

OZONE IN DRINKING WATER TREATMENT

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Summary

Ozone is a strong oxidant and an excellent disinfectant. Ozone is used at water treatment plants throughout the world to address disinfection, disinfection by-products, taste and odor, color, micro-coagulation, and other water treatment needs. Ozone can effectively destroy bacteria and inactive viruses more rapidly than any other disinfectant chemical. Ozone reacts to oxidize a number of inorganic compounds including iron, manganese, sulfides, nitrite, arsenic, bromide ion, and iodide ion. Iron and manganese can be reduced to very low, safe levels in water supplies through ozone oxidation. This same process is used to liberate organically bound heavy metals, which otherwise are not easily removed. All ozone applications involve oxidative reactions, whether ozone is used for disinfection or oxidation of specific contaminants. Difficult-to-oxidize organic compounds include many solvents, most pesticides, and compounds that cause tastes and odors (2-methylisoborneol and geosmin), which are by-products of algal growth and decomposition. This saturated organic matter cannot be oxidized rapidly by ozone alone. However, they can be oxidized by the hydroxyl radical ($\text{OH}\cdot$). When naturally occurring concentrations of hydroxyl radicals are insufficient or when offensive taste-and-odor compound concentrations are excessive, hydrogen peroxide can be added, along with an increased ozone dose, to create additional $\text{OH}\cdot$. Organic compounds oxidized by ozone or by $\text{OH}\cdot$ form shorter-chained organic molecules. Fortunately, many of these shorter-chained organics are readily biodegradable and can be removed in biological filters.

1. Introduction

Drinking water supplies are based on lakes and dam reservoirs, on river waters and ground waters. Groundwater resources associated with hard rock geology are localized and small, so supplies come mainly from surface waters such as rivers and impounding reservoirs. A problem with water quality can be defined as a failure of a water supply to meet the minimum standards laid down in the European Council (EC) Drinking Water Directive.

Council Directive 98/83/EC, the Drinking Water Directive (DWD), concerns the quality of water intended for human consumption. The objective of the Drinking Water Directive is to protect the health of the consumers in the European Union (EU) and to make sure the water is wholesome and clean. To make sure drinking water everywhere in the EU is indeed healthy, clean and tasty, the Drinking Water Directive sets standards for the most common substances (so-called parameters) that can be found in drinking water. In the DWD a total of 48 microbiological and chemical parameters must be monitored and tested regularly. In principle World Health Organization (WHO) guidelines for drinking water are used as a basis for the standards in the Drinking Water Directive. Member States are not allowed to set lower standards as the level of protection of human health should be the same within the whole EU. Member States have to monitor the quality of the drinking water supplied to their citizens and of the water used in the food production industry. This has to be done mainly at the tap inside

private and public premises. Member States report at three yearly intervals the monitoring results to the European Commission. The Commission assesses the results of water quality monitoring against the standards in the Drinking Water Directive. After each reporting cycle the Commission produces a synthesis report, which summarizes the quality of drinking water and its improvement at a European level.

Water problems can arise at four different points in the supply cycle: at the resource, the treatment stage, during distribution to the customer's house, and within the household plumbing system. As a general rule the cleaner the raw water, the cheaper the finished water is to produce, and the safer it is to drink. So where the concentration of contaminants is excessively high then the resource may be rejected due to the cost of adequate treatment. Wherever people work and live there will be an increase in toxic substances, non-toxic salts and pathogens entering the water cycle. Industrial contamination, although more localized, is often more serious. The extensive nature of agriculture makes it the most serious threat to drinking water quality, mainly due to the diffuse nature of such pollution, making it difficult to control. Any material or chemicals that find their way into the resource may need to be removed before supply, their removal generally being technically difficult and expensive.

All water sources contain natural organic matter (NOM). Concentrations (usually measured as dissolved organic carbon, DOC) differ from 0.2 to more than 10 mg L⁻¹. NOM creates direct problems, such as odor and taste in water, but also indirect problems such as organic disinfection by-product formation, bacterial regrowth in the distribution system. To produce pure drinking water, the removal of NOM is a prior task in modern water treatment. Odor and taste production in drinking water can have several causes. Odor and taste forming compounds can be present in raw water, but they can also be formed during water treatment. These compounds may derive from the decomposition of plant matter, but normally they are a result of the activity of living organisms present in the water. Inorganic compounds such as iron, manganese, copper and zinc can also generate some taste. Another possibility is that the chemical oxidation leads to an unpleasant tastes and odors. Odor and taste forming compounds are often very resistant. This causes elimination to be a very intensive process.

