
9

DISINFECTION

General

Rate of kill—disinfection parameters

Status of U.S. drinking water

Chlorine

Ozone

Ultraviolet light

Other disinfecting compounds

GENERAL

The purpose of disinfection is the protection of the microbial water quality. The ideal disinfectant should have high bacterial toxicity, be inexpensive, and not be too dangerous to handle, and should have a reliable means of detecting the presence of a residual.

Chlorine is one of the oldest disinfection agents used, which is one of the safest and most reliable. It has extremely good properties, which conform to many of the aspects of the ideal disinfectant as mentioned above.

RATE OF KILL—DISINFECTION PARAMETERS

Chick's Law

The idea behind disinfection is to kill or to inactivate harmful bacteria and viruses.

The time kill rate is a differential equation:

$$dN/dt = -kN$$

where k is a rate constant, and N is the number of living organisms. Note that the expression is specific to the type of organisms.

This gives $\ln(N_2/N_1) = -kt$ and $t = (2.3/k) \log(N_1/N_2)$, where the subscripts on N refer to the number of organisms at the respective times.

The rate of disinfection k is dependent upon the concentration of the disinfectant and the coefficient of dilution. The rate constant can also be affected by the temperature as shown in the Arrhenius equation:

$$k = Ce^{-(\Delta H_a/RT_a)}$$

where ΔH_a = activation energy (cal); R = gas constant (1.99 cal/°C); T_a = absolute temperature (K), and C is a determined constant.

The equation is evaluated by plotting **log k** versus **$1/T_a$** ; factors such as nutrient concentration, pH, and osmotic pressure all affect the constants and the rate.

The death rate of microorganisms is a first-order differential equation with respect to time.

Problem: The following table shows the disinfection of poliomyelitis virus using hypobromite as a disinfectant.¹ Determine Chick's constant and the time required to reduce the concentration of viable poliovirus to 1/10,000 of the original concentration.

Viable Poliovirus Concentrations	
$t(\text{s})$	N/N_o
4	0.07690
8	0.00633
12	0.00050

Solution: Plot the $-\ln(N/N_o)$ against time (Fig. 9.1)

Execute linear regression for experimental points. This yields the slope of the line ($k = 0.634/\text{s}$). The time required for a 10,000-fold reduction is

$$t = [-\ln(N/N_o)/k = -\ln(1/10,000)/0.634 \text{ s} = 15 \text{ s}$$

¹<http://www.nbif.org/course/env-engr/index.html>.

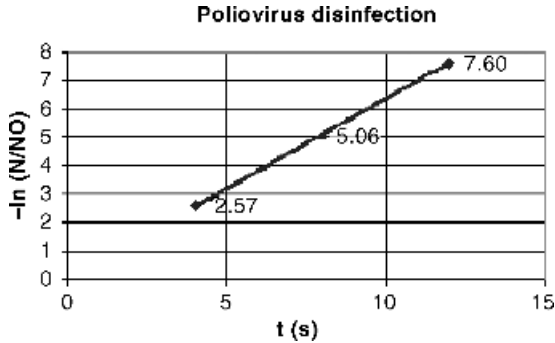


FIGURE 9.1 Sample plot of poliovirus survival ratio in disinfection experiment.

The basic organism often used in measuring disinfection efficiency is *Escherichia coli* (*E. coli*) but the USEPA has recently begun to focus on a number of different organisms that are more resistant than *E. coli*.

We cannot get into a discussion of disinfection without some considerations of human health factors.

For a number of years, the basic problem was *E. coli* and the principal concern was and largely still is fecal contamination of drinking water, bathing water, and so on. The *E. coli* organism was and still is the most frequent indicator of fecal contamination. However, in the past few years we have discovered that fecal streptococcus (*Streptococcus faecalis* and *S. faecium*; a subset of the fecal streptococci considered more feces specific) is a better indicator of human fecal contamination.

Giardia lamblia is a protozoan found in the feces of humans and animals that can cause severe gastrointestinal ailments. It is a common contaminant of surface waters. For a number of years, it went unnoticed because the principal focus was on coliform organisms. In 1981, the World Health Organization classified *Giardia* as a pathogen (capable of causing disease).

Physically, *Giardia* is a cyst former and can survive outside the body for long periods of time. If viable cysts are ingested, *Giardia* can cause the illness known as giardiasis, an intestinal illness, which can cause nausea, anorexia, fever, and severe diarrhea. The symptoms last for several days only and the body can naturally rid itself of the parasite in 1-2 months. However, for individuals with weakened immune systems the body often cannot rid itself of the parasite without medical treatment.²

²<http://www.ladwp.com/bizserv/water/quality/topics/giardia/giardia.htm>.

In the United States, *Giardia* is the most commonly identified pathogen in waterborne disease outbreaks—but that may be because of the attention given to *E. coli*. *Giardia* is not host-specific contrary to some forms of coliform organisms. *Giardia* can jump species, and the viable cysts excreted by animals can infect and cause illness in humans if it enters their drinking water. There are two ways in which *Giardia* can infect humans. Both involve inadequately treated (inadequately disinfected) drinking water: One way is through animal feces in the watershed entering the drinking water, and the second way is through human sewage entering the drinking water. In both the cases, the control mechanism is the adequate disinfection.

The effective control of *Giardia* is accomplished by chlorine and ozone, combined with filtration. Filtration may be sufficient by itself, but that assumes that the filtration will be sufficient to remove all the *Giardia*. The USEPA has focused on the inactivation of *Giardia* as being one key to safe drinking water.³

The following Web site gives more specific information on diseases and the potential problems: <http://www.unc.edu/courses/envr191/191-1999.htm>. The Web site has a number of specific links and good information on human pathogens, which are potential problems from waterborne diseases.

