

CE 474 / 574

Other Disinfection Methods

Except from
"Droste"

16.4 OZONE

Ozone is a more powerful oxidizing agent than other disinfectants discussed in this chapter and a very effective biocide. Ozone has been used for drinking water treatment on a municipal scale since 1906, when it was installed in treatment facilities in Nice, France (Singer, 1990). More than 2 000 water treatment works, primarily in France and other European countries, now use ozone for disinfection and taste and odor control (Tate, 1991). There are currently more than 50 plants in Canada and more than 40 plants in the United States using ozone.*

* This number already much larger

l.
discussed in
r problem
amples of

tates from
0° latitude
blems in
nes. Chlo-
e sensitive
al release

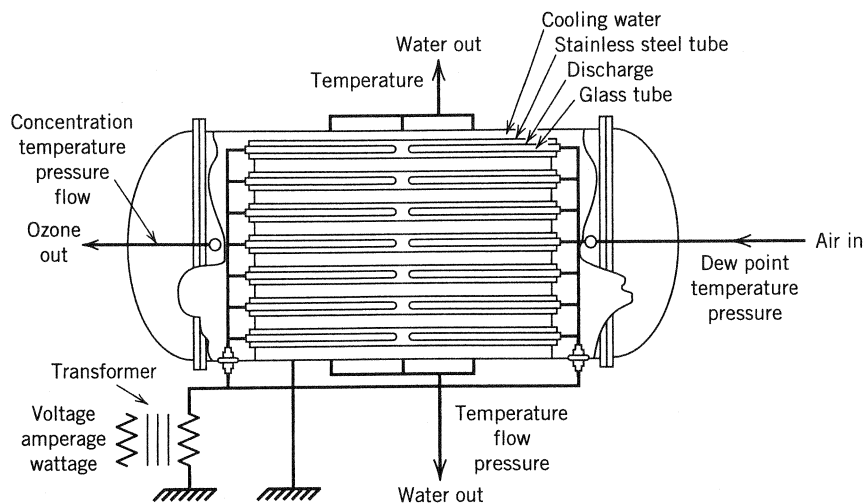


Figure 16.5 Horizontal tube ozone generator. After R. Gerval, "Specifications and Performance Control for Ozone Generators," in *Ozonization Manual for Water and Wastewater Treatment*, W. J. Masschelein, ed., copyright 1982, John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Ltd.

Ozone is created by an electrical discharge (corona discharge is most efficient) in a gas containing oxygen. Ultraviolet irradiation (wavelengths <200 nm) of a gas containing oxygen is an alternative method. The equation for ozone formation is



The rate of ozone production is a function of the oxygen concentration and impurities such as dust and water vapor in the gas.

A common horizontal tube ozone generator is shown in Fig. 16.5. A high alternating current is applied to produce voltages from 6 to 20 kV across glass dielectric tubes that are internally metal coated to conduct the current. The influent gas is dried. The quantity of energy required lies between 15 and 20 W-h/g of ozone produced from air (Masschelein, 1982a). Other types of ozonators are discussed in Masschelein (1982b). The ozone is held in contact with the water through a variety of technologies but the most common contact system in North America is a bubble diffusion system with water depths in the range of 4.5–7.3 m (14.8–24 ft) (Ferguson et al., 1991). Other contactors are over and under or around the end baffled basins, packed contactors, and deep U-tubes. Ozone in the offgas from contactors must be destroyed. Thermal systems or more commonly thermal-catalytic systems are used in North America for destroying ozone (Tate, 1991).

The mass transfer coefficient ($K_L a$) in a gas-sparged CM reactor was found to lie in the range of 0.25 – 0.45 min^{-1} except at very low gas flow rates (Grasso et al., 1990). The rate of ozone decomposition has been found to follow an autocatalytic model (Grasso and Weber, 1989):

$$\frac{d[\text{O}_3]}{dt} = -k_1[\text{O}_3] - k_2[\text{O}_3]^2 \quad (16.16)$$

The rate constants in the above equation are functions of $[\text{OH}^-]$ other alkalinity ions, the amount of UV radiation, and hydrogen peroxide concentration, which all have been found to catalyze ozone decomposition. If the solution pH is not well

buffered k_2 will vary with rate constants associated with a number of intermediate reactions in ozone decomposition (Grasso and Weber, 1989). The rate constants should be empirically assessed for each situation. The decomposition of ozone to oxygen is quite rapid and it is impossible to maintain free ozone residuals in a water for any significant length of time. The half-life of ozone is near 20 min at typical conditions.

