Watertec Engineering Pty Ltd

Information Sheet

<u>Ozone in General</u>

Ozone

What is Ozone?

Ozone, first discovered in 1840, received its name from the Greek word "Ozein", which means to smell.

Ozone is a triatomic allotrope of oxygen (a form of oxygen in which the molecule contains three atoms instead of two). Its chemical formula is O3 and it is always present in trace quantities in the Earth's atmosphere.

Ozone is produced when oxygen molecules (O2) are split into two oxygen atoms (O1) while in the presence of other oxygen molecules. These oxygen atoms (O1) then combine with molecular oxygen (O2) to yield ozone, O3.

Ozone is generated naturally by short-wave solar ultraviolet radiation, and appears in our upper atmosphere (ozonosphere) in the form of gas. Ozone also may be produced naturally by passing an electrical discharge such as lightning through oxygen.

The History of Ozone in Water Treatment

1785; Odor of ozone gas is recognized emanating from electrical machinery.
1886: The ability of ozone to disinfect polluted water is recognized in Europe.
1891: Test results from Germany show that ozone is effective against bacteria.
1893: First Full scale application using ozone for drinking water in the Netherlands.
1897: French chemist obtains his doctorate degree for his thesis on ozone. Same chemist creates the first ozone generator manufacturing facility.
1903: Niagara Falls, NY plant goes on-line.
1915: At least 49 major ozone installations are on line throughout Europe.

Circa: World War 1. ! Poisonous gas research leads to the development of inexpensive chlorine gas. Interest in ozone for water begins to decline.
1957: Ozone is implemented for oxidation of iron and manganese in Germany.
1964: Spontaneous flocculation in ozone contact chambers led to France constructing an ozone plant to enhance particulate removal.
1965: Scotland employs ozone for color control in surface water.
Switzerland uses ozone to oxidize micro pollutants such as phenolic compounds and several pesticides.
1970: French exploit use of ozone for algae control.

Ozone's Current Role in Water Treatment (as of 1990)

In Western Europe, over 40 full-scale municipal ozone facilities are installed each year. France alone has over 700 water treatment plants equipped with ozone. Switzerland has over 80 plants online for disinfecting contaminated water and oxidizing organics in heavily contaminated surface waters. Germany has over 70 installations using ozone.

As of 1990, there were no less than 40 full-scale ozone installations in the United States.

The Future of Ozone in Water Treatment

Revived interest in ozone is probably greatest in the United States. One of other main reasons for this is the 1986 Amendments to the Safe Drinking Water Act (SDWA). Municipal water systems around the world are being reengineered to incorporate the use of ozone to restrict the formation of carcinogenic disinfection by-products (DBPs) such as Trihalomethanes (THMs), thus providing safe, palatable water.

The list of applications for ozone in water treatment is extensive. Several of the water treatment applications not yet mentioned will be addressed in the following pages. The list of applications for ozone other than water treatment is even longer but will not be addressed in this manual.

US EPA Update Surface Water 1996: US EPA has plans to focus on the inactivation of the Cryptosporidium Oocyst, Giardia, and the formation of THMs relative to the SWTR. Applying ozone to surface waters will be beneficial to the end users in the years to come.

Ground water 1997: US EPA intends to implement mandatory disinfection of ground water and disinfection requirements that will provide protection from hepatitis.

In the year 2002, Stage II of Disinfection Byproducts, a reevaluation will lead to lower maximum contamination levels (MCLs).

Characteristics of Ozone

Oxidation Potential: 2.07 V in alkaline solution
Odor: Detectable in concentrations as low as 0.01 PPM in air.
Color: Pale-blue in color.
Density: 150% that of oxygen.
Gas: Ambient temperature.
Liquid: At – 170^{o} F condenses to a dark blue liquid.

Solid: At -420° F, ozone will freeze.

Decomposition: Decomposes readily in the presence of certain catalysts of at temperatures exceeding 212° F.
Stability: Time and temperature dependent. At room temperatures, unreacted ozone will revert back to molecular oxygen completely within hours. Ozone is an unstable gas with a ½ life on the order of minutes.

Oxidizer: Strongest stand alone oxidizer currently available to the applications addressed in this manual, and is 152% stronger than chlorine.

Disinfection: Destroys microorganisms, viruses, and cysts quickly, with little effect on reaction form pH or turbidity. Destroys E. Coli 3,125 times faster than chlorine.

Why Use Ozone?

Safety

Ozone is produced on site. There are no dangerous chemicals to transport, store or handle. Perhaps even more important, the chance of overdosing with dangerous and hazardous chemicals is limited.

California's South coast Air Quality District, the largest and most stringent air pollution district in the U.S., recognizes the many beneficial aspects of ozonation. A report prepared by the executive committee indicated that ozone "… is a new water treatment technology likely to play a significant role in future water treatment and supply. The ozone emissions are considered to be insignificant and dissipate as soon as released into the atmosphere". On August 1, 1992, the district voted to exempt ozone systems from any permitting requirements within their jurisdiction.

Generally Recognizes As Safe (GRAS) as listed by the United States Food and Drug Administration (USFDA) as a disinfectant for bottled waters.

Disinfection

Bacteria-

Ozone kills microorganisms with a process known as "cellular lysis". In the oxidation process, ozone ruptures the cellular membrane of microorganisms and disperses the bacterial cytoplasm into solution, thus making reactivation impossible. This process takes place in about 2 seconds. Chlorine must first diffuse through the bacterial cell wall after which oxidation of the bacterium's enzymes by hypoclorous ions causes death. This process takes much more time for disinfection and is also dependent on other factors of water quality.

Ozone destroys E. Coli 3,125 times faster than chlorine.