STATUS OF U.S. DRINKING WATER

The following is excerpted from a CDC report on disinfection of water systems in the United States:

Surveillance for Waterborne-Disease Outbreaks—United States, 1995–1996

by Deborah A. Levy, Ph.D., M.P.H.^{1,2} Michelle S. Bens, M.P.H.² Gunther F. Craun, M.P.H.³ Rebecca L. Calderon, Ph.D., M.P.H.⁴ Barbara L. Herwaldt, M.D., M.P.H.² ¹Epidemic Intelligence Service, Epidemiology Program Office, CDC; ²Division of Parasitic Diseases, National Center for Infectious Diseases, CDC; ³Gunther F. Craun & Associates, Staunton, Virginia; ⁴Human Studies Division, National Health and Environmental Effects Laboratory, U.S. Environmental Protection Agency.

Abstract Problem/Condition:

“Since 1971, CDC and the U.S. Environmental Protection Agency have maintained a collaborative surveillance system for collecting and periodically reporting data that relate to occurrences and causes of waterborne-disease outbreaks (WBDOs).

³<http://www.fc.net/~tdeagan/water/one.html#GIARDIASIS>.

Reporting Period Covered:

This summary includes data for January 1995 through December 1996 and previously unreported outbreaks in 1994. Description of the System: The surveillance system includes data about outbreaks associated with drinking water and recreational water. State, territorial, and local public health departments are primarily responsible for detecting and investigating WBDOS and for voluntarily reporting them to CDC on a standard form. Results: For the period 1995–1996, 13 states reported a total of 22 outbreaks associated with drinking water. These outbreaks caused an estimated total of 2,567 persons to become ill. No deaths were reported. The microbe or chemical that caused the outbreak was identified for 14 (63.6%) of the 22 outbreaks. *Giardia lamblia* and *Shigella sonnei* each caused two (9.1%) of the 22 outbreaks; *Escherichia coli* O157:H7, *Plesiomonas shigelloides*, and a small round structured virus were implicated for one outbreak (4.5%) each. One of the two outbreaks of giardiasis involved the largest number of cases, with an estimated 1,449 ill persons. Seven outbreaks (31.8% of 22) of chemical poisoning, which involved a total of 90 persons, were reported. Copper and nitrite were associated with two outbreaks (9.1% of 22) each and sodium hydroxide, chlorine, and concentrated liquid soap with one outbreak (4.5%) each. Eleven (50.0%) of the 22 outbreaks were linked to well water, eight in non-community and three in community systems.

Only three of the 10 outbreaks associated with community water systems were caused by problems at water treatment plants; the other seven resulted from problems in the water distribution systems and plumbing of individual facilities (e.g., a restaurant). Six of the seven outbreaks were associated with chemical contamination of the drinking water; the seventh outbreak was attributed to a small round structured virus. Four of the seven outbreaks occurred because of backflow or backsiphonage through a cross-connection, and two occurred because of high levels of copper that leached into water after the installation of new plumbing. For three of the four outbreaks caused by contamination from a cross-connection, an improperly installed vacuum breaker or a faulty backflow prevention device was identified; no protection against backsiphonage was found for the fourth outbreak.

Thirty-seven outbreaks from 17 states were attributed to recreational water exposure and affected an estimated 9,129 persons, including 8,449 persons in two large outbreaks of cryptosporidiosis. Twenty-two (59.5%) of these 37 were outbreaks of gastroenteritis; nine (24.3%) were outbreaks of dermatitis; and six (16.2%) were single cases of primary amebic meningoencephalitis caused by *Naegleria fowleri*, all of which were fatal. The etiologic agent was identified for 33 (89.2%) of the 37 outbreaks. Six (27.3%) of the 22 outbreaks of gastroenteritis were caused by *Cryptosporidium parvum* and six (27.3%) by *E. coli* O157:H7. All of the latter were associated with unchlorinated water (i.e., in lakes) or inadequately chlorinated water (i.e., in a pool). Thirteen (59.1%) of these 22 outbreaks were associated with lake water, eight (36.4%) with swimming or wading pools, and one (4.5%) with a hot spring. Of the

nine outbreaks of dermatitis, seven (77.8%) were outbreaks of *Pseudomonas dermatitis* associated with hot tubs, and two (22.2%) were lake-associated outbreaks of swimmer's itch caused by *Schistosoma* species.

Interpretation:

WBDOs caused by *E. coli* O157:H7 were reported more frequently than in previous years and were associated primarily with recreational lake water. This finding suggests the need for better monitoring of water quality and identification of sources of contamination. Although protozoan parasites, especially *Cryptosporidium* and *Giardia*, were associated with fewer reported outbreaks than in previous years, they caused large outbreaks that affected a total of approximately 10,000 persons; all of the outbreaks of cryptosporidiosis were associated with recreational water, primarily swimming pools.

Prevention of pool-associated outbreaks caused by chlorine-resistant parasites (e.g., *Cryptosporidium* and to a lesser extent *Giardia*) is particularly difficult because it requires improved filtration methods as well as education of patrons about hazards associated with fecal accidents, especially in pools frequented by diaper-aged children. The proportion of reported drinking water outbreaks associated with community water systems that were attributed to problems at water treatment plants has steadily declined since 1989 (i.e., 72.7% for 1989–1990, 62.5% for 1991–1992, 57.1% for 1993–1994, and 30.0% for 1995–1996). This decrease might reflect improvements in water treatment and in operation of plants. The outbreaks attributed to contamination in the distribution system suggest that efforts should be increased to prevent cross-connections, especially by installing and monitoring backflow prevention devices.

Actions Taken: Surveillance data that identify the types of water systems, their deficiencies, and the etiologic agents associated with outbreaks are used to evaluate the adequacy of current technologies for providing safe drinking and recreational water. In addition, they are used to establish research priorities and can lead to improved water-quality regulations.

Some organisms are harder to inactivate than others. This is especially true of the spore formers and the protozoans. An example for heat disinfection is shown in Table 9.1.