Because of its excellent disinfection and oxidation qualities, ozone is widely used for drinking water treatment. It has been used continuously in drinking water treatment for about 100 years, beginning in Nice, France, in 1906. Since then, ozone was applied in Nice continuously, causing Nice to be called the place of birth of ozonation for drinking water treatment. Today, Europe has about three thousand ozonation facilities and ozone is used at water treatment plants throughout the world to address disinfection, disinfection by-products (DBPs), taste and odor, color, micro-coagulation, and other water treatment needs. Ozone will effectively destroy bacteria and inactive viruses more rapidly than any other disinfectant chemical. Ozone is used at drinking water treatment plants for various reasons. The only reason that ozone has not totally replaced chlorine in municipal water treatment is its low solubility in water, and therefore its inability to provide a residual disinfection power all the way to the opposite end of the system in a municipal application. When ozone is applied as a gas for drinking water treatment, it is done primarily because of its oxidative strength. Ozone can react to oxidize a number of inorganic compounds including iron, manganese, sulfides, nitrite, arsenic, bromide ion,

and iodide ion. Iron and manganese can be reduced to very low, safe levels in water supplies through ozone oxidation. This same process is used to liberate organically bound heavy metals, which otherwise are not easily removed.

All ozone applications involve oxidative reactions, whether ozone is used for disinfection or oxidation of specific contaminants. Difficult-to-oxidize organic compounds include many solvents, most pesticides, and compounds that cause tastes and odors (2-methylisoborneol (MIB) and geosmin), which are by-products of algal growth and decomposition. This saturated organic matter cannot be oxidized rapidly by ozone alone. However, they can be oxidized by the hydroxyl radical (OH•). When naturally occurring concentrations of hydroxyl radicals are insufficient (the ozone molecule decomposes to form free radicals which react quickly to oxidize organic and inorganic compounds) or when offensive taste-and-odor compound concentrations are excessive, hydrogen peroxide can be added, along with an increased ozone dose, to create additional OH•.

Organic compounds oxidized by ozone or by OH• form shorter-chained organic molecules. Fortunately, many of these shorter-chained organics are readily biodegradable and can be removed in biological filters.

2. Disinfection Treatment

Microbial contamination is the most critical risk factor in drinking water quality with the potential for widespread waterborne disease. Illness derived from chemical contamination of drinking water supplies is negligible when compared to the number due to microbial pathogens.

In the past, the primary emphasis of disinfection was to control waterborne diseases through the control of associated bacterial indicator organisms such as *coliforms*. With use of disinfectants, epidemic outbreaks of diseases such as cholera and typhoid have been virtually unknown for decades. Two findings made in the 1970s have resulted in significant reevaluation of this long established disinfection practice. The first finding was that disinfection by-products, formed in the reaction of disinfectants and certain source water organic matter, might be harmful to human health. The second finding was the discovery of newly recognized waterborne disease-causing organisms that could not be effectively controlled by the then accepted disinfection procedures. These new concerns require a high level of understanding of what disinfection is and how it can be accomplished with minimal side effects. In many instances, design studies will have to be carried out to result in treatment plants that will not only meet current regulations, but also be flexible enough to adjust to new regulations as more is learned.

Disinfection may be defined as the inactivation of (pathogenic) microorganisms. Inactivation means that even though the pathogenic organism might physically exist in the finished water supply, it has been rendered dead, inactive or incapable of reproduction.

The major and first disinfection step normally employed in the treatment of drinking water is primary disinfection. In essence, primary disinfection is intended to completely

kill pathogens present in the source water, thereby preventing the introduction of such pathogens into the water distribution network. A supplemental effect may also be accomplished by the separation and removal of pathogens in the filtration of drinking water.

