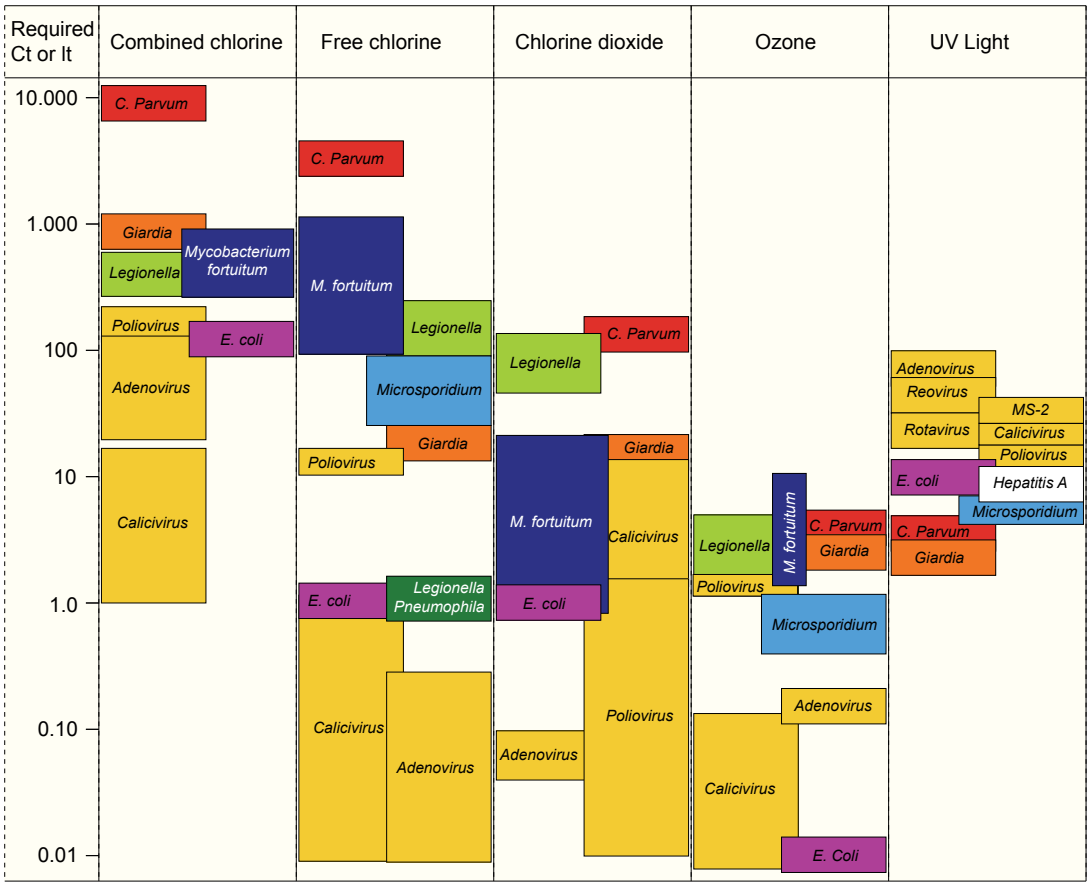
WATER TREATMENT

Disinfection



Framework

This module will describe the aspects of water disinfection. For this, the purpose of disinfection will be given, the kinetics, and the practical application.
The content of this module is abstracted from Alternative Disinfectants and Oxidants Guidance Manual (EPA 1999) and Water treatment: Principles and design (MWH 2005).

Contents

This module has the following contents:

1 Introduction

The most important use of disinfectants in water treatment is to limit waterborne diseases and inactivate pathogenic organisms in water supplies.
The first use of disinfection as a continuous process in water treatment took place in a small town in Belgium in the early 1900s (White, 1992), where chlorine was used as the disinfecting reagent.
Since the introduction of filtration and disinfection at water treatment plants, waterborne diseases, such as typhoid and cholera, have been virtually eliminated. For example, in Niagara Falls, NY, USA, between 1911 and 1915, the number of typhoid cases dropped from 185 deaths per 100,000 people to nearly zero following the introduction of filtration and chlorination (White, 1986).

For nearly a century, chlorine gas or chlorine reagents (hypochlorite, etc.) were, by far, the most commonly used disinfectant chemicals for drinking water production
In 1974, researchers in the Netherlands and the United States demonstrated that trihalomethanes (THMs) were being formed as a result of drinking water chlorination (Rook, 1974; Bellar et al., 1974).
THMs form when chlorine or bromide reacts with organic compounds in the water. THMs and other disinfection byproducts (DBPs) have been shown to be carcinogenic, mutagenic, etc. These health risks may be small but need to be taken seriously, when you consider the large population being exposed.

As a result of DBP concerns from chlorine, the water treatment industry has placed more emphasis on the use of disinfectants other than chlorine.
Some of these alternative disinfectants, however, have also been found to produce DBPs as a result of either reactions between disinfectants and compounds in the water or as a natural decaying process of the disinfectant itself (McGuire et al., 1990; Legube et al., 1989).
These DBPs include:

- halogenated organics, such as THMs, haloacetic acids, haloketones, and others that are produced primarily as a result of chlorination
- organic oxidation byproducts such as aldehydes, ketones, assimilable organic carbon (AOC), and biodegradable organic carbon (BDOC) that are associated primarily with strong oxidants such as ozone, chlorine, and advanced oxidation
- inorganics such as chlorate and chlorite associated with chlorine dioxide, and bromate that is associated with ozone, and has also been found when chlorine dioxide is exposed to sunlight.

The type and amount of DBPs produced during treatment depends largely on the type of disinfectant, water quality, treatment sequences, contact time, and environmental factors such as temperature and pH.

When considering the use of alternative disinfectants, systems should ensure that the inactivation of pathogenic organisms is not compromised.
Pathogens pose an immediate critical public health threat due to the risk of an acute disease outbreak.
Although most identified public health risks associated with DBPs are chronic, long-term risks, many systems will be able to lower DBP levels without compromising microbial protection.

In this module the purpose of disinfection is presented first. Thereafter, the DBPs are discussed, since they play an important role in the selection of the disinfection method.
After this, disinfection kinetics are presented.
Finally, an overview is given of the different disinfection methods, in which the pros and cons of the major methods are provided.

2 Purpose of disinfection

2.1 Diseases and drinking water

Although the epidemiological relationship between water and disease had been suggested as early as the 1850s, it was not until the development of the germ theory of disease by Pasteur in the mid-1880s that water as a carrier of disease-producing organisms was understood.