The type of disinfectant is also important. The following generally holds true:

Microbe type: vegetative bacteria–viruses–protozoan cysts, spores, and eggs

least resistant ----- most resistant

Disinfectant: O₃–ClO₂–iodine/freechlorine–chloramines

Giardia: best -----worst

TABLE 9.1 Comparison of Bacterial Disinfection Rates

Organism	Relative Resistance
<i>E. Coli</i>	1
Bacterial spores	3,000,000
Mold spores	2–10
Viruses and bacteriophages	1–5

Source: O. Rahn, Physical Methods of Sterilization of Microorganisms. Bacteriological Reviews, vol. 9, 1945, pp. 1–7.

The effectiveness of the disinfectant varies with the type of microbe and chemical and environmental factors.

Microbial aggregation: protects interior microbes from inactivation

Water quality: Particulates: protect microbes from inactivation

Dissolved organics: protects; consumes disinfectant; coats microbes.

Inorganic compounds and ions: effects vary with disinfectant

pH: effects depend on disinfectant.

Free chlorine more biocidal at low pH where HOCl predominates.

Chlorine dioxide more microbiocidal at high pH.

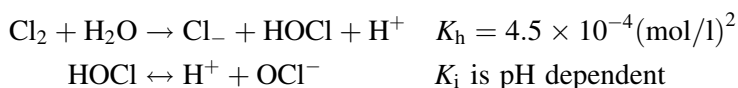
Free chlorine is still the most commonly used disinfectant.

Maintaining disinfectant residual during treated water storage and distribution is essential. It is a problem for O₃ and ClO₂ because they do not leave residuals and the water can be reinfected fairly easily. For these compounds, a secondary disinfectant must be used to provide a satisfactory residual. Most commonly the disinfectant chosen is chlorine.

See Figures 9.2 and 9.3 on virus and bacterial inactivation. These figures are taken from the WEF MOP #8 on Wastewater Treatment Plant Design.

CHLORINE

Silver and heat are probably the oldest disinfectants, but chlorine has got the most acceptance. Chlorine disassociates in water. The reactions are as follows:



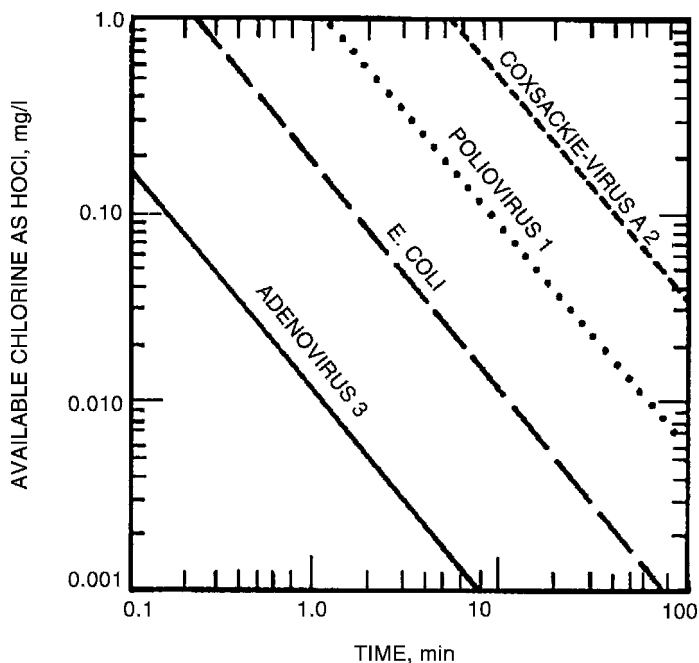


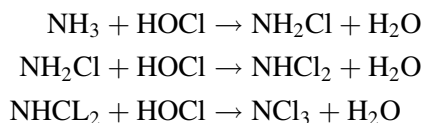
FIGURE 9.2 Time vs. concentration for 99% kill of *E. coli* and three viruses of hypochlorous acid at 0°C–6°C.

Consider the following:

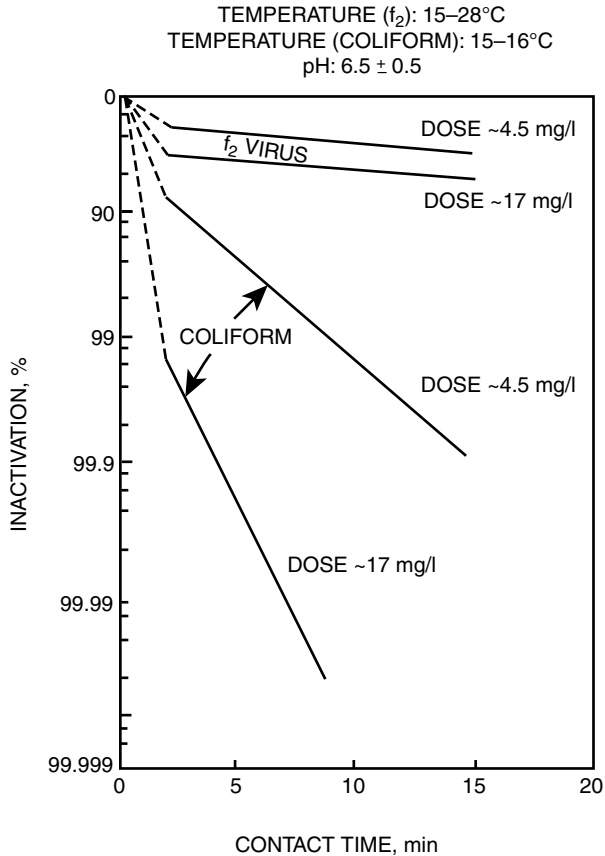
The most effective form of disinfectant is the HOCl form. By applying the pH and speciating the OCl and HOCl forms, it is possible to calculate the required dose of chlorine for a specific kill based upon pH (Fig. 9.4).

Ammonia, Chlorine, and Chloramines

Free ammonia combines with the HOCl form of chlorine to form chloramines in a three-step reaction.



When the $\text{pH} > 6$ and $[\text{HOCl}]/[\text{NH}_3]$ is around 1, monochloramine predominates. The reason for the detailed explanation is that chloramines are also a form of disinfectant—not as effective as HOCl, but as a disinfectant nonetheless.



