Review of literature to determine the uses for ozone in the treatment of water and wastewater: Executive Summary

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This paper responds to a CREW call down request submitted by Scottish Water.

A review of literature to determine the uses for ozone in the treatment of water and wastewater; in particular:

- point of use disinfection of water supplies
- inactivation of cryptosprodium oocysts
- bulk disinfection of potable water supplies at treatment works
- oxidation of organics, iron and manganese
- other uses

Wastewater:

- impact of ozone on filamentous bacteria
- disinfection of final effluent
- other uses

Disinfection of potable water using ozone

In most water treatment plants ozone is used for multiple applications. Ozone is now used as a disinfectant, an oxidant of organic and inorganic molecules, a coagulant aid, removing taste and odour, a means of controlling algae and as a way of biologically stabilising water. Ozone is very effective for disinfection against bacteria, viruses and protozoa. However, when used in a disinfection capacity, it is often used when contaminants are highly resistant to more conventional disinfectants.

It has been described as the only chemical form of disinfection to provide effective inactivation of *Cryptosporidium* and *Giardia* at doses similar to those used routinely for water treatment. For drinking water, the CT concept or derivations of it are usually suitable for determining the required dosage. Inactivation of *Cryptosporidia* in final effluent following wastewater treatment differs from drinking water treatment due to the different water quality parameters. This renders the CT approach much less effective for wastewater disinfection.

There is substantial variability across studies on ozone inactivation of *Cryptosporidium* spp. which makes them difficult to summarise or directly compare. This is due to differences in the way studies are performed (e.g. lab *vs*. pilot *vs*. full scale; synthetic or real water sources, artificial seeding with oocysts and continuous *vs*. discontinuous ozone supply) and way in which the values are reported, for example applied or transferred/residual ozone doses; differences in the level of detail with respect to water quality parameters.

Despite this, log inactivation of *Cryptosporidium* following ozone application is frequently reported to be within the 2-3 log range. Of the literature data evaluated graphically (45 data points from 12 studies), 61 % showed greater than 2-log inactivation. The CT relationship was not clear due to the study differences highlighted above. Because *Cryptosporidium* is highly resistant to external stressors including disinfectants, log inactivation cannot be reliably derived from studies of other pathogens or indicator organisms. For example, in a study evaluating *Cryptosporidium* inactivation in river water, Owens et al (2000) demonstrated that the CT required for 2-log inactivation of *Cryptosporidium* (*C. parvum* and *C. muris*) was 12 times greater than that required for the same degree of inactivation of *Giardia muris* cysts*. Bacillus subtilis* spores show some promise as conservative indicators for *Cryptosporidium* inactivation, however.

Sequential disinfection schemes involving two disinfectants have been proposed to provide a certain level of synergism, which may allow greater levels of inactivation to be achieved in drinking water treatment plants (Gyurek et al., 1996; 1997; Liyanage et al., 1997). Rennecker et al. (1999b) indicated that sequential disinfection with ozone followed by free chlorine was promising for the treatment of oocysts.

A number of water quality parameters strongly influence the efficacy of the ozone to disinfect:

- Temperature: as temperature increases, the disinfecting power of ozone increases. Temperature influences inactivation of *Cryptosporidium*, with a 4.5-fold increase in CT suggested for a 10 degree C rise in water temperature.
- pH: changes in water pH changes the balance of available O_3 and OH. An increase in pH from 6 to 9 reduces the amount of O_3 available for disinfection by a factor of 40 (Elovitz *et al*., 1999). There is conflicting evidence in the literature relating to the effect of pH on inactivation of *Cryptosporidium*. It has been suggested that in batch systems, increasing pH is correlated with increasing inactivation, but where ozone is continuously bubbled through the system there is limited effect of pH. Inactivation rates of different *Cryptosporidium* species were not substantially different, although a few studies have noted that oocysts of different ages may show differential responses to ozonation.
- Suspended solids and other ozone scavengers: the presence of contaminants other than the target microorganisms may consume ozone and reduce the disinfection capacity of the water. As for other disinfectants, constituents within the water, primarily NOM, EfOM, BDOC, bromide, synthetic organic compounds and alkalinity exert an ozone demand. It is therefore critical to know what is in the water to understand ozone doses and contact necessary to achieve a specific water quality objective.

When applying ozone at a WTW facility, there are four requisite components: (1) oxygen gas feed system (either air or pure oxygen); (2) ozone production and delivery, (3) an ozone contactor and (4) ozone off gas destruction.