Table 1 - Waterborne diseases from bacteria

Causative agent	Disease	Symptoms
Salmonella typhosa	Typhoid fever	Headache, neasea, loss of appetite, constipation or diarrhea, insomnia, sore throat, bronchitis, abdominal pain, nose bleeding, shivering and increasing fever, rosy spots on trunk. Incubation period: 7 - 14 days.
S. paratyphi *S. schottinulleri* *S. hirschfeldi C.*	Paratyphoid fever	General infection characterized by continued fever, diarrhea disturbances, sometimes rosy spots on trunk. Incubation period: 1 - 7 days.
Shigella flexneri *Sh. dysenteriae* *Sh. sonnei* *Sh. paradysinteriae*	Bacillary dysentery	Acute onset with diarrhea, fever, tenesmus and stool frequently containing mucus and blood. Incubation period: 1 - 7 days.
Vibrio comma *V. Cholerae*	Cholera	Diarrhea, vomiting, rice water stools, thirst, pain, coma. Incubation period: a few hours to 5 days.
Pasteurellla tularensis	Tularemia	Sudden onset with pains and fever; prostration. Incubation period: 1 - 10 days.
Brucella melitensis	Brucellosis (undulant fever)	Irregular fever, sweating, chills, pain in muscles.
Pseudomonas pseudomallei	Melioidosis	Acute diarrhea, vomiting, high fever, delerium, mania.
Leptospira icterohaemorrhagiae (spirochaetales)	Leptospirosis (Well's disease)	Fevers, rigors, headaches, nausea, muscular pains, vomiting, thirst, prostration and jaundice may occur.
Enteropathogenic *E. coli*	Gastroenteritis	Water diarrhea, nausea, prostration and dehydration.

In the 1880s, while London was experiencing the "Broad Street Well" cholera epidemic, Dr. John Snow conducted his now famous epidemiological study. Dr. Snow concluded that the well had become contaminated by a visitor with the disease who had arrived in the vicinity.
Cholera was one of the first diseases to be recognized as capable of being waterborne.
Also, this incident was probably the first reported disease epidemic attributed to the direct recycling of non-disinfected water.

Now, over 100 years later, the list of potential waterborne diseases due to pathogens is considerably longer, and includes bacterial, parasitic, and viral microorganisms, as shown in Tables 1, 2 and 3, respectively.

A major cause for the number of disease outbreaks in potable water is contamination of the distribution system from cross-connections and back siphoning with non-potable water. However, outbreaks resulting from distribution system contamination are usually quickly contained and result in relatively few illnesses compared to the many cases of illness per incident when there is contamination of the source water or a breakdown in the treatment system.
When considering the number of cases, the major causes of disease outbreaks are source water contamination and treatment deficiencies (White, 1992). For example, in 1993 a Cryptosporidiosis outbreak affected over 400,000 people in Milwaukee, Wisconsin (USA). The outbreak was associated with deterioration in the raw water

Table 2 - Waterborne diseases from Parasites (Protozoa)

Causitive agent	Disease	Symptoms
Ascario lumricoidis (round worm)	Ascariasis	Vomiting, live worms in feces.
Cryptosporidium muris *Cryptosporidium parvum*	Cryptosporidiosis	Acute diarrhea, abdominal pain, vomitin, and low-grade fever. Can be life-threatening in immunodeficient patients.
Entamoeba histolytica	Amebiasis	Diarrhea alternating with constipation, chronic dysentery with mucus and blood.
Giardia lamblia	Giardiasis	Intermittent diarrhea.
Naegleria gruberi	Amoebid menigoecephalitis	Death.
Schistosoma mansoni	Schistosomiasis	Liver and bladder infection.
Taenia saginata (beef tapeworm)	Taeniasis	Abdominal pain, digestive disturbances, loss of weight.

Table 3 - Waterborne diseases from Human Enteric Viruses

Causative agent	Disease	Symptoms
Enterovirus Polio (3)	Muscular paralysis	Destruction of motor neurons
	Aseptic meningitis	Inflammation of meninges from virus
	Febrille episode	Viremia and viral multiplication
Enterovirus Echo (34)	Aseptic meningitis	Inflammation of meninges from virus
	Muscular paralysis	Destruction of motor neurons
	Guillain-Barre's Syndrome[1]	Destruction of motor neurons
	Exanthem	Dilation and rupture of blood vessels
	Respiratory diseases	Viral invasion of parechymiatous of respiratory tracts and secondary inflammatory responses intestinal infections
	Diarrhea	Not well known
	Epidemic myalgia	Viral invasion of cells with secondary infammatory responses
	Pericardits and myocarditis	Invasion of parencheyma cells
	Hepatitis	
Enterovirus Coxsackie (>24)	Herpengina[2]	Viral invasion of mucosa with secondary inflammation
Enterovirus A	Aculte lymphatic pharyngitis	Sore throat, pharyngeal lesions
	Aseptic meningitis	Inflammation of meninges from virus
	Muscular paralysis	Destruction of motor neurons
	Hand-foot-mouth disease[3]	Viral invasions of skin cells of hands-feet-mouth
	Respiratory disease	Viral invasion of parenchymiatous of respiratory tracts and secondary infammatory responses
		Viral invasion of cells of mucosa
	Infantile diarrhea	Viral invasion of parenchyma cells
	Hepatitis	Viral invasion of cells with secondary inflammatory responses
	Pericarditis and myocarditis	
Enterovirus B (6)	Pleurodynia[4]	Viral invasion of muscle cells
	Aseptic meningitis	Inflammation of meninges from virus
	Muscular paralysis	Destruction of motor neurons
	Meningoencephalitis	Viral invasion of cells
	Pericarditis, endocarditis, myocarditis	Viral invasion of cells with secondary inflammatory responses
	Respiratory disease	Viral invasion of parenchymiatous of respiratory tracts and secondary inflammatory responses
		Invasion of parenchyma cells
	Hepatitis or Rash	Viral invasion of vascular cells
	Spontaneous abortion	Viral invasion of insulin-producing cells
	Insulin-dependent diabetes	Viral invasion muscle cells
	Congenital heart anomalies	
Reovirus (6)	Not well known	Not well known
Adenovirus (31)	Respiratory diseases	Viral invasion of parenchymiatous of respiratory tracts and secondary inflammatory responses
		Viral invasion of cells and secondary inflammatory responses
	Acute conjunctivitis	Viral invasion of mucosa cells
		Viral invasion of lymph nodes
	Acute appendicitis	Viral invasion of parenchyma cells
	Intussusception	Sarcoma in hamsters
	Subacute thyroiditis	
	Sarcoma in hamsters	
Hepatitis (>2)	Infectious hepatitis	Invasion of parenchyma cells
	Serum hepatitis	Invasion of parenchyma cells
	Down's syndrome	Invasion of cells

quality and a simultaneous decrease in the effectiveness of the coagulation-filtration process (Kramer et al., 1996; MacKenzie et al., 1994).

Historically, about 46 percent of the outbreaks in public water systems are found to be related to deficiencies in source water and treatment systems, with 92 percent of the causes of illness due to these two particular problems.

All natural waters support biological communities. Because some microorganisms can be responsible for public health problems, the biological characteristics of the source water are one of the most important parameters in water treatment.

In addition to public health problems, microbiology

Table 4 - Attributes of the three waterborne pathogens of concern in water treatment

Organism	Size (μm)	Mobility	Point(s) of origin	Resistance to disinfection	Removal by sedimentation, coagulation and filtration
Bacteria	0.1 - 10	Motile, Nonmotile	Humans and animals, water and contaminated food	Type specific - bacterial spores typically have the highest resistance whereas vegetative bacteria have the lowest resistance	Good, 2 to 3 - log removal
Viruses	0.01 - 0.1	Nonmotile	Humans and animals, polluted water, and contaminated food	Generally more resistant than vegetative bacteria	Poor, 1 to 3 - log removal
Protozoa	1 - 20	Motile, Nonmotile	Humans and animals, sewage, decaying vegetation, and water	More resistant than viruses or vegetative bacteria	Good, 2 to 3 - log removal

can also affect the physical and chemical water quality and treatment plant operation.