Viral and bacterial inactivation at a 5700 m^3/day (1.5 mgd) conventional activated sludge plant conditions. The f_2 bacterial virus was seeded in the secondary settling basin at a titer of approximately 10^6 plaque forming units/ml. Chlorine dosages were approximately 4.5 and 17 mg/l.

FIGURE 9.3 f_2 Virus and coliform inactivation in a chlorine contact tank under controlled conditions. Viruses are often more difficult to kill than are coliform and nonspore forming organisms.

When the molar ratio of chlorine to ammonia is substantially above 2, dechlorination of the hypochlorite / hypochlorous ions occurs because of the formation of chloramines. The concentration of residual chlorine first rises then falls then rises again, as shown in Figure 9.5.

Chloramines have some disinfecting power, but their ability to inactivate viruses and especially spore formers such as *Giardia* is quite limited. Chloramines have been in use as disinfectants since the early 1900s but the

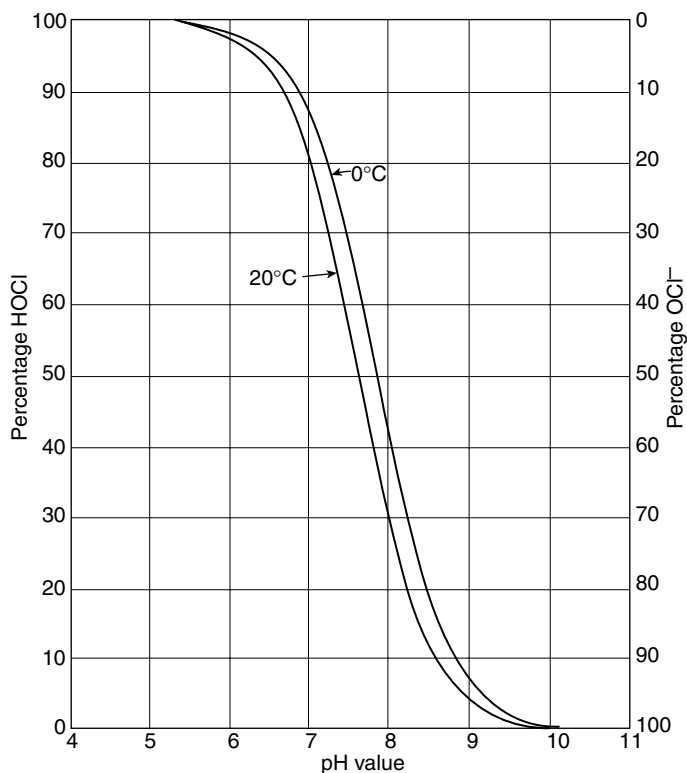
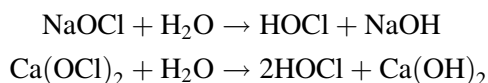


FIGURE 9.4 Distributions of hypochlorous and hypochlorite ions in water at various pH levels.

use is limited because of the expense of generation and relatively poor effectiveness against several common types of pathogens.

Other Types of Chlorine

Chlorine comes in a variety of forms. The most common are calcium hypochlorite (tablet and powder) and sodium hypochlorite (liquid). Both compounds are basic. The disassociation reactions are as follows:



Sodium hypochlorite (concentrated liquid bleach) and calcium hypochlorite tablet and powder (dry bleach and disinfecting tablets and powders) can react violently with organics and fuels, and are corrosive to clothing.

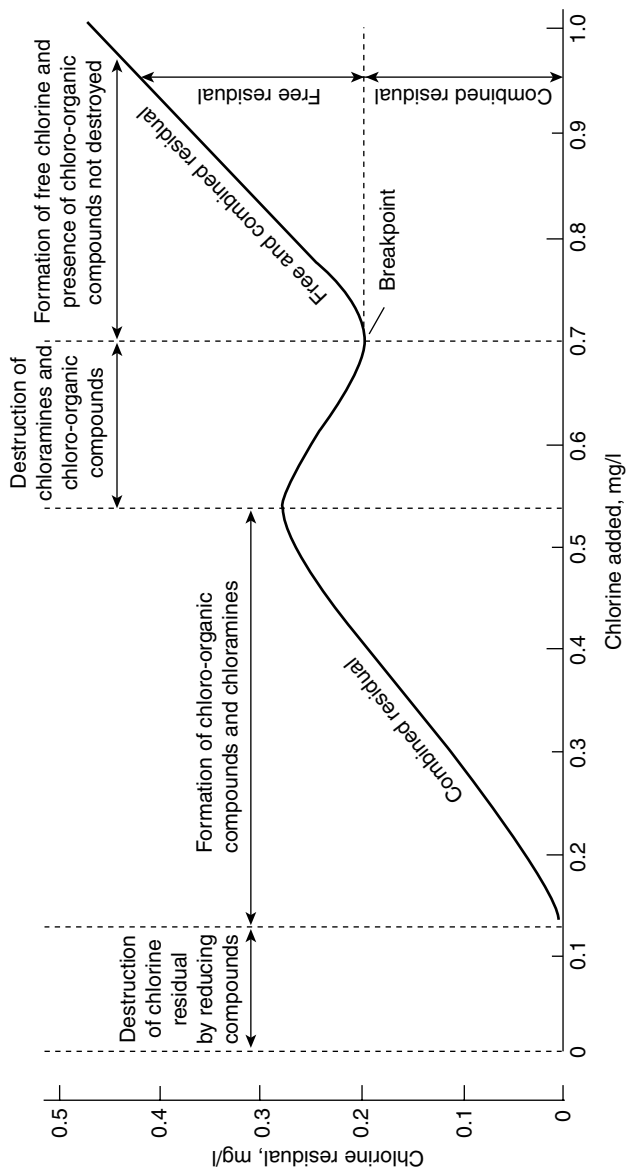


FIGURE 9.5 Break point chlorination by the formation of chloramines. The free chlorine residuals first rises then falls until the reaction with ammonia have been completed. As additional chlorine is applied and ammonia is consumed, the chlorine residual again rises.