One of the key challenges faced when using ozone as an oxidising agent is the formation of disinfection by-product (DBPs) compounds. Ozone tends to produce DBPs in the categories of oxyhalides, aldehydes and carboxylic acids. While many organic and inorganic ozonation disinfection/ oxidation by-products have been identified, bromate is generally considered to be of greatest concern (von Gunten, 2003) and aldehydes are also important although they are not currently regulated (Silva et al., 2010). Where bromide is present in raw waters, bromo-organic by-products can form during ozonation.

There are a number of factors that influence bromate formation. These are:

- Bromine concentration: given that bromide is oxidised by ozone to bromate, an increase in bromide leads to an increase in bromate for a constant ozone dose and contact time.
- pH: As the pH of the water is increased during ozonation, more bromate is formed.
- Alkalinity: The presence of inorganic carbon (IC) species increases bromate formation.
- Ammonia concentration: Ammonia can remove a significant intermediary from the bromate formation path and reduce the amount of bromate formed.
- Transferred ozone dose and contact time: The relationship between bromate formation and CT follows a linear function, with an increase in CT leading to an increase in bromate formation

The formation of disinfection by products of ozonation has been studied with respect to water reclamation and is also pertinent where treated effluent significantly influences raw water for abstraction.

In a study evaluating DBP concentrations across 12 drinking water treatment plants in the US in which sites using all four major disinfectants (chlorine, chloramines, ozone, and chlorine dioxide) were covered, the highest concentration of the DBP dichloroacetaldehyde occurred at a plant using chloramine and ozone disinfection. Therefore, although the use of alternative disinfectants minimized the formation of the four regulated THM, some unregulated DBPs were present in higher levels than where traditional chlorine disinfection was applied. The literature is contradictory, and ozonation can increase THMS where organic loadings of wastewater are still high, however it has also been shown to reduce the formation of both THMs and HAAs where ozone is introduced in combination with chlorination of effluent.

Oxidation of contaminants in water

Compounds present in water can react with ozone directly or indirectly through OH• radicals. Direct ozonation is usually the most important oxidative reaction if the radical reactions are inhibited due to the lack of initiating compounds to begin the chain reaction or due to the presence of too many radical scavengers. The direct pathway normally dominates under acidic conditions (pH <4) and changes to the indirect pathways above pH 10. Both pathways will therefore play a role in most ground and surface waters (pH ~ 7).

A number of compounds can be directly degraded by ozone. These include taste and odour compounds (geosmin and methylisoborneol (MIB)), phenolic compounds and pesticides such as atrazine. The importance of ozonation in the treatment of industrial wastewaters targeting the degradation of dyes, pharmaceuticals and personal care products has also grown in recent years. Ozone is also used for oxidation of organic macropollutants and its application is used for bleaching of colour, increasing the biodegradability of organic compounds, removal of THM precursors and reducing total organic halide formation potential or chlorine demand. One of the most important ozone applications in water treatment is the oxidation of iron and manganese.

Ozone is capable of destroying a range of volatile micropollutant compounds, in particular alkenes and aromatic organics under the conditions of treatment applied to drinking water. In the past, micropollutant removal was not a primary task for ozone but was considered a positive side effect.

However, due to ever lowering detection limits and stricter regulatory requirements for more chemicals in drinking water, the interest in micropollutants has grown in recent years.

The most common taste and odour associated compounds are MIB and geosmin and these have a very low reactivity with ozone. However, despite this, studies with natural waters have shown good removal efficiencies of these compounds when using ozone. It is likely that ozonation is most effective in waters that support the OH• radical pathway. However, the action of ozone in natural waters is variable and depends on the quality of organics present as well as the treatment conditions.

It has been observed for more than 30 years that pre-ozonation ahead of solid-liquid separation processes can improve the removal of particles. Positive effects of pre-ozonation are also seen for algae removal. Ozone readily kills or lyses many types of algae and it has also been observed to enhance the removal of algae by coagulation and settling. Ozone can also be applied to inactivate zooplankton and actinomycetes. A number of laboratory studies have reported the effect of ozonation on the removal of cyanotoxins and it was shown that complete removal of the toxins can be achieved when ozone is included in the treatment process. Ozoflotation is a new process combining the physical phenomenon of flotation with the oxidising properties of ozone and is usually used as a pre-treatment stage in order to reduce the treatment load.