Used for disinfection, ozone may also provide secondary benefits:
- Prevent THM formation (a problem with chlorine)
- Oxidation of inorganics
- Taste and odor control
- Microflocculation
- Oxidizing synthetic and volatile organic chemicals

Streptococcus Fecalis is easily destroyed with low ozone dosages.

Legionalla pneumophila (the bacteria responsible for Legionnaires disease) is destroyed with relatively low dosages of ozone. This is one of the many reasons ozone has become so popular in the treatment of cooling tower water.

Virus Inactivation-

Pioneered by French public officials, it has been found that inactivation of viruses in excess of 3-log (99.9%) can be achieved by maintaining a 0.4 residual of ozone for a minimum of 4 minutes.

Spores –

Inactivation of Bacillus and Clostridium spores for sterilization is achievable with ozone at relatively high dosages and high contact time.

Cryptosporidium and Giardia

Cryptosporidium and Giardia are protozoan oo/cysts that can infect the digestive tract of humans and other warm-blooded animals. They were the cause of the Sydney water crisis of 1998.

While both chlorine and ozone readily inactivate bacteria, viruses and Giardia, research has demonstrated that Cryptosporidium is much more readily inactivated by ozone than by chlorine. A comparison is given in the following Table 2:-

	CT Value*	
Micro-organism	**Ozone**	**Chlorine**
E. Coli	0.02	0.03
Poliovirus 1	0.1	1.1
Giardia Lamblia cysts	0.5	30
Cryptosporidium oocysts	2.5	7200

Table 2 CT values (mg. min/L) for a 99% (2 log) Inactivation at Temperature 25^{o} and pH Range 6.0 to 7.0

*****CT is the product of the residual disinfectant concentration C (mg/L) and the contact time T (mins).

Ozone is therefore more than 2,800 times more effective than chlorine against Cryptosporidium.

Taste and Odor Control

Ozone is the disinfectant of choice for most water bottling plant operations. Unlike chlorine, ozone leaves no undesirable taste or odor.

Taste and odor by-products such as unsaturated aldehydes are readily oxidizable with ozone. Ozone can sometimes solve taste and odor problems without filtration.

Algae Control

Ozonation will disrupt the metabolic processes of many types of algae by oxidizing essential organic components.

Oxidation

Inorganics-
Oxidation of inorganics with ozone will not result in the removal of metals, but it does facilitate their precipitation and subsequent removal through filtration.

Iron and manganese are easily and readily oxidized into a particulate for filtration downstream.

Sulfides are rapidly oxidized to sulfates, thus eliminating the “rotten egg” taste and odor associated with sulfides.

Heavy metals such as arsenic, copper, and lead are easily reduced to below detection limits with ozonation followed by filtration.

Trace metal removal of cadmium and zinc through oxidation with ozone and subsequent filtration has been found to be effective in reaching MCL levels established by the USEPA in the SDWA.

Nitrite ion is oxidized very quickly to nitrate as are organic nitriles, nitrites, nitrous compounds, hydroxylamines and the like.

Organics

The USEPA has identified over 700 individual organic compounds, many of which may be readily oxidized to carbon dioxide by ozone, while others are not affected at all. The use of ozone on organics is typically followed by filtration with granular activated carbon (GAC).

Advanced Oxidation Process (AOP) refers to increasing the reactivity of ozone in water. This is performed by forcing ozone to react via a free radical pathway. There are two methods commonly used to attain AOP:

1. Hydrogen Peroxide (O3 + H202)
2. Ultraviolet Radiation (O3 + UV)

Many molecules that are resistant to ozone alone are degraded by this free radical process. AOP utilized on organics that normally react to ozone will reduce the initial ozone dosage required by approximately 20%. AOP is used most often to control organics (taste, odor, color, THM precursors, micro pollutants and pesticides). This is not to say that AOP is required for oxidation of organics, but in some instances it may be preferred.

Trihalomethanes (THM) precursors (humic and fulvic acids) are formed until they are chlorinated. Therefore, it is best to control the THM precursors prior to chlorination (if required after ozonation) by partially oxidizing them with small amounts of ozone. Normally, the ozonated water is then pasted through sand and/or GAC filtration. The partially oxidized THM precursors are biologically degraded in the sand and/or GAC filters.

Volatile Organic Contaminants (VOCs) may be reduced dramatically (up to 97%) by ozonation followed by GAC.

Synthetic Organic Contaminants (SOCs)/Micro pollutants – Ozone or AOP is capable of removing many SOCs. This removal leads to the transformation of these molecules into toxic or non-toxic by-products which are easily removed through subsequent GAC filtration.

Color derived from the decomposition of naturally occurring humic materials (organics) is easily removed with ozone followed by GAC filtration.

Pesticides such as phosolone and aldrin are oxidized to destruction.

Toxic Cyanide ions are readily oxidized by ozone to the much less toxic cyanate ion.

Turbidity/Microflocculation

Ozone, used as an aid to coagulation prior to the injection of chemicals, enhances the process through microflocculation and reduces chemical demand. Ozone should not be mistakenly applied as a replacement to the coagulation process, but as a superior coagulant aid.

Acknowledgements

The two major sources of information relating to ozone in water treatment is The American Water Works Association Research Foundation (AWWARF) and the International Ozone Association (IOA) have gone to great lengths in researching ozone and its effects on constituents found in water. It is the information provided by these sources that assists the water treatment professional working with smaller applications (POE or light industrial) to dispel the mystery associated with the use of ozone.

Much of the information presented herein is referenced from the work of others. This information may be found in “Ozone in Water Treatment-Application and Engineering”, a cooperative research report available from Lewis Publishers.