When reacted with acids, violent explosions have been known to occur. The resulting gas is chlorine gas and hydrogen. Because it is a powerful oxidizer, it must be properly stored away from any potential fuels or reactive metals, including aluminum. There are a number of situations when people have been killed from the explosion resulting from the accidental mixing of drain cleaner [usually a sodium salt of sulfuric acid (NaHSO_4)] or the acid itself (H_2SO_4) and powdered bleach ($\text{Ca}(\text{OCl})_2$) in trying to clean out a toilet bowl. There are an equally large number of cases of reported fires when a homeowner attempts to store oily rags in a container of calcium hypochlorite disinfecting powder, which has not been properly cleaned out and still contains powder residues.

Other Reactions with Chlorine

Chlorine in water will oxidize iron, manganese, chromium, arsenic, and a variety of other compounds. In the case of the latter two compounds the higher valence is of more toxic. It is extremely effective in oxidizing these compounds, especially at pH less than 7. It will also react with natural organic compounds such as tannins from leaves and will form trihalomethanes, chloroform, and other probable human carcinogens.⁴ However, the use of the word “probable” is subject to interpretation. Various lobby groups are against the use of chlorine for a variety of reasons, and while some of the halomethanes are actual carcinogens, there is scant evidence that chlorinated drinking water will cause cancer from halomethanes, especially when the risk of not using chlorine is considered.

Chlorine forms chlorate ions that are also “suspect” compounds. The EPA is currently regulating disinfection by-products (DBP’s) in municipal water supplies.

Chlorine Safety

Chlorine gas is corrosive, oxidizing, toxic, and denser than air and should be handled accordingly, with extreme caution. It can react violently with a number of compounds.

The EPA has designated chlorine as a toxic gas under Section 313 of SARA and Section 112r of the Clean Air Act. As such, anyone handling quantities in excess of 200 lb may have to fulfill special notification requirements under Section 313 and if the total quantity stored is in excess of 2500 lb of chlorine, special evacuation and community notification plans will be mandatory

⁴<http://www.epa.gov/safewater/mbdp/mbdptg.html#disinfect>.

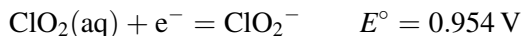
under U.S. law. It is important to note that in the United States a one-ton cylinder of chlorine may create a “theoretical” evacuation distance around the source of almost 2 miles.⁵

Chlorine Dioxide

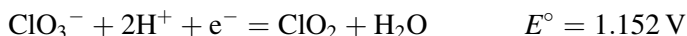
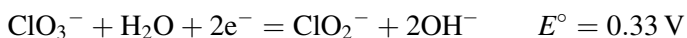
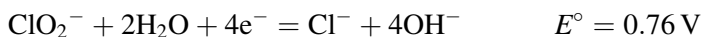
Chlorine dioxide (ClO_2) is a neutral compound of chlorine in the +IV oxidation state. It disinfects by oxidation; however, it does not chlorinate. It is a relatively small, volatile, and highly energetic molecule, and a free radical even while in dilute aqueous solutions. At high concentrations, it reacts violently with reducing agents. However, it is stable in dilute solution in a closed container in the absence of light.

Chlorine dioxide functions as a highly selective oxidant owing to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-).

The $\text{p}K_a$ for the chlorite ion, chlorous acid equilibrium, is extremely low at pH 1.8. This is remarkably different from the hypochlorous acid/hypochlorite base ion pair equilibrium found near neutrality and indicates that the chlorite ion will exist as the dominant species in drinking water. The oxidation-reduction of some key reactions are as follows:



Other important half reactions are



Chlorine dioxide is always generated on-site because it is explosive when compressed. It also reacts violently with sunlight and/or UV light with explosive decomposition. It is generated from sodium chlorite and sodium chlorate.

Chlorine dioxide is less pH sensitive than chlorine and may be equally as effective as a disinfectant. However, it costs substantially more than chlorine. Because of the air hazards associated with chlorine, and the problems associated with the treatment of various by-products of disinfection and concerns about the formation of dioxins from chlorination, chlorine dioxide has seen a

⁵See 40 CFR 68 for requirements and threshold requirements.

resurgence in the paper industry in the pulp bleaching area. However, it is still not as economical as chlorine.

OZONE

Ozone has the following properties:

Ozone exists as a gas at room temperature. The gas is colorless with a pungent odor readily detectable at concentrations as low as 0.02 ppm–0.05 ppm (by volume), which is below concentrations of health concern. Ozone gas is highly corrosive and toxic.

Ozone is a powerful oxidant, second only to the hydroxyl free radical, among chemicals typically used in water treatment. Therefore, it is capable of oxidizing many organic and inorganic compounds in water. These reactions with organic and inorganic compounds cause an ozone demand in the water treated, which should be satisfied during water ozonation prior to developing a measurable residual.

Ozone is slightly soluble in water. At 20°C, the solubility of 100% ozone is only 570 mg/l as compared with about 11.3 mg/l for oxygen. Typical concentrations of ozone found during drinking water treatment range from <0.1 mg/l to 1 mg/l, although higher concentrations can be attained under optimum conditions.

Ozone decomposes spontaneously during water treatment by a complex mechanism that involves the generation of hydroxyl free radicals. The hydroxyl free radicals are among the most reactive oxidizing agents in water, with reaction rates in the order of 10^{10} – $10^{13} \text{ M}^{-1} \text{ s}^{-1}$. The half-life of hydroxyl free radicals is in the order of microseconds; therefore, concentrations of hydroxyl free radicals can never reach levels above 10^{-12} M .

- In the presence of many compounds commonly encountered in water treatment, ozone decomposition forms hydroxyl free radicals. The oxidation of many types of naturally occurring organic matter leads to the formation of aldehydes, organic acids, and aldo- and ketoacids.
- Ozone can mineralize some organic materials if the pathway is predominantly one of hydroxyl radical oxidation.
- Oxidation of bromide ion leads to the formation of hypobromous acid, hypobromite ion, bromate ion, brominated organics, and bromamines.
- Bicarbonate or carbonate ions, commonly measured as alkalinity, will scavenge the hydroxyl radicals and form carbonate radicals.