Usually a secondary or final disinfection step is added to the treatment train to maintain a disinfectant residual concentration throughout the water distribution system. The role of this disinfectant residual is to provide protection against subsequent microbial intrusion or regrowth following treatment. Sufficient disinfectant is added to the flow leaving the treatment facilities to ensure that some residual is available throughout a distribution system. The basic presumption is that the specific combination of disinfectant concentration and contact time (CT) will result in a certain degree for inactivation of the target pathogen groups.

2.1. Microorganism Inactivation with Ozone

Ozone must be generated on site, and the gas stream is applied to the water flow using appropriate gas/liquid contacting conditions. Ozone is thought to achieve disinfection largely through oxidation reactions that damage and destroy critical components of microorganisms. Although the general effects of disinfectants on bacteria and other organisms are known, the precise mechanisms are not as firmly established. Ozone is thought to exert its strong oxidizing capability to achieve disinfection by disrupting the function of the bacterial cell membrane, although enzyme and other internal cell interactions are also possible. With respect to viral disinfection, ozone is thought to achieve viral disinfection through oxidative attack of the protective protein coating; possible interactions with deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) may be a factor as well.

The primary purpose of ozonation at many water treatment plants is to achieve disinfection log-inactivation credit for viruses, *Giardia*, and *Cryptosporidium* at regulated or above-regulated levels.

The value of 1-log inactivation is the same as 90 % inactivation, 2 log is 99 %, 3 log is 99.9 %, etc. The term log removal or log inactivation, instead of percent removal, is used in regulations for ease in disinfection reporting.

Eq. (1) is the fundamental equation for determining the number of organisms that are still viable after exposure to any disinfectant, including ozone.

$$N = N_0 \times 10^{-k_p C^n T^m} \quad (1)$$

where:

N – number of organisms that remain viable,

N_0 – initial number of viable organisms,

k_p – pathogen inactivation rate constant, $\log(N/N_0)/CT$,

C – residual concentration of the disinfectant, mg L^{-1} ,

T – exposure time, min,

n – allows the relative impact of C to be adjusted upward or downward,

m – allows the relative impact of T to be adjusted upward or downward.

Most researchers have found that the values of n and m are equal to 1.0; therefore, by rearranging Eq. (1) and by inverting N and N_0 , the negative sign is eliminated from the equation and the result is positive value (Eq. (2)).

$$\log\left(\frac{N_0}{N}\right) = k_p \times C \times T \quad (2)$$

where:

$\log(N_0/N)$ – log-inactivation credit,

k_p – pathogen log-inactivation rate,

$C \times T$ – disinfection "power", or ozone residual (mg L^{-1}) times time (min).

Various methods are available for calculating CT values. The method chosen depends largely on available information concerning ozone residual characteristics and hydrodynamic features of the ozone contactor. For chemical disinfection, the Environmental Protection Agency (EPA) regulates inactivation using CT tables, which provide oxidant exposure values (CT in min mg L^{-1}) for different oxidants and target microorganisms.

Two types of primary disinfecting credit are considered for ozone. The first type of credit is based on measured CT as with other disinfectants. However, ozone is also thought to achieve a very rapid initial kill that does not appear to be characterized by a CT relationship. In recognition of this phenomenon, EPA criteria provide a second type of credit for at least 1 log virus inactivation and 0.5 log *Giardia* inactivation within the first stage of a multistage contacting system as long as specified minimum ozone residuals are provided at the discharge from that stage. These credits are not specifically related to contact time and are available as long as the first stage is equal to or greater in volume than subsequent stages. Note that this credit can be extremely important for the widely used countercurrent porous gas diffusion type of contacting system. In this type of contactor, ozone is not introduced until flow reaches the bottom of the first stage and the ozone concentration at the top is very low. As a consequence of this arrangement, much of the contactor volume of the first stage contains only limited quantity of ozone. Credit available from CT calculations would, therefore, be extremely limited for this type of system.

The CT tables include temperature ranges typically encountered in water treatment, but they do not account for changes in inactivation response that may result from changes in pH, turbidity levels, or the presence of different sources of dissolved organic matter.