Ozone reacts with most organic matter. Ozone attacks organic matter directly or free radical species (such as the hydroxyl radical, OH) formed by ozone decomposition oxidize organic matter. Byproducts formed from ozone attack with human health significance in water treatment are organic peroxides, unsaturated aldehydes, and epoxides (Singer, 1990). On the other hand, ozonation destroys the precursors of most halogenated byproducts, e.g., THMs, haloacetic acids, and haloacetonitriles, that can be formed by subsequent chlorination. A UV-ozone oxidation treatment unit is shown in Fig. 16.6.

Partial oxidation of organic matter by ozone produces more readily biodegradable compounds. As a consequence, using ozone as a final disinfectant can lead to extensive biological regrowth in the distribution system. If the ozone treatment is followed by a porous media treatment such as filtration or granular activated carbon treatment, biological growth in the bed is enhanced (Section 14.11) and a biologically stable water, not subject to regrowth, will be produced (Singer, 1990).

Ozone is effective in oxidizing inorganic substances. The presence of significant carbon dioxide-associated alkalinity improves ozone's ability to destroy organics and as a disinfectant (Singer, 1990) and results in more rapid consumption of ozone as noted above. Ozonation was found to be effective for removing musty, earthy, fishy, and muddy tastes and odors from water that had been chlorinated, coagulated, and sand filtered; astringent and plastic tastes were not significantly removed. However, ozonation was responsible for the development of fruity odors with high intensities

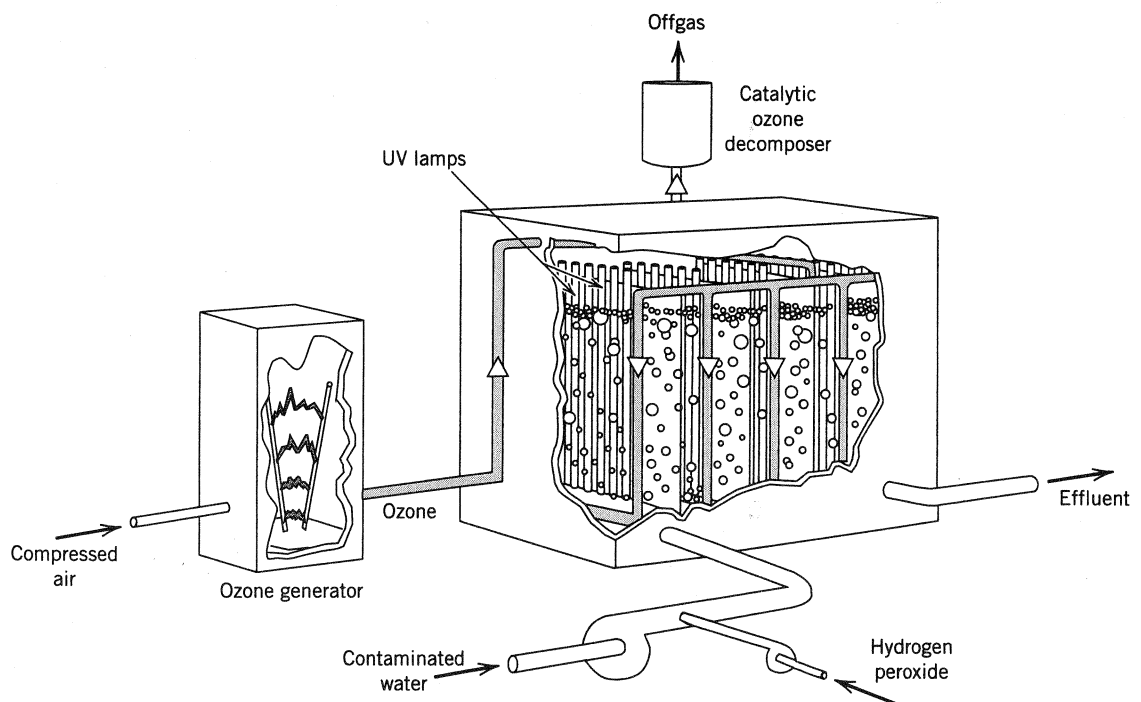


Figure 16.6 UV-ozone oxidation system for treatment of drinking water or wastewater. Courtesy of Zimpro Environmental, Inc.