Ozone Production

Because ozone is an unstable molecule, it should be generated at the point of application for use in water treatment. It is generally formed by combining an oxygen atom with an oxygen molecule (O_2):



This reaction is endothermic and requires a considerable input of energy. Ozone was first discovered by the electrolysis of sulfuric acid. Ozone can be produced by several ways, although one method, corona discharge, predominates in the ozone generation industry. Ozone can also be produced by irradiating an oxygen-containing gas with ultraviolet light and electrolytic reaction.

Corona discharge, also known as silent electrical discharge, consists of passing an oxygen-containing gas through two electrodes separated by a dielectric and a discharge gap. Voltage is applied to the electrodes, causing an electron flow through across the discharge gap. These electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone. The following figure shows a basic ozone generator (Fig. 9.6).

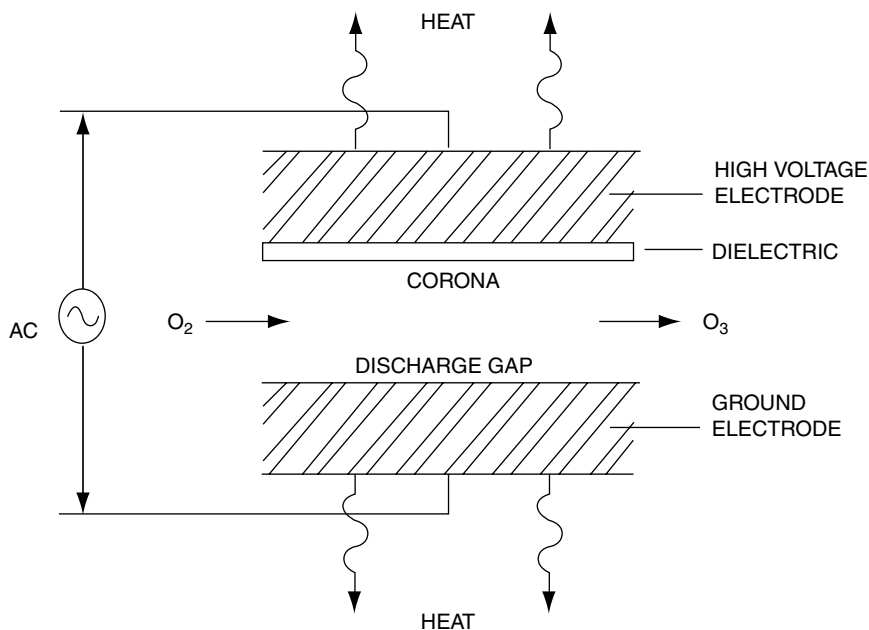


FIGURE 9.6 Schematic drawing of corona discharge method for making ozone.

ULTRAVIOLET LIGHT

Ultraviolet or UV light is a bacterial disinfectant. It carries no residual. It requires clear, un-turbid, and noncolored water for its use. Most commercial disinfection systems operate low to medium powered UV lamps and the technology currently in use focuses on a wavelength of about 354 nm (Figs. 9.7 and 9.8).

The UV dosage is calculated as

$$D = I \cdot t$$

where D = UV dose ($\text{mW} \cdot \text{s}/\text{cm}^2$); I = Intensity (mW/cm^2); t = exposure time (s).

Research indicates that when microorganisms are exposed to UV radiation, a constant fraction of the living population is inactivated during each progressive increment in time. This dose–response relationship for germicidal effect indicates that high-intensity UV energy over a short period of time would provide the same kill as a lower intensity UV energy at a proportionally longer period of time.

The UV dose required for effective inactivation is determined by site-specific data relating to the water quality and log removal required. On the basis of first-order kinetics, the survival of microorganisms can be calculated as a function of dose and contact time.

The advantage of UV is that, for waters with high transmittance, it is directly effective against the DNA of many organisms, is not reactive with other forms of carbonaceous demand, and can give good bactericidal kill values while not leaving any residue or chlorites, or trihalomethanes.

The advantage is often the disadvantage, because power fluctuations, variations in hydraulic flow rates, and color or turbidity can cause the treatment to be ineffective. Also recently, some discussion of cell recovery and repair from UV exposure, with a consequent rapid recovery and regrowth of the damaged organisms because of the inactivation of their predators and competitors, has come to light.

OTHER DISINFECTING COMPOUNDS

Potassium Permanganate

Potassium permanganate is highly reactive under conditions found in the water industry. It will oxidize a wide variety of inorganic and organic substances. Potassium permanganate (Mn^{7+}) is reduced to manganese

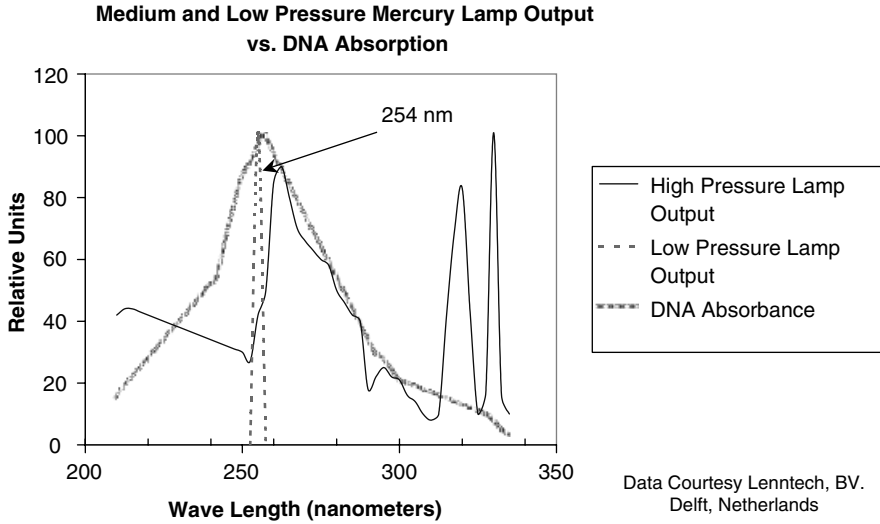
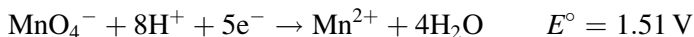


FIGURE 9.7 UV spectra for various lamps. The medium pressure lamp has the spectra almost precisely at the 357nm range where the disinfection is most effective.