2.2 Pathogens of primary concern

Table 4 shows the attributes of three groups of pathogens of concern in water treatment, namely bacteria, viruses, and protozoa.

Bacteria

Bacteria are single-celled organisms typically ranging in size from 0.1 to 10 μm.
Shape, components, size, and the manner in which they grow can characterize the physical structure of the bacterial cell.

Most bacteria can be grouped by shape into four general categories: spheroid, rod, curved rod or spiral, and filamentous.
Cocci, or spherical bacteria, are approximately 1 to 3 μm in diameter.
Bacilli (rod-shaped bacteria) vary in size and range from 0.3 to 1.5 μm in width (or diameter) and from 1.0 to 10.0 μm in length.
Vibrios, or curved rod-shaped bacteria, typically vary in size from 0.6 to 1.0 μm in width (or diameter) and from 2 to 6 μm in length.
Spirilla (spiral bacteria) can be found in lengths up to 50 μm, whereas filamentous bacteria can occur in lengths in excess of 100 μm.

Viruses

Viruses are microorganisms composed of the genetic material deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) and a protective protein coat (single-, double-, or partially double-stranded).

All viruses are obligate parasites, unable to carry out any form of metabolism and are completely dependent upon host cells for replication.
Viruses are typically 0.01 to 0.1 μm in size and are very species specific with respect to infection, typically attacking only one type of host.
Although the principal modes of transmission for the hepatitis B virus and poliovirus are through food, personal contact, or exchange of body fluids, these viruses can also be transmitted through potable water.
Some viruses, such as the retroviruses (including the HIV group), appear to be too fragile for water transmission to be a significant danger to public health (Riggs, 1989).

Protozoa

Protozoa are single-cell eucaryotic microorganisms without cell walls that utilize bacteria and other organisms for food.

Most protozoa are free-living in nature and can be encountered in water; however, several species are parasitic and live on or in host organisms.
Host organisms can vary from primitive organisms such as algae to highly complex organisms such as human beings.
Several species of protozoa known to utilize human beings as hosts are shown in Table 5.

2.3 Recent waterborne outbreaks

Within the past 40 years, several pathogenic

agents never before associated with documented waterborne outbreaks have appeared in the drinking water industry.

Enteropathogenic *E. coli* and *Giardia lamblia* were first identified as the etiological agents responsible for waterborne outbreaks in the 1960s.
The first recorded *Cryptosporidium* infection in humans occurred in the mid-1970s. Also during that time was the first recorded outbreak of pneumonia caused by *Legionella pneumophila* (Centers for Disease Control, 1989; Witherell et al., 1988).

Recently, there have been numerous documented waterborne disease outbreaks that have been caused by *E. coli, Giardia lamblia, Cryptosporidium*, and *Legionella pneumophila*.

E-coli
The first documented case of waterborne disease outbreaks associated with enteropathogenic *E. coli* occurred in the 1960s in the United States.
Various serotypes of *E. coli* have been implicated as the etiological agent responsible for disease in newborn infants, usually the result of cross-contamination in nurseries.
Now, there have been several well-documented outbreaks of *E. coli* (serotypes 0111:B4 and 0124:B27) associated with adult waterborne disease (AWWA, 1990, and Craun, 1981).
In 1975, the etiologic agent of a large outbreak at Crater Lake National Park was *E. coli* serotype 06:H16 (Craun, 1981).

Giardia lamblia
Similar to *E. coli*, *Giardia lamblia* was first identified in the 1960s to be associated with waterborne outbreaks in the United States.
Giardia lamblia is a flagellated protozoan that is responsible for Giardiasis, a disease that can range from being mildly to extremely debilitating.

Giardia is currently one of the most commonly identified pathogens responsible for waterborne disease outbreaks.
The life cycle of *Giardia* includes a cyst stage when the organism remains dormant and is extremely resilient (i.e., the cyst can survive some extreme environmental conditions).
Once ingested by a warm-blooded animal, the life cycle of *Giardia* continues with excystation.
The cysts are relatively large (8-14 µm) and can be removed effectively by filtration using diatomaceous earth, granular media, or membranes.

Giardiasis can be acquired by ingesting viable cysts from food or water or by direct contact with fecal material.
In addition to humans, wild and domestic animals have been implicated as hosts.
Between 1972 and 1981, 50 waterborne outbreaks of Giardiasis occurred with about 20,000 reported cases (Craun and Jakubowski, 1986).
Currently, no simple and reliable method exists to assay *Giardia* cysts in water samples.
Microscopic methods for detection and enumeration are tedious and require examiner skill and patience. *Giardia* cysts are relatively resistant to chlorine, especially at higher pH levels and low temperatures.

Cryptosporidium
Cryptosporidium is a protozoan similar to *Giardia*. It forms resilient oocysts as part of its life cycle. The oocysts are smaller than *Giardia* cysts, typically about 4-6 µm in diameter. These oocysts can survive under adverse conditions until ingested by a warm-blooded animal, and then continue with excystation.

Due to the increase in the number of outbreaks of Cryptosporidiosis, a tremendous amount of research has focused on *Cryptosporidium* within the last 10 years.
Medical interest has increased because of its occurrence as a life-threatening infection to individuals with depressed immune systems.

As previously mentioned, in 1993, the largest documented waterborne disease outbreak in United States history occurred in Milwaukee and was determined to be caused by *Cryptosporidium*.
An estimated 403,000 people became ill, 4,400 people were hospitalized, and 100 people died.

The outbreak was associated with deterioration of the raw water quality and a simultaneous decrease in effectiveness of the coagulation-filtration process, which led to an increase in the turbidity of treated water and the inadequate removal of *Cryptosporidium* oocysts.

Legionella pneumophila

An outbreak of pneumonia occurred in 1976 at the annual convention of the Pennsylvania American Legion. A total of 221 people were affected by the outbreak, and 35 of those afflicted died.

The cause of the pneumonia was not determined immediately, despite an intense investigation by the Centers for Disease Control. Six months after the incident, microbiologists were able to isolate a bacterium from the autopsy lung tissue of one of the Legionnaires.

The bacterium responsible for the outbreak was found to be distinct from other known bacterium and was named *Legionella pneumophila* (Witherell et al., 1988).

Following the discovery of this organism, other *Legionella*-like organisms were discovered. All together, 26 species of *Legionella* have been identified, and seven are etiologic agents for Legionnaires' disease (AWWA, 1990).

Legionnaires' disease does not appear to be transferred from person-to-person. Epidemiological studies have shown that the disease enters the body through the respiratory system.

Legionella can be inhaled via water particles less than 5μm in size from facilities such as cooling towers, hospital hot water systems, and recreational whirlpools (Witherell et al., 1988).