2.2. pH Influence

pH can be an important factor in ozone disinfection. This may not be immediately apparent since the disinfecting properties at a given ozone solution concentration are not thought to vary significantly with pH, at least up to a pH of 9. On the other hand, it is important to recognize that the actual ozone dosage required to achieve a target disinfecting concentration for ozone will vary since ozone decomposition rates increase with pH, especially above pH 8. Disinfection may still be achieved under high pH conditions since the action of ozone is relatively rapid. Some supplemental site-specific testing of key pathogen indicators may be necessary to establish the relative disinfecting condition of ozonation under such conditions.

2.3. Influence of Turbidity

Some laboratory studies have indicated that specific types of test particulates might not interfere with ozone disinfection, for example there was no significant impact on the inactivation of *Bacillus subtilis* as a result of increasing turbidity. Clean kaolinite was added to produce a target turbidity of 2.5 NTU and 5 NTU, corresponding to approximately 2.5 mg/L and 5 mg/L kaolinite.

But this might not be the case under some conditions encountered in full-scale water treatment applications. For example, decreased capability for inactivation of *Giardia* at elevated turbidity (greater than 1.1 NTU for this water) was indicated. Greater than 99 % inactivation was achieved in low-turbidity water, whereas more erratic results, with some removals at less than 90 %, were reported in higher-turbidity waters. Possible protection of *Giardia* cysts by clumps of debris was suggested as one explanation of reduced efficiency under the higher-turbidity condition. This condition may have been further aggravated by auto flocculating phenomena that can occur under some conditions with ozone.

2.4. Secondary Disinfection Requirements

From the standpoint of secondary disinfection applications, ozone does not provide a lasting residual in distribution systems due to its short half-life, which eliminates it from consideration for this type of application. Therefore, a separate secondary disinfectant is typically added if ozone is used as the primary disinfectant. One effect of using ozone as the primary disinfectant or as a pre-oxidant is that the oxidant demand, and possibly the precursor content for formation of disinfection by-products are frequently reduced, a condition that can reduce the required dosage of the secondary disinfectant and the associated formation of disinfection by-products. Because the most likely secondary disinfecting agents are chlorine and chloramines, such dosage reductions can have beneficial implications insofar as reducing formation of halogenated by-products.

Additional benefits are achieved if ozone is used with a biological activated carbon (BAC) process to provide removal of biologically degradable material. Ozone/BAC combination limits microbial regrowth in the distribution piping and results in more stable secondary disinfecting residuals. These benefits may justify use of ozone by some utilities regardless of disinfection by-product considerations.

2.5. Point of Ozone Application

Selection of the location of ozone application for meeting disinfection goals depends on site-specific factors. In many pretreatment oxidation applications of ozone, particularly in waters with low ozone demand, it may be reasonable to provide an ozone residual over the contact time that also provides the CT required for primary disinfection requirements. However, where the ozone demand exerted in these pretreatment oxidation applications causes rapid depletion of the residual, ozone disinfection is often hampered. In such situations, ozone may have to be added at a second downstream location to accomplish disinfection. Such additional application points to consider are downstream of either the sedimentation or filtration processes, where both the oxidant demand and turbidity levels are much lower. When these alternatives are considered, caution should be exercised at locations downstream of the filter that are discussed in the subsequent section, Ozone Application Points.

When the location of an ozone disinfection step within a water treatment process sequence is selected, consideration should also be given to the pH level, especially in finished water where elevated pH levels might be used for corrosion control. This is because of the rapid depletion of ozone that may occur under excessively alkaline pH conditions.

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Biographical Sketch

Marina Kritševskaja was born in Tallinn, Estonia in 1974. Received degrees: Diploma in Chemical Engineering *Cum Laude*, Tallinn University of Technology (TUT), Tallinn, Estonia, 1996; Master of Science in Engineering, Lappeenranta University of Technology (LUT), Lappeenranta, Finland, 1996; Master of Science in Engineering, TUT, Tallinn, Estonia, 1998; Doctor in Engineering, Chemical Technology, TUT, Tallinn, Estonia, 2003. Her work experience includes: Senior Researcher at TUT, Researcher at LUT and TUT Chemistry Institute. Research interests: Photocatalytical oxidation of toxic

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