FIGURE 9.8 Horizontal lamps in a UV disinfection unit. The other potential configuration is with vertical lamps. In both cases, the flow is along the length of the lamps.

dioxide (MnO_2) (Mn^{4+}), which precipitates out of solution. All reactions are exothermic. Under acidic conditions the oxidation half-reactions are



Under alkaline conditions, the half-reaction is



Reaction rates for the oxidation of constituents found in natural waters are relatively fast and depend on temperature, pH, and dosage.

Potassium permanganate is a good oxidant but not a very good disinfectant. Its primary uses are taste and odor control, and like HOCl it is more effective as a disinfectant under acidic conditions down to a pH of about 5.9. Under alkaline conditions, it is very powerful as an oxidant but less so as a disinfectant.

Hydrogen Peroxide and Ozone

Hydrogen peroxide is a liquid with the formulation H_2O_2 . There is a bit of a debate over the exact mechanism of disinfection. Hydrogen peroxide is not much of a disinfectant by itself, but in combination with ozone it has powerful disinfection properties. The combination is called peroxone. Until recently there was a large debate on whether or not peroxones even existed. One school of thought discusses the formation of peroxones, another school of thought states that the peroxones do not exist.⁶ Hydrogen peroxide or ultraviolet radiation accelerates the decomposition of ozone and increases the hydroxyl radical concentration. By adding hydrogen peroxide, the net production of hydroxyl free radicals is 1.0 mole hydroxyl radical per mole ozone. The two principal methods of disinfection are (1) direct oxidation of compounds by aqueous ozone ($\text{O}_{3(\text{aq})}$) and (2) oxidation of compounds by hydroxyl radicals produced by the decomposition of ozone. Dosage levels for peroxide and ozone are generally in the order of 5 mg/l each with ratios of peroxide/ozone between 0.5 and 0.8 and detention times greater than 5 min but less than 20 min.

The two oxidation reactions compete for substrate (i.e., compounds to oxidize). The ratio of direct oxidation with molecular ozone is relatively slow (10^{-5} – $10^7 \text{ M}^{-1} \text{ s}^{-1}$) compared with hydroxyl radical oxidation

⁶A paper by Xin Xu and William A Goddard III published in the November 2002, Proc. National Academy of Sciences, Vol. 99, No. 24 has done much to identify the complex formation of peroxones—see “Peroxone Chemistry: Formation of H_2O_3 and ring $(\text{HO}_2)(\text{HO}_3)$ from $\text{O}_3/\text{H}_2\text{O}_2$.”

(10^{12} – 10^{14} M⁻¹ s⁻¹). The hydroxyl radical reactions are very fast, but the concentration of hydroxyl radicals under normal ozonation conditions is relatively small.

A key difference between the ozone and peroxone processes is that the ozone process relies heavily on the direct oxidation of aqueous ozone while peroxone relies primarily on oxidation with hydroxyl radical, which is a powerful oxidant in its own right. In the peroxone process, the ozone residual is short-lived because the added peroxide greatly accelerates the ozone decomposition. The oxidation by the hydroxyl radical more than compensates for the reduction in direct ozone oxidation because the hydroxyl radical is much more reactive. The net result is that oxidation is more reactive and much faster in the peroxone process compared with the ozone molecular process. However, because an ozone residual is required for determining disinfection CT credit, peroxone may not be appropriate as a pre-disinfectant.

Because the ozone peroxide radical oxidation is much more vigorous and effective than with ozone oxidation alone, it is being used to treat organics, which are difficult to oxidize, such as taste and odor compounds and chlorinated organics (PERC and TCE) and reactive materials including explosives in the groundwater.

Neither ozone nor peroxone significantly destroys TOC. Peroxone will oxidize the saturated hydrocarbons and produce by-products such as aldehydes, ketones, peroxides, bromate ion, and biodegradable organics. However, because the peroxone is a “more powerful and rigorous oxidant,” the organic material is subsequently rendered more amenable to hydrolysis and subsequent oxidation by bacterial compounds and can be biodegraded.

pH and bicarbonate alkalinity play a major role in peroxone effectiveness because the carbonate/bicarbonate system competes for hydroxyl radical at high alkalinity and at high pH levels. The presence of fine particulate solids causing turbidity does not affect the effectiveness of peroxone treatment, and the presence of peroxones will not necessarily reduce turbidity.

Table 9.2 summarizes the key differences between ozone and peroxone as they relate to their application in drinking water treatment.⁷ The comparisons are similar for wastewater treatment.

Bromine and Iodine

Bromine Bromine has been used as a disinfectant in a number of applications. It has good toxicity, is a liquid at room temperatures (while chlorine is a gas at room temperature) is somewhat easier to handle than chlorine.

⁷Alternative Disinfectants and Oxidants Guidance Manual EPA 815-R-99-014, April 1999.

TABLE 9.2 Comparison Between Ozone and Peroxone Oxidation

Process	Ozone	Peroxone
Ozone decomposition rate	“Normal” decomposition producing hydroxyl radical as an intermediate product	Accelerated ozone decomposition increases the hydroxyl radical concentration above that of ozone alone
Ozone residual	5–10 min	Very short-lived owing rapid reaction
Oxidation path	Usually direct aqueous molecular ozone oxidation	Primarily hydroxyl radical oxidation
Ability to oxidize iron and manganese	Excellent	Less effective
Ability to oxidize taste and odor compounds	Variable	Good, hydroxyl radical more reactive than ozone
Ability to oxidize chlorinated organics	Poor	Good, hydroxyl radical more reactive than ozone
Disinfection ability	Excellent	Good, but systems can only receive CT credit if they have a measurable ozone residual
Ability to detect residual for disinfection monitoring	Good	Poor, cannot calculate CT value for disinfection credit

The chemistry of bromine is similar in many respects to the chemistry of chlorine; however, bromine cannot be used for shock treating (high dose disinfection) in the same manner as chlorine is used.