2.4 Mechanisms of pathogen inactivation

The three primary mechanisms of pathogen inactivation are to:

- destroy or impair cellular structural organization by attacking major cell constituents, such as destroying the cell wall or impairing the functions of semi-permeable membranes
- interfere with energy-yielding metabolism through enzyme substrates in combination with prosthetic groups of enzymes, thus rendering the enzymes non-functional
- interfere with biosynthesis and growth by preventing synthesis of normal proteins, nucleic acids, coenzymes, or the cell wall.

Depending on the disinfectant and microorganism type, combinations of these mechanisms can also be responsible for pathogen inactivation.

In water treatment, it is believed that the primary factors controlling disinfection efficiency are:

(1) the ability of the disinfectant to oxidize or rupture the cell wall.

(2) the ability of the disinfectant to diffuse into the cell and interfere with cellular activity (Montgomery, 1985).

2.5 Other uses of disinfectants in water treatment

Disinfectants are used for more than just disinfection in drinking water treatment.

While inactivation of pathogenic organisms is a primary function, disinfectants are also used as oxidants in drinking water treatment for several other functions:

- control of nuisance Asiatic clams and zebra mussels
- prevention of algal growth in sedimentation basins and filters
- removal of taste and odors through chemical oxidation
- improvement of coagulation and filtration efficiency
- oxidation of iron and manganese
- removal of color
- prevention of regrowth in the distribution system and maintenance of biological stability.

2.6 Current practice of disinfection (and oxidation)

USA

In the USA, most water treatment plants disinfect water prior to distribution.

The 1995 Community Water Systems Survey (USEPA, 1997a) reported that 81 percent of all community water systems provide some form of treatment on all or a portion of their water sources.
The survey also found that virtually all surface water systems provide some treatment of their water.
Of those systems reporting no treatment, 80 percent rely on groundwater as their only water source.

The most commonly used disinfectants/oxidants are chlorine, chlorine dioxide, chloramines, ozone, and potassium permanganate.
Table 5 displays a breakdown of the chemical usage based on the survey's data. Note that the table shows the percentages of systems using the particular chemical as a disinfectant or in some other role. The table shows the predominance of chlorine in surface and groundwater disinfection treatment systems with more than 60 percent of the treatment systems using chlorine as a disinfectant/oxidant.

Potassium permanganate, on the other hand, is used by many systems, but its application is primarily for oxidation rather than for disinfection.

Table 5 - Disinfection practice (USA)

Treatment	Ground-water	Surface water
Number of systems	31,579	3,347
Pre-disinfection	1%	4%
Primary disinfection/oxidation	66%	90%
Chlorine	64%	64%
Chlorine dioxide	0%	6%
Chloramines	0%	3%
Ozone	0%	1%
$KMnO_4$	2%	16%
Post-disinfection	32%	80%
Chlorine	31%	68%
Chlorine dioxide	0%	2%
Chloramines	0%	8%
Post-disinfection combinations	0%	3%

Permanganate will have some beneficial impact on disinfection since it is a strong oxidant that will reduce the chemical demand for the ultimate disinfection chemical.

Chloramine is used by some systems and is more frequently used as a post-treatment disinfectant.

In the USA, the most common uses for ozone are for oxidation of iron and manganese and for taste and odor control.
Twenty-four of the 158 ozone facilities used GAC following ozonation.
In addition to 158 operating ozone facilities in the USA in 1997, 19 facilities were under construction and another 30 under design.
In May 1998, 264 drinking water plants in the United States were using ozone.

Europe
In the Netherlands, as well as in most other Western European countries, the practice regarding disinfection and oxidation is completely different from what happens in the USA.
In Europe, disinfection of groundwater is seldom applied. The water is abstracted by hygienic means (closed wells, etc.), and the treatment and storage facilities are covered and protected. Oxidation of iron, ammonia and manganese is, in nearly every case, performed by oxygen (after aeration) instead of by chemical oxidants.
Since 2006, chlorination is no longer applied to surface water in the Netherlands, as mandated by the drinking water regulations. For primary disinfection in direct treatment systems (without infiltration or river bank infiltration), UV is used, either by itself or in combination with peroxide. Sometimes, ozone is used.
Whenever post-disinfection occurs, in most cases chlorine dioxide is applied.

Gaseous chlorine is rarely used in Western Europe, in keeping with safety regulations.

2.7 Disinfection byproducts

Table 6 is a list of disinfection residuals and dis-

Table 6 - Chemicals with health risks related to disinfection

Chemical	Carcinogen
Disinfection residuals	
Free chlorine	
Monochloramine	
(Ammonia)	
Hydrogen peroxide	
Chlorine peroxide	
Inorganic byproducts	
Chlorate	
Chlorite	
Bromate	+
Iodate	
Organic oxidation byproducts	
Aldehydes	+
Carboxylic acids	
Assimilable Organic Carbon (AOC)	
Nitrosoamines	
Halogenated organic byproducts	+
Trihalomethanes (THM)	+
Haloacetic acids (HAA)	?
Haloacetonitriles	
Haloketones	+
Chlorophenols	
Chloropicrin	?
Chloral hydrate	
Cyanogen chloride	
N-Organochloramines	
MX	

infection byproducts (DBP) that may be of health concern.

Formation of DBPs

Halogenated organic byproducts are formed when natural organic matter (NOM) reacts with free chlorine or free bromine.

Free chlorine can be introduced to water directly as a primary or secondary disinfectant, with chlorine dioxide, or with chloramines.

Free bromine results from the oxidation of the bromide ion in source water.

Factors affecting formation of halogenated DBPs include the type and concentration of natural organic matter, oxidant type and dose, time, bromide ion concentration, pH, organic nitrogen concentration, and temperature.

Organic nitrogen significantly influences the formation of nitrogen containing DBPs such as the haloacetonitriles, halopicrins, and cyanogen halides (Reckhow et al., 1990; Hoigné and Bader, 1988).

The parameter TOX represents the concentration of total organic halides in a water sample (calculated as chloride). In general, less than 50 percent of the TOX content has been identified, despite evidence that several of these unknown halogenated byproducts of water chlorination may be harmful to humans (Singer and Chang, 1989).

Non-halogenated DBPs are also formed when strong oxidants react with organic compounds found in water.

Ozone and peroxone oxidation of organics leads to the production of aldehydes, aldo- and keto-acids, organic acids, and, when bromide ion is present, brominated organics (Singer, 1992).

Many oxidation byproducts are biodegradable and appear as biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC) in treated water.

Bromide ion plays a key role in DBP formation.

Ozone or free chlorine oxidizes bromide ion to hypobromate ion/hypobromous acid, which subsequently forms brominated DBPs.

Brominated organic byproducts include compounds such as bromoform, brominated acetic acids and acetonitriles, bromopicrin, and cyanogen bromide. Only about one third of the bromide ions incorporated into byproducts has been identified.

DBP precursors

Numerous researchers have documented that NOM is the principal precursor of organic DBP formation (Stevens et al., 1976; Babcock and Singer 1979; Christman et al., 1983).