Point of Use systems

There are a range of commercially available point of use (POU) and point of entry (POE) ozonation devices. There is limited scientific literature available on the performance and reliability of these devices and most of the below information has been taken from commercial sources and, as such, limited validation of performance can be gleaned from this data. Independent testing of POU ozone devices is required because to date, most, if not all, claims made by manufacturers have not been verified.

Application of ozone in wastewater treatment

Similarly to drinking water treatment, ozone can be applied to satisfy a number of objectives in wastewater treatment, including:

- Disinfection
- Oxidation of inorganic compounds
- Oxidation of organic compounds
- Enhancement of sludge degradability

Ozone disinfection mechanisms in wastewater are less well understood. Ozone reacts strongly with many substances, therefore it is generally deemed more appropriate for use on pre-treated effluents (Paraskeva and Graham, 2002). In a wastewater of high organic content, inactivation of total and faecal coliforms and *E. coli* has been reported at an applied ozone dose of 10 mg/L for a 5 minute contact time. Ozone doses commonly presented in the literature ranged from 0.3 µg/L to fully saturated, with contact times generally between 1.5 and 18 minutes. This provided a range of inactivation rates, broadly in the range of 1-2.5 log inactivation for coliforms, *Enterococci* and *Clostridia,* while some higher reductions were noted for bacteriophages used as surrogates for human viruses

The critical parameter for disinfection of indicator organisms appears to be the optimisation of mass transfer of ozone, which is usually low due to its poor solubility. Hydraulic retention time appears less important. Meeting the initial ozone demand leads to a substantial microbial inactivation as the microbial cells actually exert a significant proportion of that ozone demand (Xu et al 2002).

Filamentous organisms are a normal part of the activated sludge microflora and, in low numbers, are thought to promote floc formation. Excessively long filaments or presence in high numbers can lead to sludge bulking (Eckenfelder, 1992). Ozone can be used as a “non-specific” approach to reducing filamentous organisms and therefore reducing bulking and foaming in activated sludge systems. Low dose ozonation can inhibit the activity of filamentous bacteria and has been applied to control bulking and improve floc settling (Foladori et al, 2010).

The efficiency of sludge ozonation depends on the following parameters (Foladori et al; 2010):

- Wastewater or Sludge quality
- Reactor configuration
- Ozone gas flow rate and concentration
- Sludge flow rate and solids concentration
- Ozone transfer efficiency
- Contact time
- Ozone dosage per mass of TSS

Studies have reported improved floc structure directly after the start-up of ozone treatment with few filamentous bacteria remaining inside the sludge flocs. One author reported the number of filaments to be an order of magnitude lower in the ozonated treatment than the control. The authors also indicted that ozonation promoted nitrification and biological removal of organic material without affecting phosphate removal.

The influence of ozone on other wastewater treatment parameters is critical to the success of its use to reduce filaments or excess sludge. Paul and Debellefontaine (2007) noted that there was a linear relationship between the log of biomass activity (reported as maximal oxygen uptake rate) and log ozone dose between 0.001 and 0.2 g O_3 transferred per g COD in the sludge). They concluded that ozonation does not affect any of the capabilities of an AS biological process; however other studies have reported contrary indications. For example, a decrease in nitrification rate has been shown to be proportional to increasing ozone dose (Dyctzak et al (2007), although other studies indicate no effects on nitrification. Reid et al (2007) suggested that a more cost effective ozone process for excess sludge reduction would follow the principle “partial oxidation as low as possible and biological oxidation as high as possible”. This minimises the use of ozone but maximises conversion of solids into biodegradable materials which can then be removed in cheaper biological reactors.

Water quality and ozone demand can be used to determine the best point of application. Broadly, high ozone demand in raw water, indicative of high levels of organic material can lead to increased biodegradability of natural organic matter (NOM) (Beltrán et al. 1999; Ternes et al. 2006) following ozonation. This may then require a biological treatment step to remove BDOC which can lead to bacterial growth in the distribution system. Water with a high ozone demand and high turbidity would be considered the most difficult water to treat with ozone, for example, surface water with a high loading of organic material and inorganic particles therefore selecting a point in the treatment train where particulates and organic matter have been removed substantially would be advisable. However, because ozone can also break down organic material, antibiotics and pharmaceuticals, incorporating ozonation at more than one stage of treatment may be effective. Thus low doses of ozone prior to existing treatment can capitalise on some of these effects.

