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 water as well as man-made organic compounds such as phenols and some pesticides, humics and organic acids 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 ozoneation with filtration through media such as granular activated carbon (GAC) allow development of a bioma on the GAC that, in turn, converts significant amounts (up to 40–60 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. 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 matter ions.

**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 material. Generally, organic byproducts formed by any strong oxidizing agent added to water (chlorine, chlorine dioxide, ozone) include organic acids, aldehydes, ketones, alcohols, chloroform, monoo-, di- and tribrominated organic 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 minorization 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 factor (such as bromoform, monoo-, di- and tribromomethanes), during ozonation of water containing bromide ion, the formed HOB or also can produce brominated organics such as bromoform and mono-, di- and possibly tribromomethanes. 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 (BrO₃⁻), which has been determined to be carcinogenic to certain laboratory test animals. Consequently, BrO₃⁻ has been listed by the U.S. Environmental Protection Agency (EPA) as a probable human carcinogen. 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.

Another technique to minimize bromate formation during ozonation is to adjust the ozonation conditions to minimize the levels of residual acid. In this manner, other water contaminants tend to outcompete 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. Figure 1 summarizes the mechanisms of formation of bromate ion and methods to minimize its formation during ozonation.

**Recent Developments in Potable Water Treatment**

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
utilities for ensuring that any disinfectant used for inactivating Giardia cysts and enteric viruses actually was doing its job. In this concept, the term “Ct” 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 plant operators can control disinfection online rather than wait for after-the-fact microorganism counts.

With ozone, the Ct value for inactivation of three-log 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-log 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. 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. This article was edited and reprinted with permission from the Third NSF International Symposium and Technology Expo (2001).

References available online at www.waterinfocenter.com.

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