Chlorine reacts with NOM to produce a variety of DBPs, including THMs, haloacetic acids (HAAs), and others.

Ozone reacts with NOM to produce aldehydes,

organic acids, and aldo- and keto-acids; many of these are produced by chlorine as well (Singer and Harrington, 1993).
Natural waters contain mixtures of both humic and nonhumic organic substances. NOM can be subdivided into a hydrophobic fraction composed of primarily humic material, and a hydrophilic fraction composed of primarily fulvic material.

The type and concentration of NOM are often assessed using surrogate measures.
Although surrogate parameters have limitations, they are used because they may be measured more easily, rapidly, and inexpensively than the parameter of interest, often allowing on-line monitoring of the operation and performance of water treatment plants.
Surrogates used to assess NOM include:

- Total and dissolved organic carbon (TOC and DOC)
- Specific ultraviolet light absorbance (SUVA), which is the absorbance at 254 nm wavelength (UV-254) divided by DOC (SUVA = (UV-254/DOC)*100, in L/mg-m)
- THM formation potential (THMFP) -- a test measuring the quantity of THMs formed with a high dosage of free chlorine and a long reaction time
- TTHM Simulated Distribution System (SDS)-- a test to predict the TTHM concentration at some selected point in a given distribution system, where the conditions of the chlorination test simulate the distribution system at the point desired.

On average, about 90 percent of the TOC is dissolved.
DOC is defined as the TOC able to pass through a 0.45 µm filter.
UV absorbance is a good technique for assessing the presence of DOC because DOC primarily consists of humic substances, which contain aromatic structures that absorb light in the UV spectrum.
Oxidation of DOC reduces the UV absorbance of the water due to oxidation of some of the organic bonds that absorb UV absorbance.
Complete mineralization of organic compounds to carbon dioxide usually does not occur under water treatment conditions; therefore, the overall TOC concentration is usually constant.

3 Disinfection kinetics

3.1 Chick's Law

In 1908 Ms. Harriet Chick found that her disinfection experiments could best be described by a first-order reaction:

$$\frac{dN}{dt} = -k \cdot N$$

or:

$$\ln(N/N_o) = -k \cdot t$$

in which:

N	=	concentration of organism	[- / m^3]
N_O	=	initial concentration of organism	[- / m^3]
t	=	time	[s]
k	=	rate constant	[1/s]

The rate constant k differs per disinfectant, disinfectant concentration, organism and temperature.
The rate of inactivation depends upon such factors as the penetration of the cell wall, and the time needed to penetrate vital centers. Each species of microorganism, therefore, will have a different sensitivity to each disinfectant.
According to this relationship, known as Chick's Law, you can achieve a doubling of the log-removal by providing for a contact time twice as long, assuming a constant disinfectant concentration (Figure 1).

It should be noted that Chick's Law resembles the formula for natural decay. Disinfection increases the decay constant k.

A complete inactivation of the microorganism is not feasible according to this model.

Efficiency of disinfection
The efficiency of disinfection is reported in terms

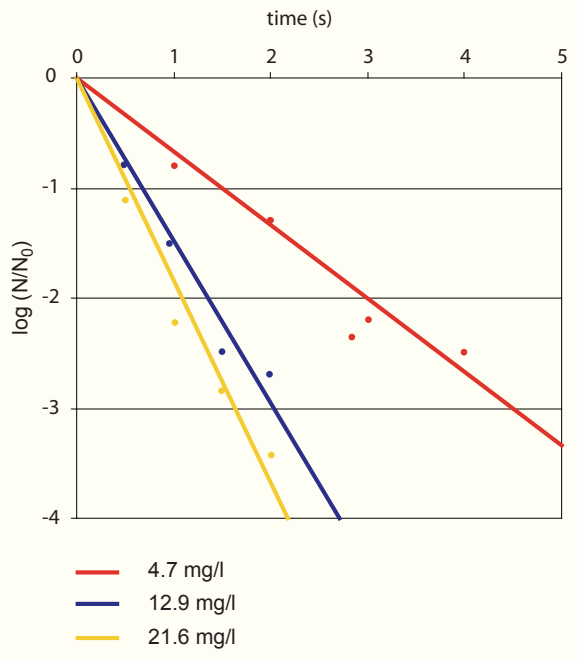


Figure 1 - Disinfection of Poliovirus Type 1 with 3 concentration Br_2

of the ratio of microorganisms inactivated to the original number, such as 99 % (2 logs) or 99.99 % (4 logs) removal.
In view of the substantial removal of microorganisms required in disinfection, log-removal is typically mentioned.

3.2 Chick-Watson model

Also in 1908, Mr. Herbert Watson proposed his disinfection law:

$$C^n \cdot t = K_r$$

in which:

C	=	concentration of disinfectant	[mg/l]
n	=	empirical constant	[-]
t	=	time	[s]
K_r	=	empirical value for a percentage of inactivation (e.g., 99%)	

In many cases, the empirical constant n can be assumed to be 1 (Figure 2).
This means that for a requested inactivation, a certain C t -value is required, in which time t and concentration C are equally important.

Combining both laws (with n=1) gives the Chick-

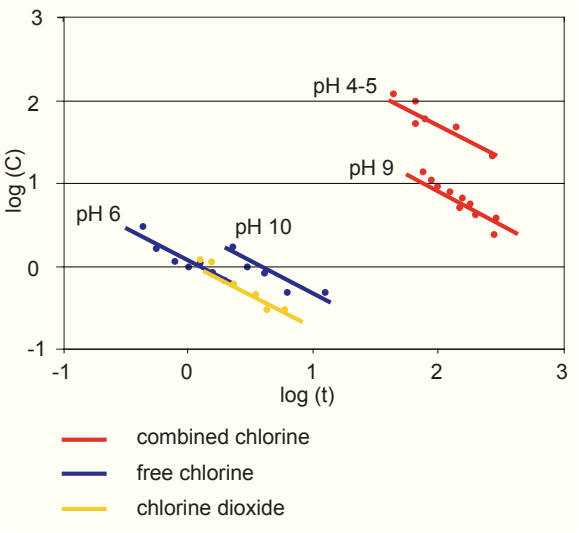


Figure 2 - Watson plot for 99% inactivation of Polio- virus Type 1

Watson law:

$$\ln(N/N_0) = -K_{CW} \cdot C \cdot t$$

in which:

K_{CW}	=	specific lethality	[l/mg.s]

In Figure 3, the data of Figure 1 is plotted according to the Chick-Watson model.
For a limited inactivation, the model fits the data rather well. The lower inactivation for the higher

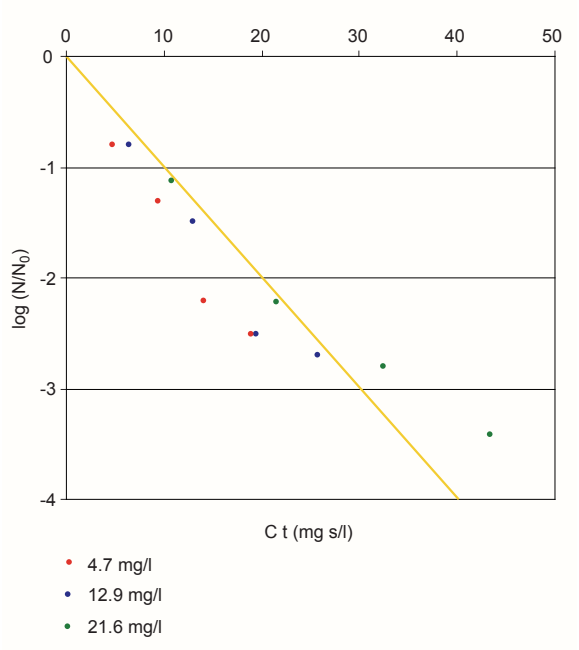


Figure 3 - Disinfection of Poliovirus Type 1 with 3 concentration Br_2 (Chick-Watson plot)

dose indicates a value n<1 (0.8-0.9). For higher inactivation, the required C t -value is more than the model assumes.