For wastewater, ozonation is often part of a multistage treatment process to reduce ozone consumption. Most often a chemical-biological process includes biodegradation at least before and also often after the chemical oxidation step (Gottschalk et al, 2010). Ozone quantities and generation costs tend to be reduced when utilising these combined systems.

Dissolved organic carbon (DOC) concentrations are typically greater in wastewater than in surface water, resulting in faster O_3 decomposition rates and increased hydroxyl radical ($\bullet$OH) exposures (Buffle et al., 2006). As a result, higher O_3 dosages are required to meet wastewater treatment goals, potentially leading to increased DBP formation.

One of the aims of ozone application in wastewater treatment is to remove toxic inorganic substances and this mainly involves the removal of cyanide (CN-) mostly associated with metal processing and electronics industry wastewaters. Nitrite (NO_2^-) and sulphide (H_2S/S^{2-}) react quickly with ozone and therefore their removal is sometimes carried out using ozonation, however more cost-efficient biological treatment alternatives are more often employed for these contaminants.

Most often in industrial wastewater treatment, ozone is applied to remove target organic compounds that can be present at a wide range of concentrations. These wastewaters include landfill leachate, textile, pharmaceutical and chemical industry wastewaters that can contain many refractory organics including humic compounds, aromatic compounds containing metals, pesticides and surfactants. The main aims of ozonation in this case are (Gottschalk et al., 2000):

- The transformation of toxic organics that are often present in low concentrations and as complex mixtures
- The improvement of biodegradability of refractory organics by partial oxidation
- The removal of colour

Ozonation is a widely used chemical method to improve anaerobic degradability of sludge. Ozonation has also been combined with anaerobic digestion as a pre-treatment or post-treatment with a recycle back to the anaerobic digester. Better performance and lower ozone consumption has been observed in the case of post-treatment and recycling in the digester. The advantages of ozonation pre-treatment of secondary sludge is that it can improve the sludge solubilisation and it can also simultaneously degrade organic pollutants.

Conclusions and recommendations

- Key consideration of ozone treatment for any of the above processes include improved ozone transfer technologies, correct dosage and an awareness of the importance of key water quality parameters such as organic, particulate and bromide loadings.
- Implementation of ozone treatments is likely to be most effective if evaluated on a site by site basis as this not only promotes a thorough evaluation of how to implement the technology for effective disinfection, but would also allow the operators to determine

whether ozone interventions at multiple points would be more cost effective for overall treatment and/or whether the inclusion of additional treatment stages before or after ozonation would be required.

- Ozone disinfection of drinking water is highly effective against a wide range of pathogens, including *Cryptosporidium*.
- Cyst and sporular forms of protozoans and bacteria present the most difficult treatment challenge for ozone disinfection. High CT values can control these pathogens, but it is recommended that a physical barrier is also provided for water sources containing these micro-organisms.
- The main limitation of applying ozone in drinking water systems is the production of bromate as a DBP. Methods of controlling bromate formation have been developed, principally through controlling pH and understanding prevailing water quality conditions.
- POU/POE systems are widely available, mainly from North American suppliers that can generate and deliver ozone from mains electricity. A filtration system needs to be supplied after the ozone when these are used in order to prevent precipitated solids from being present in treated water – it is not always evident that the proprietary systems have these as supplied. Who manages and replaces spent filtration systems and adequate off-gas control must therefore be also considered for POU systems.
- A wide range of organic and inorganic contaminants can be degraded by ozone. High concentrations of ozone are needed for effective degradation of bulk natural organic matter and is therefore not recommended for this application. The most effective use of ozone is for oxidation of metals and organic micro pollutants in combination with a physical/adsorptive process.
- The higher contaminant and scavenging load in wastewater means that much higher doses must be applied for these waters in order to achieve satisfactory levels of removal/disinfection. There are many examples of ozone having been used in wastewater for small scale and pilot treatment systems, but few cases of large WWTWs using ozone due to the high cost of having to add such high concentrations of ozone.
- Ozonation of final effluent can be effective, however higher ozone doses tend to be required which increases the likelihood of formation of disinfection by products.
- Ozone can be an effective non-specific inhibitor of filamentous organisms in activated sludge systems but effects on the overall treatment process are variable
- Ozone is a widely used chemical in water and wastewater treatment as well as numerous industrial applications. The ability of ozone to effectively oxidise a wide range of contaminants and disinfect a broad sweep of micro-organisms have made it an essential component of many treatment flowsheets across the world.

Key words

Disinfection, iron, manganese, ozone, oxidation, point of use, wastewater, water.