Bromine has a pH of 4.0–4.5. When bromine is added to water and an oxidizer is present, the bromine forms hypobromous acid (HOBr) and hypobromite ions (OBr). Like chlorine, the percentage of each is affected by pH. However, the effect is not as strong as it is with chlorine. Like chlorine, bromine combines with organic impurities to form combined bromine or bromamines. However, combined bromine is still an effective sanitizer, and it does not smell as strongly as chlorine. Bromine is substantially more expensive than chlorine. Consequently, it has fallen out of use as a commercial disinfectant except in swimming pools where it is still used, because it reportedly has less eye irritation than chlorine, but it has seen a resurgence in popularity because of the perceived hazards associated with chlorine gas. Bromine’s disinfectant power is also dependent upon pH as shown in Table 9.3.

TABLE 9.3 Ion Species of Bromine with pH (Compare to Fig. 9.4 for Chlorine)

HOBr Hypobromous Acid % Bromine as HOBr	pH	OBr ⁻ Hypobromite Ion % Bromine as OBr ⁻
100.0	6.0	0.0
99.4	6.5	0.6
98.0	7.0	2.0
94.0	7.5	6.0
83.0	8.0	17.0
57.0	8.5	43.0

Iodine⁸ Iodine kills bacteria and disease-causing organisms. Iodine is, however, ineffective as an algicide. Iodine has been in use to disinfect water since the early 1900s. In its natural state, iodine is a solid black crystal. The simplest method of disinfecting water with iodine is by dissolving iodine in water to form a saturated solution and then injecting the iodine solution into a water system.

Iodine does not kill bacteria on contact; a holding time of at least 20 min is needed depending on the iodine concentration. An iodine residual of 0.5–1.0 mg/l should be maintained, and iodine at this level gives the water little or no iodide taste or odor. Iodine can be removed from water with a carbon filter just before drinking.

Iodine dosage is highly temperature dependent—iodine crystals are more soluble at higher temperatures. Iodine remains effective over a wide range of pH and does not lose effectiveness until the pH of water reaches 10. Iodine residuals in water can easily be measured using a test kit that indicates a color change.

Iodine tablets were developed during World War II to disinfect small amounts of water for emergency or temporary use. A few drops of tincture of iodine or iodine tablets are popular with campers and the military for disinfecting water.

Types of Iodinator

Iodine solutions are injected into a water system using bypass saturator systems or injection pumps. A holding tank or coil of pipe is used after iodine injection to provide the necessary holding time.

⁸http://www.ag.ohio-state.edu/~ohioline/b795/b795_10.html.

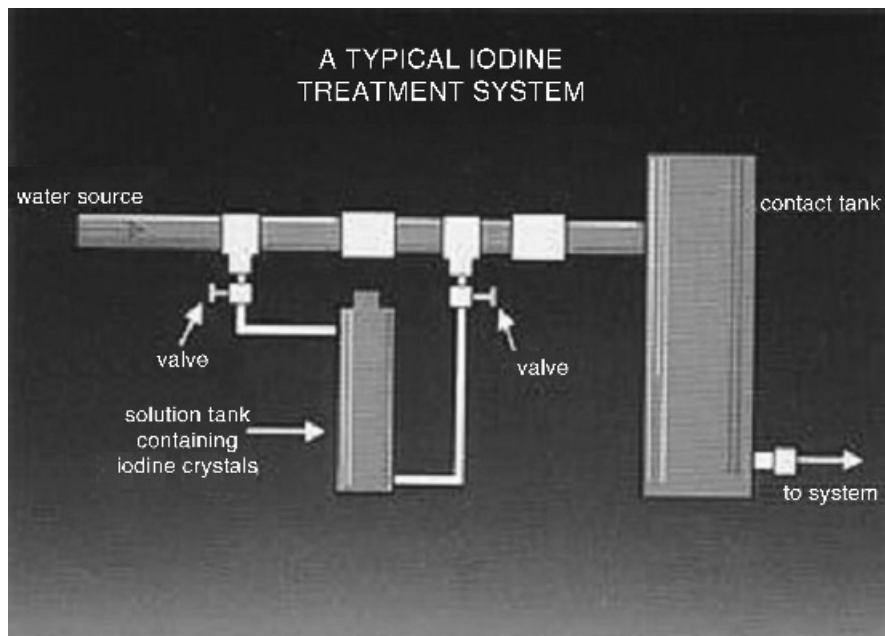


FIGURE 9.9 Schematic drawing of a bypass iodinator—United States patent 4555347.

The most common type of iodinator is called a bypass saturator and consists of a solution tank containing iodine crystals. Bypass saturators do not require any electrical connections. The solution tank is connected to the water system and diverts a small amount of water through it and back into the water line. Valves are placed on either side of the iodinator to control the iodine dose. Fluctuation in water temperature affects the solubility of iodine. Adjustments in the bypass rate are needed if water temperature changes.

Chemical injection pumps can also be used to inject iodine solutions for individual water treatment. These are the same injection systems that are used for chlorine.

Iodinators are in-line systems that are sized to treat all the water used in a household (Fig. 9.9).

Careful Use of Iodine

The question of possible health effects of iodine is still unanswered. No adverse health effects have been shown, yet continuous consumption of iodine-treated water is not recommended. Carbon filters can be used to

remove iodine just before drinking. Iodine is also appropriate for occasional use in vacation homes, campgrounds, and restaurants. Iodine treatment of drinking water supplies to dairy cattle is also a concern. Because dairy cattle can drink from 15 gallons to 30 gallons of water a day, and normal levels of iodine used for disinfection may cause iodine carryover into milk.