3.3 Other models

Alternative models have been developed over the years to get better fits between model and data.

Rennecker-Mariñas model

For inactivation of oocysts and endospores, often a certain lag concentration is observed. Below this lag concentration of disinfectant, no disinfection is obtained.
This phenomenon is incorporated in the Rennecker-Mariñas model, which uses a "net disinfectant concentration" in the Chick-Watson model:

$$C = C_{actual} - C_{lag}$$

Collins-Selleck model

Collins and Selleck developed a model to describe the inactivation of coliform organisms in wastewater disinfection. They observed that increased C t -values were required for very large inactivation (log 4 to 6). This is probably due to the encapsulation of a small part of these organisms, making it less approachable for disinfectants.

Hom-Haas model

In the Hom-Haas model, Cp tq is used instead of C t.
With this extension, a better fit can be obtained, but more empirical constants should be determined for different conditions.

3.4 C t -values

In most cases the C t -value is used as the basis for disinfection.
This approach is also used for disinfection with UV radiation, for which the C t -value is modified into UV light intensity (mW/cm^2) multiplied by the time of exposure (s), giving the dose (mJ/cm^2).

For many pathogens and disinfectants, information can be found on C t -values and inactivation.

The US EPA began the practice of specifying C t -values that must be met as a way of regulating the control of pathogens within the Surface Water Treatment Regulations.
At present, they have published tables for critical pathogens (e.g. *Giardia*, *Cryptosporidium*, viruses) for all relevant disinfection methods, and different log inactivation credits, at different water temperatures and pH.

An impression of the required C t -values for different disinfectant methods is shown in Figure 4.
Notice that *Cryptosporidium Parvum* and *Giardia* are difficult to inactivate with chemical disinfectants (high C t required) and easy to inactivate with UV radiation (low I t).
The opposite is true for viruses.

The required C t -values for chemical disinfectants show large variations (range 10^3 – 10^6).
For UV radiation, this variation is much smaller (range 10^2).

Declining concentration

Chemical disinfectants are oxidants reacting with components in the water. Therefore, the concentration of the disinfectant declines in time.
Additionally, the disinfectant/oxidant might decompose. Because ozone naturally decomposes so fast, this is an important consideration for the disinfection process.

To calculate the disinfection credits based on C t -values, reductions in the disinfectant concentration should be taken into account.

Temperature

At lower temperatures, disinfection requires higher C t -values for the same inactivation.
At 1 to 5 °C, the required C t -value might be some 5 – 10 times higher than the C t -value at 25 °C.

Short-circuiting

The C t -values are based on batch lab experiments in which the concentration and residence time are controlled.
In practice, disinfection is applied in full-scale

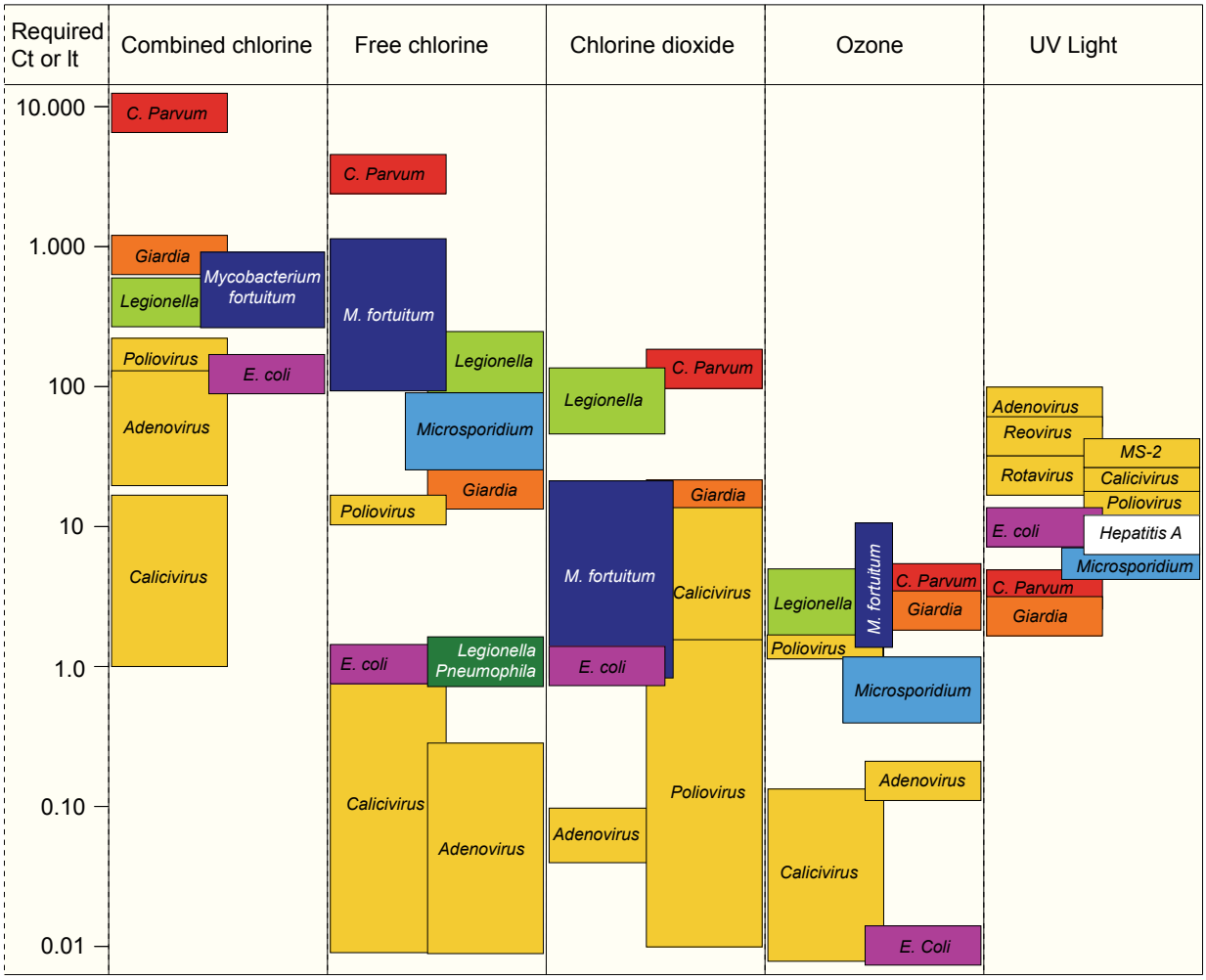


Figure 4 - Disinfection requirements for 99% inactivation (min mg/l or mJ/cm²)

contact tanks, having non-ideal residence times (residence time distribution, short-circuiting).

