction.

Increasing the ozone level at the injection point to raise residual level downstream is not recommended. The higher ozone concentration may destroy the water treatment chemicals, increase corrosion near the injection area and destroy seals, gaskets, or other components in the system.

Ozone is limited in penetrating biofilm. It may burn the surface of the biofilm, protecting the microorganisms underneath from further destruction. Therefore, they will survive and will likely continue to cause localized corrosion. This situation may be remedied by adding a good bio-dispersant to penetrate and disperse the biofilm, including the bacteria living under the biofilm.

Ozone does not discriminate in terms of what it oxidizes. If ozone is used as a disinfectant in water loaded with other non-biological organic matters, they will also consume ozone. As such, there may not be enough ozone residual to accomplish the intended disinfection. The remedy is to generate more ozone to supply the total ozone demand. However, this increases costs in both operating and capital. As such, ozone may not be cost effective for these types of applications.



Potential Health Hazards

According to the EPA, “the same chemical properties that allow high concentration of ozone to react with organic material outside the body give it the ability to react with similar organic material that makes up the body. When inhaled, ozone can damage the lungs. Relatively low amounts can cause chest pain, coughing, shortness of breath, and throat irritation. Ozone may worsen chronic respiratory diseases such as asthma and compromise the ability of the body to fight respiratory infections.”

EPA makes a distinction between ozone in the upper and lower atmosphere. Ozone in the upper atmosphere, referred to as stratospheric ozone, helps filter out damaging ultraviolet radiation from the sun. Conversely, ozone in the lower atmosphere, – the air we breathe – can be harmful to the respiratory system.

OSHA has issued a threshold limit value (TLV) on ozone exposure to 0.1 mg/L over eight hours per day and five days per week, or 0.3 mg/L for a 15-minute continuous exposure. Because of the potential health hazards, it is crucial to destroy any excess ozone in a safe way.

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