(Anselme et al., 1989). In general ozone is highly effective as an oxidant of off-flavors compared to chlorine derivatives or permanganate oxidants (Ferguson et al., 1991). Ozone is also very effective for color removal.

Ultraviolet irradiation greatly enhances the ability of ozone to decompose humic acids and other organic compounds. In one study the destruction of dissolved organic substances with UV and ozone proceeded at least 10 times faster than in the presence of ozone alone (Kusakabe et al., 1990). Major final products of decomposition were acetic acid, formic acid, and oxalic acid, which are refractory to ozone attack and are not precursors of THMs. This is an example of an advanced oxidation process using ozone that yields free radical oxidizing species upon decomposition. The process is accelerated by addition of hydroxide ion, hydrogen peroxide, or UV irradiation. Advanced oxidation processes can be used to reduce TOC levels.

16.5 ULTRAVIOLET AND IONIZING RADIATION

Ultraviolet radiation, which is electromagnetic radiation in the shorter wavelength range of the spectrum from 5 to 400 nm, causes dieoff of microorganisms and leaves no residual radiation (and thus no residual disinfecting power) in a water. Ultraviolet radiation has been used since the turn of this century to disinfect water. In the past 20 years there has been an increase in the application of UV radiation to wastewater treatment plant effluents.

Ultraviolet radiation is not effective against *Giardia* cysts. Current United States' regulations (SWTR) for capability of inactivating *Giardia* cysts preclude UV radiation as a primary disinfectant for surface waters where potential for *Giardia* contamination exists (USEPA, 1990). Ultraviolet radiation is appropriate as a primary disinfectant for groundwaters that do not contain *Giardia*.

There is no chemical consumption for UV disinfection and no harmful byproducts are formed. Ultraviolet radiation was observed to have effects equivalent to a residual by Lund and Hongve (1994). The growth of heterotrophic bacteria was inhibited in water that had been irradiated. The effect lasted for 1 week or more and was explained by the production of oxidizing reagents such as hydroxyl radicals formed by UV irradiation of humic substances.

The penetrating power of UV radiation is not as great as ionizing radiation. Ultraviolet rays cause damage to nucleic acids; some cells may be able to recover after exposure to UV radiation. Water and constituents in water affect the transmission and absorption of UV rays. The Beer-Lambert law (Section 5.6) applies. Suspended solids not only reduce the transmission of UV radiation but also shield bacteria from exposure, particularly bacteria within suspended particulates. The correlations between transmittance and turbidity or suspended solids in clarified secondary effluent may be weak at these low concentrations (less than 20 mg/L) (Darby et al., 1993) and the dose of UV radiation may have to be empirically established.

Some bacteria have the ability to repair UV induced damage to DNA. The process is thought to occur in the following manner (Lindenauer and Darby, 1994). Ultraviolet light absorption produces photoproducts, the most important of which are pyrimidine dimers formed from adjacent pyrimidine molecules on the same strand of DNA. With light, a photoreactivating enzyme can split the dimers, causing the repair of the DNA. Lindenauer and Darby (1994) found that the percentage of photoreactivation of total coliforms in wastewater inversely related to UV dose. The overall extent of recovery was less than 1% for all UV doses.

