

Developments in Ozone Technology

Small Systems Adopt Ozone Technology to Protect Against Cryptosporidium, Giardia

Ozone technology developments have opened new applications for these established water treatment technologies. Driving these changes has been the identification of new, more disinfection-resistant microorganisms such as *Giardia* and *Cryptosporidium* cysts and governmental regulations designed to protect the public health from the hazards of ingestion of these microorganisms. Additionally, the desire to prevent or minimize the formation of halogenated disinfection byproducts formed during chlorination has stimulated new interest in the use of ozone. Combinations of ozone with hydrogen peroxide and/or ultraviolet (UV) radiation can destroy many contaminants present in ground water.

Early on, ozone's uses for water treatment began with disinfection for potable water plants. Other (oxidative) applications for ozone in drinking water have developed including the oxidation of iron, manganese, sulfide, cyanide and nitrite in ground waters as well as man-made organic compounds such as phenols and some pesticides, humics and organics discharged in industrial waste waters.

In recent years, the use of small amounts of ozone for coagulation assistance (microflocculation) and of slightly larger dosages for partial oxidation of organic contaminants to increase their biodegradability has developed. Following ozonation with filtration through media such as granular activated carbon (GAC) allow development of a biomass on the GAC that, in turn, converts significant amounts (up to 40–45 percent) of the partially oxidized dissolved organic materials into carbon dioxide and water. This process, known as "ozone-biofiltration," only has developed within the past 30 years.^{1,2,3} After ozone-biofiltration, smaller amounts of chlorine or chloramine usually are added to provide a stable residual because of the removal of chlorine-demanding organic materials.

Byproducts of Ozonation

Organic oxidation products. Most organic byproducts of ozonation contain more oxygen than did their parent compounds. As such, they usually are less toxic and more easily biodegradable than the starting materials. Generally, organic byproducts formed by any strong oxidizing agent added to water (chlorine, chlorine dioxide, ozone) include organic acids, aldehydes, ketones, alcohols,

aldehyde-acids, keto-acids, alcohol-acids, etc. Advantages of ozone for oxidation of organics over chlorine are that ozone is a stronger oxidizing agent and, therefore, forms higher quantities of the oxidized organics than does chlorine—and these oxidized organics readily are "mineralized" (e.g., converted to carbon dioxide and water during biofiltration). When residual chlorine is present, the biomass cannot form effectively and, therefore, no mineralization of chlorine-oxidized organics can take place.

Although the formation of organic oxidation byproducts from natural humic-type precursors during ozonation might appear to be something of a negative fac-

tor for ozone, it actually is an advantage. The oxidized organics produced during ozonation of natural organics have simpler molecular structures than do the parent humics. These simpler organics readily are mineralized (converted to carbon dioxide and water) biochemically during the passage through a biofilter. Once these oxidation-produced simple organic compounds have been removed from solution, the chlorine demand of the biofiltered water is lower than that of the water prior to ozonation and biofiltration.

Bromate anion. When bromide ion is present in water to be ozonated, hypobromite ion (OBr^-) and hypobromous acid (HOBr) are formed (similarly with chlorine). HOBr is a brominating agent capable of producing brominated organics of various types. During chlorination of waters containing bromide ion, mixed bromo-chloro-organics are produced (such as two of the trihalomethanes and several of the haloacetic acids) as well as bromo-organics not containing chlorine

(such as bromoform, mono-, di- and tribromoacetic acids). During ozonation of waters containing bromide ion, the formed HOBr also can produce brominated organics such as bromoform and mono-, di- and possibly tribromoacetic acids. To date, however, only traces of bromoform have been identified in some ozonated water containing high levels of bromide ion.

In the presence of ozone, OBr^- can be further oxidized to bromate ion (BrO_3^-), which has been determined to be carcinogenic to certain laboratory test animals. Consequently, BrO_3^- has been listed by the U.S. Environmental Protection Agency (EPA) as a *probable* human car-

bromate ion drastically is lowered or even eliminated. If bromate formation is a potential problem in treating potable water supplies with ozone, one technique for minimizing or eliminating bromate formation is to conduct the ozonation at pH 6.5 or less, then adjust pH up at a later stage of treatment.⁴

Another technique to minimize bromate formation during ozonation is to adjust the ozonation conditions to minimize the levels of residual ozone. In this manner, other water contaminants tend to out-compete the OBr^- for the ozone. Still a third technique to minimize ozone production of bromate ion is to add a trace of ammonia to the water prior to ozonation. When HOBr is produced during ozonation, it will react immediately with the added ammonia, producing monobromamine, which is much more slowly oxidized by ozone to yield bromide ion again.⁵ Figure 1 summarizes the mechanisms of formation of bromate ion and methods to minimize its formation during ozonation.