The Chick-Watson model can be used to determine the effect of a non-ideal flow in a disinfection reactor.
As an example we compare the disinfection efficiency of a full plug flow reactor with a reactor in which half the flow has a residence time of 60%, and the other half a residence time of 140%. Assume that the plug flow reactor has an inactivation of log 4. The water at low residence time has an inactivation of (4*0.6=) 2.4, while the water in the high residence time has an inactivation of (4*1.4=) 5.6. The total inactivation is ($-\log(10^{2.4}+10^{5.6})/2$ =) 2.8.
This shows that short-circuiting has a substantial negative effect on the efficiency of disinfection, particularly when a high inactivation is required.

The t_{10} concept

Because of the effect of short-circuiting, the detention time in the US EPA regulations are defined as being the detention time in which 10% of the flow has passed the contactor (t_{10}).
In poorly designed contactors, this greatly reduces the disinfection credits.

In order to improve these reactors, better plug flow conditions can be achieved by proper flow splitting, baffling, and/or by designing long and narrow contactors.

Bypassing

Calculations can be made on the effect of bypassing, which occurs, for instance, when part of the flow does not receive any disinfectant. Bad mixing can occur when there is an uneven distribution of

the flow.
If 1% of the flow is bypassing a log 4 disinfection reactor, the overall efficiency can be calculated as being log 2.
(influent, and bypass 10,000 organisms, disinfected main stream 1 organism, overall effect 10,000*0.01+1*0.99=100.99 organisms or log(100.99/10,000) = -1.996).

This example shows the dramatic reduction in disinfection caused by bypassing, in particular at a high disinfection requirement.

4 Disinfection methods

In the following section the advantages and disadvantages of different disinfection methods for drinking water are presented.

Because of the wide variation of system sizes, water quality, and dosages applied, some of these advantages and disadvantages may not apply to all systems.

4.1 Chlorine

Advantages
- Oxidizes soluble iron, manganese, and sulfides
- Enhances color removal
- Enhances taste and odor
- May enhance coagulation and filtration of particulate contaminants
- Is an effective biocide
- Is the easiest and least expensive disinfection method, regardless of system size
- Is the most widely used disinfection method, and, therefore, the best known
- Is available as calcium and sodium hypochlorite. Use of these solutions is more advantageous for smaller systems than chlorine gas because they are easier to use, are safer, and need less equipment compared to chlorine gas
- Provides a residual

Disadvantages
- May cause a deterioration in coagulation/filtration of dissolved organic substances
- Forms halogen-substituted byproducts
- Finished water could have taste and odor problems, depending on water quality and dosage
- Chlorine gas is a hazardous corrosive gas
- Special leak containment and scrubber facilities could be required for chlorine gas
- Typically, sodium and calcium hypochlorite are more expensive than chlorine gas
- Sodium hypochlorite degrades over time and with exposure to light
- Sodium hypochlorite is a corrosive chemical
- Calcium hypochlorite must be stored in a cool, dry place because of its reaction with moisture and heat
- A precipitate may form in a calcium hypochlorite solution because of impurities, therefore, an antiscalant chemical may be needed
- Higher concentrations of hypochlorite solutions are unstable and will produce chlorate as a byproduct
- Is less effective at high pH
- Forms oxygenated byproducts that are biodegradable and which can enhance subsequent biological growth if the chlorine residual is not maintained.
- Release of constituents bound in the distribution system (e.g., arsenic) by changing the redox state

Generation
Chlorination may be performed using chlorine gas or other chlorinated compounds that may be in liquid or solid form.
Chlorine gas can be generated by a number of processes including the electrolysis of alkaline brine or hydrochloric acid, the reaction between sodium chloride and nitric acid, or the oxidation of hydrochloric acid.
Since chlorine is a stable compound, chlorine gas, sodium hypochlorite, and calcium hypochlorite are typically produced off-site by a chemical manufacturer.

Primary uses
The primary use of chlorination is disinfection. Chlorine also serves as an oxidizing agent for taste and odor control, preventing algal growths, maintaining clear filter media, removing iron and manganese, destroying hydrogen sulfide, removing color, maintaining the water quality at the distribution systems, and improving coagulation.

Inactivation efficiency
The general order of increasing chlorine disinfection difficulty is bacteria, viruses, and then protozoa.
Chlorine is an extremely effective disinfectant for inactivating bacteria and a highly effective viricide. However, chlorine is less effective against Giardia cysts. Cryptosporidium oocysts are highly resistant to chlorine.

Byproduct formation
When added to the water, free chlorine reacts with NOM and bromide to form DBPs, primarily THMs, some haloacetic acids (HAAs), and others.

Point of application
Chlorine can be applied at different points: in the raw water storage, pre-coagulation/post-raw water storage, pre-sedimentation/ post-coagulation, post-sedimentation/pre-filtration, post-filtration (disinfection), or in the distribution system.

Special considerations
Because chlorine is such a strong oxidant and extremely corrosive, special storage and handling considerations should be considered in the planning of a water treatment plant.
Additionally, health concerns associated with the handling and use of chlorine is an important consideration.

4.2 Ozone

Advantages
- Ozone is more effective than chlorine, chloramines, and chlorine dioxide for inactivation of viruses, Cryptosporidium, and Giardia.
- Ozone oxidizes iron, manganese, and sulfides.
- Ozone can sometimes enhance the clarification process and turbidity removal.
- Ozone controls color, taste, and odors.
- One of the most efficient chemical disinfectants, ozone requires a very short contact time.
- In the absence of bromide, halogen-substitutes DBPs are not formed.
- Upon decomposition, the only residual is dissolved oxygen.
- Biocidal activity is not influenced by pH.

Disadvantages
- DBPs are formed, particularly by bromate and bromine-substituted DBPs, in the presence of bromide, aldehydes, ketones, etc.
- The initial cost of ozonation equipment is high.
- The generation of ozone requires high energy and should be generated on-site.
- Ozone is highly corrosive and toxic.
- Biologically activated filters are needed for removing assimilable organic carbon and biodegradable DBPs.
- Ozone decays rapidly at high pH and warm temperatures.
- Ozone provides no residual.
- Ozone requires higher level of maintenance and operator skill.

Generation
Because of its instability, ozone should be generated at the point of use.
Ozone can be generated from oxygen present in air or high purity oxygen. The feed gas source should be clean and dry, with a maximum dew point of -60 0C.
Ozone generation consumes power at a rate of 8 to 7 kWh/kg O3. On-site generation saves a lot of storage space.

Primary uses
Primary uses include primary disinfection and chemical oxidation. As an oxidizing agent, ozone can be used to increase the biodegradability of organic compounds destroys taste and odor

control, and reduce levels of chlorination DBP precursors.
Ozone should not be used for secondary disinfection because it is highly reactive and does not maintain an appreciable residual level for the length of time desired in the distribution system.