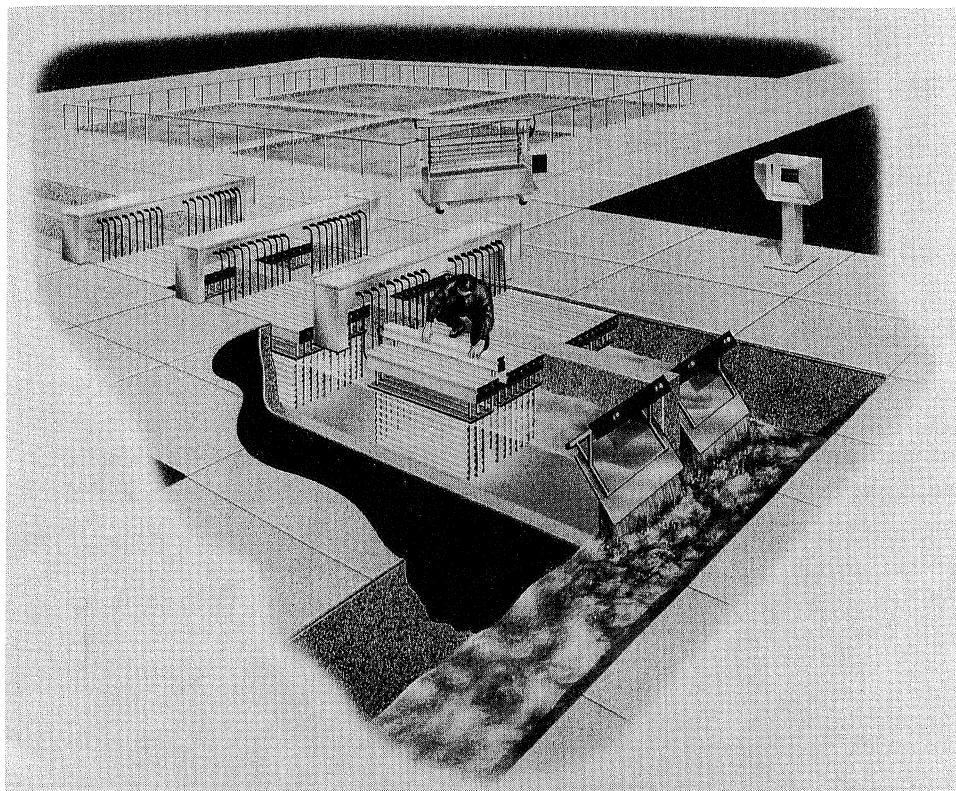


Figure 16.7 A typical UV disinfection system. Lamps are installed in modules for ease of lamp cleaning and replacement. Courtesy of Trojan Technologies Inc.

Ultraviolet radiation is generated by current flow between electrodes in ionized mercury vapor. The maximum energy output of low-pressure mercury arc lamps is at a wavelength of 253.7 nm, which is in the middle of the UV range. Depending on the intensity of the UV radiation and the degree of dispersion in the flow, the contact time necessary to inactivate microorganisms ranges from a few seconds to a few minutes. Long tubular lamps are usually used. Water flows through a bank of lamps to achieve the desired contact time (Fig. 16.7).

The output intensity of lamps is somewhat unstable during the first 100 h of operation and decays exponentially during this period. The 100% output is the output after 100 h of operation. The germicidal effectiveness of the lamps deteriorates with time, which must be considered when designing the system. Manufacturers supply curves that provide the correction factor for lamp output as a function of age of the lamp as shown in Fig. 16.8. Ultraviolet lamp output is also variable with temperature. Manufacturer's rating curves should be consulted.

The rate of inactivation of microorganisms with UV exposure is assumed to follow a first-order reaction:

$$N = N_0 e^{-kEt} = N_0 e^{-kD} \quad (16.17)$$

where

N and N_0 are the number or concentration of bacteria at time t and initially, respectively

k is an inactivation coefficient

E is average UV intensity in the reactor

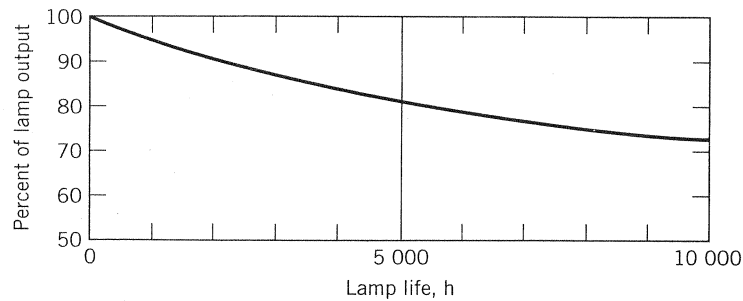


Figure 16.8 Typical UV lamp output. (Time 0 is after 100 h of operation.)

t is average detention time in the irradiated portion of the reactor
 D is radiation dose ($D = Et$)

Darby et al. (1993) found a fairly well-defined relation between UV dose (D) and log survival of coliforms in clarified secondary effluent with TSS <15 mg/L. At doses of 30 mW-s/cm² (0.054 mWh/in.²), log survival was near -3.7; log survival decreased to -4.6 at a dose of 150 mW-s/cm² (0.16 mWh/in.²). The change in survival with dose was not linear. Table 16.5 lists inactivation coefficients for a number of indicator microorganisms in effluent from a biological treatment process.