Recent Developments

in Potable Water Treatment

Until the passage of the Safe Drinking Water Act (SDWA) Amendments of 1986, the use of ozone for drinking water treatment in the United States was confined mainly to control tastes and odors. From the 1986 SDWA Amendments came a requirement from the EPA in the SWTR to control "new" microorganisms in raw water supplies (e.g., *Giardia* cysts and enteric viruses). Although these organisms can be controlled by chlorination, the increased quantities of chlorine generate increased amounts of halogenated disinfection byproducts. UV disinfection was ignored in the SWTR because of a publication indicating that UV was ineffective against *Giardia* cysts when excystation was the end point.⁶ As a result, interest in the so-called "alternative disinfectants" was stimulated, with particular attention focused on ozone and chlorine dioxide.

The number of U.S. potable water treatment plants using ozone rose starting in the late 1980s. Of interest is that of the 332 total water systems using ozone, some 194 produce less than 1 mgd, and 120 of the 194 small plants serve fewer than 600 people. (See Figure 1.)

In the 1986 SDWA Amendments and the SWTR, the EPA also introduced the "Ct" concept to U.S. drinking water

Figure 1:
194 U.S. Ozone Water Plants (≤ 1 mgd)
By Population Served — Jan. 15, 2000 — RG Rice



cinogen, and a maximum contaminant level (MCL) of $10 \mu\text{g/L}$ has been established for BrO_3^- in the Surface Water Treatment Rule (SWTR). Many source waters for water treatment plants contain bromide ion, and the more bromide ion contained therein, the more bromate ion can be produced during ozonation, particularly when the pH is greater than 6.5. Consequently, it is important for water treatment specialists to understand the chemistry of bromate formation and the various chemical techniques for minimizing its formation.

BrO_3^- can be produced during ozonation when raw waters contain bromide ion and under certain conditions of pH and ozone-demanding materials. Ozone (or chlorine for that matter) quickly oxidizes bromide ion to a mixture of HOBr and OBr^- . However, ozonation is capable of slowly oxidizing the OBr^- (not HOBr) further to bromate ion provided that the pH is above 6.5. At pH 6.5, no OBr^- can exist, and ozone-formation of



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utilities for ensuring that any disinfectant used for inactivating *Giardia* cysts and enteric viruses actually was doing its job. In this concept, the term "C" refers to the concentration of disinfectant in aqueous solution (mg/L) and "t" is the time (in minutes) the disinfectant is in contact with the aqueous solution. By adopting the Ct concept, water treatment plants operators can control disinfection online rather than wait for after-the-fact microorganism counts.

With ozone, the Ct value for inactivation of three-logs of *Giardia* cysts at 0.5° C is about 3 mg-min/L decreasing to about 0.5 mg-min/L at 25° C. Ct values for inactivating enteric viruses are less than those for inactivating corresponding numbers of logs of *Giardia* cysts. Ten years later, the 1996 SDWA Amendments required *Cryptosporidium parvum* oocysts to be disinfected in addition to those microorganisms listed 10 years earlier. However, at the time only ozone and chlorine dioxide were known to inactivate *Cryptosporidium*. Since *Cryptosporidium* oocysts are considerably more resistant to any chemical disinfectant than are *Giardia* cysts, considerably higher Ct values are required. For example, the inactivation of two-logs of *Cryptosporidium* at less than 5° C is about 20–30 mg-min/L, decreasing to about 3–7 mg-min/L at 25° C. When inactivating *Cryptosporidium parvum* oocysts, considerably higher concentrations of ozone and/or contact times are required than for the inactivation of *Giardia* cysts or enteric viruses. This means the generation of higher concentrations of organic (and sometimes inorganic) oxidation byproducts is required.

On the negative side, the bromate issue continues to act as a rein to the otherwise robust expansion of the installation of ozone. The problem is two-fold—more ozone is required to inactivate *Cryptosporidium parvum* than to inactivate *Giardia* cysts and viruses, yet more ozone usually produces more bromate ion. If the amount of ozone added to control *Cryptosporidium* produces sufficient bromate ion to exceed the current MCL of 10 µg/L, then the use of ozone becomes infeasible.

Advanced Oxidation

The term "advanced oxidation" was created to describe several processes by which hydroxyl-free radicals are generated and used for the oxidation of otherwise refractory organics in water.

The good news is that ozone is being installed for potable water treatment in an ever-increasing number of plants. In the United States alone (as of January 2000), ozone had been installed in approximately 194 small systems (less than 1 mgd). In addition, some 363 ozone systems were known to have been installed in residences and in small businesses as of January 2000.⁷ The ability to inactivate *Cryptosporidium parvum*

oocysts also is good news for ozone, since chlorine is ineffective for this purpose.

On the other hand, the bromate MCL of 10 µg/L discourages the use of ozone for *Cryptosporidium* inactivation, particularly in waters containing significant quantities of bromide ion. The Ct values for ozone inactivation of *Cryptosporidium* are some 5–10 times higher than the Ct for ozone inactivation of *Giardia lamblia* and enteric viruses.

For ground water systems contaminated with such refractory organics as TCE, PCE and probably MTBE, the coupling of ozone and UV offers considerable promise to provide both oxidation and disinfection. **WQP**

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References available online at www.waterinfocenter.com.

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