Inactivation efficiency
Ozone is one of the most potent and effective germicide used in water treatment. It is effective against bacteria, viruses, and protozoan cysts. Inactivation efficiency for bacteria and viruses is not affected by pH; at pH levels between 6 and 9.
As water temperature increases, ozone disinfection efficiency increases.

Byproduct formation
Ozone itself does not form halogenated DBPs; however, if bromide ion is present in the raw water or if chlorine is added as a secondary disinfectant, halogenated DBPs, including bromate ion may be formed.
Other ozonation byproducts include organic acids and aldehydes.

Limitations
Ozone generation is a relatively complex process.
Storage of LOX (if oxygen is to be the feed gas) is subject to building and fire codes.

Points of application
For primary disinfection, ozone addition should be prior to biofiltration/filtration and after sedimentation.
For oxidation, ozone addition can be prior to coagulation/sedimentation or filtration depending on the constituents to be oxidized.

Safety considerations
Ozone is a toxic gas and the ozone production and application facilities should be designed to generate, apply, and control this gas, so as to protect plant personnel. Ambient ozone levels in plant facilities should be monitored continuously.

4.3 UV radiation

Generation
Low pressure and medium pressure UV lamps are available.
Primary uses
Primary physical disinfectant; requires secondary chemical disinfectant for residual in distribution system.

Inactivation efficiency
This method is very effective against bacteria and viruses at low dosages (5-25 mW•s/cm^2 for 2-log removal and 90-140 mW•s/cm^2 for 4-log removal).
Much higher dosage required for Cryptosporidium and Giardia (100-8,000 mW•s/cm^2 for 2-log removal)

Byproduct formation
Minimal disinfection byproducts produced.

Limitations
Limited experience and data with large flows.
Water with high concentrations of iron, calcium, turbidity, and phenols may not be applicable to UV disinfection.

Point of application
It is preferable to apply UV radiation prior to the distribution system.

Special considerations
Extremely high UV dosages for Cryptosporidium and Giardia may make surface water treatment impractical.

4.4 Chlorine dioxide

Advantages
- Chlorine dioxide is more effective than chlorine and chloramines for inactivation of viruses, Cryptosporidium, and Giardia.
- Chlorine dioxide oxidizes iron, manganese, and sulfides.
- Chlorine dioxide may enhance the clarification process.

- Taste and odors resulting from algae and decaying vegetation, as well as phenolic compounds, are controlled by chlorine dioxide.
- Under proper generation conditions (i.e., no excess chlorine), halogen-substituted DBPs are not formed.
- Chlorine dioxide is easy to generate.
- Biocidal properties are not influenced by pH.
- Chlorine dioxide provides residuals.

Disadvantages
- The chlorine dioxide process forms the specific byproducts chlorite and chlorate.
- Generator efficiency and optimization difficulty can cause excess chlorine to be fed at the application point, which can potentially form halogen-substitute DBPs.
- Costs associated with training, sampling, and laboratory testing for chlorite and chlorate are high.
- Equipment is typically rented, and the cost of the sodium chlorite is high.
- Measuring chlorine dioxide gas is explosive, so it must be generated on-site.
- Chlorine dioxide gas is explosive, so it must be generated and measured on-site.
- Chlorine dioxide decomposes in sunlight.
- Can lead to production noxious odors in some systems.

Generation
Chlorine dioxide must be generated on-site. In most potable water applications, chlorine dioxide is generated as needed and directly educed from or injected into a diluting stream.
Generators are available that utilize sodium chlorite and a variety of feedstocks such as Cl_2 gas, sodium hypochlorite, and sulfuric or hydrochloric acid.
Small samples of generated solutions, up to 1 percent (10 g/l) chlorine dioxide can be safely stored if the solution is protected from light, chilled (<5 ^{o}C), and has no unventilated headspace.

Primary uses
Chlorine dioxide is utilized as a primary or secondary disinfectant for taste and odor control, TTHM/HAA reduction, Fe and Mn control, color removal, sulfide and phenol destruction, and Zebra mussel control.

Inactivation efficiency
Chlorine dioxide rapidly inactivates most microorganisms over a wide pH range. It is more effective than chlorine (for pathogens other than viruses) and is not pH dependent between pH 5-10, but is less effective than ozone.

Byproducts formation
When added to water, chlorine dioxide reacts with many organic and inorganic compounds. The reactions produce chlorite and chlorate as end-products (compounds that are suspected of causing hemolytic anemia and other health effects). Chlorate ion is formed predominantly in downstream reactions between residual chlorite and free chlorine when used as the distribution system disinfectant.
Chlorine dioxide does not produce THMs. The use of chlorine dioxide aids in reducing the formation of TTHMs and HAAs by oxidizing precursors, and by allowing the point of chlorination to be moved farther downstream in the plant after coagulation, sedimentation, and filtration have reduced the quantity of NOM.

Point of application
In conventional treatment plants, chlorine dioxide used for oxidation is fed either in the raw water or in the sedimentation basins, or following sedimentation.
To limit the oxidant demand, and therefore the chlorine dioxide dose and formation of chlorite, it is common to add chlorine dioxide following sedimentation.
Concerns about possible taste and odor complaints have limited the use of chlorine dioxide to provide a disinfectant residual in the distribution system. Consequently, public water suppliers who are considering the use of chlorine dioxide for oxidation and primary disinfectant applications may want to consider chloramines for secondary disinfection.

Special considerations

An oxidant demand study should be completed to determine an approximate chlorine dioxide dosage to obtain the required C t -value as a disinfectant.
In addition to the toxic effects of chlorine, chlorine dioxide gas is explosive at levels > 10% in air. The chlorine dioxide dosage cannot exceed 1.4 mg/l so as to limit the total combined concentration of ClO_2, ClO_2^-, ClO_3^-, to a maximum of 1.0 mg/l.
Under the proposed DBP regulations, the MRDL for chlorine dioxide is 0.8 mg/l and the MCL for chlorite is 1.0 mg/l. Regulations concerning the use of chlorine dioxide vary from state to state.

4.5 Other methods

Alternative disinfection methods are used during large scale water treatment for drinking water production:

- Hydrogen peroxide / Ozone (Peroxone)
- Hydrogen peroxide / UV
- Potassium permanganate
- Chloramines.

For a description of these systems, reference is made to the literature.

Further reading

- Water treatment: Principles and design, MWH (2005), (ISBN 0 471 11018 3) (1948 pgs)
- Unit processes in drinking water treatment, W. Masschelein 1992 (ISBN 0 8247 8678 5) (635 pgs)
- Water quality and treatment, AWWA 1999 (ISBN 0 07 001659 3) (1233 pgs)
- Water treatment and pathogen control, WHO 2004 (ISBN 92 4 156255 2) (139 pgs)
- Assessing microbial safety of drinking water, WHO 2003 (ISBN 1 84339 036 1) (297 pgs)
- Water disinfection, CEPIS-PAHO/WHO 2003 (208 pgs) (for small water systems)