■ Example 16.3 UV Disinfection

Assume Fig. 16.8 describes the output of a UV lamp system and find the detention time in a UV system to inactivate 99.9% of *E. coli* after 10 000 h of lamp operation. The system is designed to provide an intensity of 2 mW/cm² (12.9 mW/in.²) with new lamps (100-h operation). The rate constants in Table 16.5 apply. For this system, what removal of *E. coli* would occur with new lamps?

From Eq. (16.17), $\ln(N/N_0) = -kD$; from Table 16.5, $k = 0.013 \text{ m}^2/\text{J}$ (504 ft²/Wh).

$$D = -\frac{\ln(N/N_0)}{k} = -\frac{\ln(1/1000)}{0.013 \text{ m}^2/\text{J}} = 531 \text{ J/m}^2$$

$$\text{In U.S. units: } D = -\frac{\ln(1/1000)}{504 \text{ ft}^2/\text{Wh}} = 0.0137 \text{ Wh/ft}^2$$

The intensity of the lamps after 10 000 h (1.14 yr) of operation is approximately 72% of their intensity when new.

$$E_{1.14} = 0.72(2 \text{ mW/cm}^2) = 1.44 \text{ mW/cm}^2$$

$$\text{In U.S. units: } E_{1.14} = 0.72(12.9 \text{ mW/in.}^2) = 9.29 \text{ mW/in.}^2$$

$$Et = D \quad t = \frac{D}{E} = \left(\frac{531 \text{ J/m}^2}{1.44 \text{ mW/cm}^2}\right) \left(\frac{1000 \text{ mW}}{\text{J/s}}\right) \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2 = 36.9 \text{ s}$$

$$\text{In U.S. units: } t = \left(\frac{0.0137 \text{ Wh/ft}^2}{9.29 \text{ mW/in.}^2}\right) \left(\frac{10^3 \text{ mW}}{1 \text{ W}}\right) \left(\frac{1 \text{ ft}}{12 \text{ in.}}\right)^2 \left(\frac{3600 \text{ s}}{\text{h}}\right) = 36.9 \text{ s}$$

When the lamps are new,

$$D = Et = (2.0 \text{ mW/cm}^2)(36.9 \text{ s}) = 73.8 \text{ mW-s/cm}^2$$

$$\text{In U.S. units: } D = Et = (12.9 \text{ mW/in.}^2)(36.9 \text{ s}) = 476 \text{ mW-s/in.}^2$$

$$N = N_0 e^{-kD} \quad \frac{N}{N_0} = \exp \left[- \left(0.013 \frac{\text{m}^2}{\text{J}} \right) \left(73.8 \frac{\text{mW}\cdot\text{s}}{\text{cm}^2} \right) \left(\frac{1 \text{ J/s}}{1\,000 \text{ mW}} \right) \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 \right]$$

$$= 6.81 \times 10^{-5}$$

$$\text{In U.S. units: } \frac{N}{N_0} = \exp \left[- \left(504 \frac{\text{ft}^2}{\text{Wh}} \right) \left(476 \frac{\text{mW}\cdot\text{s}}{\text{in}^2} \right) \left(\frac{1 \text{ W}}{1\,000 \text{ mW}} \right) \left(\frac{1 \text{ h}}{3\,600 \text{ s}} \right) \left(\frac{12 \text{ in.}}{1 \text{ ft}} \right)^2 \right]$$

$$= 6.80 \times 10^{-5}$$

The survival is 0.006 8% when the lamps are new.

Ionizing radiation such as gamma radiation and X rays has wavelengths in the range of 0.001 to 100 nm. Electron beams are also ionizing. Ionizing radiation is a powerful disinfectant, causing irreversible damage to a cell. There is no residual radiation left in the water. Gamma radiation appears to produce slightly better disinfection than high-energy electron beams (Farooq et al., 1993). The application of ionizing radiation as a disinfectant in the water or wastewater industry has been limited, although gamma radiation has been used to inactivate microorganisms in food and medical products for a number of years.

