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Ozone in Cooling Water Treatment

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Introduction

When commercial ozone generators were first introduced for cooling water treatment, they were marketed as stand-alone treatment, a cure-all, a panacea. We now know this isn't true. Because there has 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 3 atoms of oxygen. The air we breath contains 2 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 2 individual oxygen atoms (O). When the individual oxygen atoms (O) merge with other oxygen molecules (O_2), they form O_3. Ozone is a very unstable molecule and will revert back to O_2 quickly.

What is the significance of ozone?

Ozone is a very powerful oxidant, even more powerful than chlorine. Below is a table comparing the Oxidizing Potential of Ozone to other oxidizing agents.

Oxidizing Agent	Oxidation Potential (volts)	Relative Power of Chlorine
Flourine (F_2)	3.06	2.25
Ozone (O_3)	2.07	1.52
Hydrogen Peroxide (H_2O_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

This table is courtesy of CEC the Ozone Company

Ozone is a very powerful oxidizing biocide, viricide, fungicide, sporicide, disinfectant, and sterilizer. It kills microorganisms on contact by cellular lysis and cytoplasmic dispersion, that is, 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 Pneumophilia, 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 hydrocarbon
- 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.

Environmental Friendly

Ozone is very friendly to the environment. The extra atom of oxygen makes ozone very unstable. Ozone has a half-life of about 20 minutes in clean water. In dirty water, its half-life is even shorter as it is consumed by the microorganism, VOC, and other compounds.

Ozone breaks down to oxygen. As such, it 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 and then to hypochlorite ion, both of which can linger on and adversely affect our hydrological system.

Since ozone reverts to oxygen very quickly 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.

Commercial production

Ozone is produced commercially in the same way ozone is formed naturally by lightning or UV radiation from the sun.

The commercial lightning method is called the ***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 merge with molecular oxygen to form ozone, while other oxygen atoms simply recombines to form O_2. A fraction of oxygen in the air is transformed into ozone. When dried air is used as feed gas, you can get ozone between 1 - 2 percent by weight in air. When oxygen is used as feed gas, you can get ozone between 6 - 12 percent by weight.

The 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 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. A static mixer is usually installed after the venturi to ensure adequate mixing, distribution, and proper contact between the ozone and water.

Another method, but less popular, is the diffuser method, where ozone is injected under pressure through diffusers creating bubble columns, much like air diffusers in aquariums.

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, which is 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 ppm over 8 hours per day and 5 days per week, or 0.3 ppm for a 15-minute continuous exposure. Because of the potential health hazards, it is crucial to destroy any excess ozone in a safe way.

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 it (carbon) is also consumed in the process. There's also a risk of fire as carbon could ignite under high exothermic condition. In ***thermal destruction***, ozone is destroyed by heating it to excess of 300^{o}C. ***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 microbio (bacteria, algae, fungi, etc) growth. And now, there's even a greater threat - the emergence of pathogenic bacteria like Legionella Pneumophilia. Microbio 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 microbio 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. When you destroy the steel structure at strategic points, the whole building implodes. Comparing this 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 them as scale inhibitor also. Needless to say, ozone failed to prevent mineral deposits under other conditions, such as supersaturation, excessive hardness, alkalinity, and others.

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 microbio. Typical non-oxidizing biocides are organo-sulfur compounds (carbamate based, thiocyanate), organotin, isothiazolone , organobromine (dibromonitrilopropionamide), organic thiocyano-azole (benzothiazole) glutaraldehyde, and quaternary ammonia. Typical oxidizing biocides are chlorine, bromine, and chlorine dioxide. Most of these 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 life, the ozone level drops off rapidly as time progresses and as it moves away from the injection point, decreasing its disinfecting efficacy as well. In systems with long piping runs, ozone may not get far enough, leaving the farthest areas vulnerable to microbio 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 a good solution. The higher ozone concentration may destroy the water treatment chemicals, increase corrosion near the injection area, and destroy seals, gaskets, etc.

Ozone does not do a good job in penetrating biofilm. It may burn the surface of the biofilm, but that would only protect the microorganisms underneath the biofilm from further destruction. Therefore, they will continue to survive and will most likely continue to cause localized corrosion. Likewise, 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 can oxidize. If ozone is used as a disinfectant in water that is loaded with other non-biological organic matters, they will also consume ozone. As such, there may not be enough ozone left to accomplish the intended disinfection. The remedy here 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 this type of applications.

Summary

We know that ozone is a great biocide and oxidizer. And we now know that ozone cannot be used successfully as a stand-alone water treatment program. And like all other biocides, ozone has advantages as well as disadvantages. If applied improperly, the protection it is intended to achieve will fail. Ozone is not the panacea it was once touted. Knowing its pros and cons, you can use the strong points to your advantage and avoid the pitfalls of its weak points. Because every facility has its own unique, evolving, and increasing challenges, such as meeting tougher environmental regulations, ozone can be a welcoming and refreshing addition to current water treatment program.