Gamma irradiation requires a radioactive source, whereas electron beam technology does not, which is a major advantage for electron beam technology. Both processes avoid problems associated with use of chemical oxidants (Farooq et al., 1993).

High-energy electron beams have been used for other applications, including aromatic hydrocarbon destruction. The principal reactive species responsible for attack on organics is the hydroxyl radical (Nickelsen et al., 1994). Toluene and benzene were decayed according to a first-order reaction with respect to adsorbed radiation dose:

$$\frac{dR}{dD} = -kR \Rightarrow R_D = R_0 e^{-kD}$$

TABLE 16.5 Inactivation Rate Constants for Indicator and Other Microorganisms for UV Radiation^a

Organism	k	
	m ² /J	ft ² /Wh
<i>Escherichia coli</i>	0.013	504
Fecal streptococci	0.006 7	260
Sulfite-reducing bacteria spores	0.001 5	58
Somatic coliphages	0.016	620
F-specific bacteriophages	0.005 3	205
MS2 bacteriophages	0.011	426
Reoviruses	0.005 5	213

^aReprinted from *Water Research*, 25, T. J. Nieuwstad, A. H. Havelaar, and M. van Olphen, "Hydraulic and Microbiological Characterization of Reactors for Ultraviolet Disinfection of Secondary Wastewater Effluent," pp. 775-783, Copyright 1991, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, OX5 1GB, UK.

where

R_D is the solute concentration at a dose D

R_0 is the initial concentration of the solute

k is a constant

The rate constant k is a function of pH and the amount of organic matter in solution. Organic matter is a scavenger for the radicals. Phenols are initial byproducts, along with a variety of hydroxylated and other highly oxidized byproducts.

16.6 OTHER DISINFECTANTS

Other disinfectants are being examined as suitable replacements for the common disinfectants. All of the halogens have disinfecting power.

16.6.1 Chlorine Dioxide and the Other Halogens

Chlorine dioxide (ClO_2 , with the bonding structure $\text{O}=\text{Cl}=\text{O}$) is a powerful oxidizing agent with nearly 2.5 times the oxidizing power of chlorine. Historically, chlorine dioxide has been primarily used for the removal of taste and odor caused by phenolic compounds (White, 1992). Research has shown that chlorine dioxide does not produce THMs and that the production of precursors for THMs is reduced. This has sparked new interest in chlorine dioxide as a disinfectant. The disinfection efficiency of chlorine dioxide does not vary with pH, in contrast to chlorine, which is converted to pH-sensitive HOCl , and chlorine dioxide does not oxidize bromide (Hoigné and Bader, 1994). Chlorine dioxide is also superior to chlorine for the oxidation of iron and manganese. For the removal of iron and manganese, chlorine dioxide is added as a treatment preceding flocculation and sedimentation.

The benefits of chlorine dioxide for disinfection with THM reduction are potentially offset by its production of disinfection byproducts. As chlorine dioxide exerts its oxidizing power, it degrades into chlorite (ClO_2^-) and to a lesser extent chlorate (ClO_3^-) and chloride ions. Because the concentration of chlorine added with chlorine dioxide is smaller than the amount of chlorine that would be required for a given amount of oxidizing power, the potential for formation of chloroorganics is reduced (see Problem 19). But chlorite ion can oxidize hemoglobin and cause methemoglobinemia. Infants are more susceptible to this disease because they have a reduced capability of reducing methemoglobin. Furthermore, hemolytic anemia, which is a decrease in the blood concentration of hemoglobin, is induced at low concentrations of chlorite ion. Dialysis patients may be particularly susceptible to this condition. There have been studies, with chlorite ion doses well above those found in water disinfection applications, that have found no adverse effects on the exposed population. White (1992) has discussed various studies. Clearly, there is need for more research to quantify the risks and benefits for chlorine dioxide against other disinfectants.

There is no evidence that chlorine dioxide is mutagenic or carcinogenic. However, Eckhardt et al. (1982) found that chlorate was mutagenic to a strain of *Salmonella typhimurium* and to *Drosophila*. But Meier et al. (1985) found that neither chlorite nor chlorate were mutagenic to mouse micronuclei, mouse sperm head, or mouse bone marrow chromosomes.

Chlorine dioxide application in water treatment plants has been practiced for many years at installations throughout the world. There have been many installations that have adopted chlorine dioxide as a disinfectant during the past 25 years.

END