2. DISINFECTANT USE IN WATER TREATMENT

To comply with the SDWA regulations, the majority of PWSs use some form of water treatment. The 1995 Community Water Systems Survey (USEPA, 1997a) reports that in the United States, 99 percent of surface water systems provide some treatment to their water, with 99 percent of these treatment systems using disinfection/oxidation as part of the treatment process. Although 45 percent of ground water systems provide no treatment, 92 percent of those ground water plants that do provide some form of treatment include disinfection/oxidation as part of the treatment process. The most commonly used disinfectants/oxidants (in no particular order) are chlorine, chlorine dioxide, chloramines, ozone, and potassium permanganate.

Disinfectants are also used to achieve other specific objectives in drinking water treatment. These other objectives include nuisance control (e.g., for zebra mussels and Asiatic clams), oxidation of specific compounds (i.e., taste and odor causing compounds, iron, and manganese), and use as a coagulant and filtration aid.

The purpose of this chapter is to:

- Provide a brief overview of the need for disinfection in water treatment.
- Provide basic information that is common to all disinfectants;
- Discuss other uses for disinfectant chemicals (i.e., as oxidants);
- Describe trends in DBP formation and the health effects of DBPs found in water treatment;
- Discuss microorganisms of concern in water systems, their associated health impact, and the inactivation mechanisms and efficiencies of various disinfectants; and
- Summarize current disinfection practices in the United States, including the use of chlorine as a disinfectant and an oxidant.

2.1 Need for Disinfection in Water Treatment

Although the epidemiological relation between water and disease had been suggested as early as the 1850s, it was not until the establishment of the germ theory of disease by Pasteur in the mid-1880s that water as a carrier of disease-producing organisms was understood. In the 1880s, while London experienced 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 direct recycling of non-disinfected water. Now, over 100 years later, the list of potential waterborne diseases due to pathogens is considerably larger, and includes bacterial, viral, and parasitic microorganisms, as shown in Table 2-1, Table 2-2 and Table 2-3, respectively.

A major cause for the number of disease outbreaks in potable water is contamination of the distribution system from cross connections and back siphonage with non-potable water. However, outbreaks resulting from distribution system contamination are usually quickly contained and result in relatively few illnesses compared to contamination of the source water or a breakdown in the treatment system, which typically produce many cases of illnesses per incident. 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. The outbreak was associated with deterioration in the raw water 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 the 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, biological characteristics of the source water are one of the most important parameters in water treatment. In addition to public health problems, microbiology can also affect the physical and chemical water quality and treatment plant operation.

2.1.1 Pathogens of Primary Concern

Table 2-4 shows the attributes of three groups of pathogens of concern in water treatment, namely bacteria, viruses, and protozoa.

2.1.1.1 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) are variable 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 length in excess of 100 μm.

Table 2-1. Waterborne Diseases from Bacteria

Causative Agent	Disease	Symptoms	Reservoir
Salmonella typhosa	Typhoid Fever	Headache, nausea, loss of appetite, constipation or diarrhea, insomnia, sore throat, bronchitis, abdominal pain, nose bleeding, shivering and increasing fever. Rose spots on trunk. Incubation period: 7-14 days.	Feces and urine of typhoid carrier or patient.
S. paratyphi *S. schottinulleri* *S. hirschfeldi* C.	Paratyphoid fever	General infection characterized by continued fever, diarrhea disturbances, sometimes rose spots on trunk. Incubation period: 1-10 days.	Feces and urine of carrier or patient.
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.	Bowel discharges of carriers and infected persons.
Vibrio comma *V. cholerae*	Cholera	Diarrhea, vomiting, rice water stools, thirst, pain, coma. Incubation period: a few hours to 5 days.	Bowel discharges, vomitus, carriers.
Pasteurella tularensis	Tularemia	Sudden onset with pains and fever; prostration. Incubation period: 1-10 days.	Rodent, rabbit, horsefly, woodtick, dog, fox, hog.
Brucella melitensis	Brucellosis (undulant fever)	Irregular fever, sweating, chills, pain in muscles.	Tissues, blood, mold, urine, infected animal.
Pseudomonas pseudomallei	Melioidosis	Acute diarrhea, vomiting, high fever, delirium, mania.	Rats, guinea pigs, cats, rabbits, dogs, horses.
Leptospira icterohaemorrhagiae (spirochaetales)	Leptospirosis (Well's disease)	Fevers, rigors, headaches, nausea, muscular pains, vomiting, thirst, prostration and jaundice may occur.	Urine and feces of rats, swine, dogs, cats, mice, foxes, sheep.
Enteropathogenic *E. coli*	Gastroenteritis	Water diarrhea, nausea, prostration and dehydration.	Feces of carrier.

Sources: Salvato, 1972; Geldreich, 1972.

Table 2-2. Waterborne Diseases from Human Enteric Viruses

Group	Subgroup	No. of Types or Subtypes	Disease Entities Associated with These Viruses	Pathological Changes in Patients	Organs Where Virus Multiplies
Enterovirus	Poliovirus	3	Muscular paralysis	Destruction of motor neurons	Intestinal mucosa, spinal cord, brain stem
			Aseptic meningitis	Inflammation of meninges from virus	Meninges
			Febrile episode	Viremia and viral multiplication	Intestinal mucosa and lymph
	Echovirus	34	Aseptic meningitis	Inflammation of meninges from virus	Stem
			Muscular paralysis	Destruction of motor neurons	Intestinal mucosa, spinal cord, brain
			Guillain-Barre's Syndrome[1]	Destruction of motor neurons	Spinal cord
			Exanthem	Dilation and rupture of blood vessels	Skin
			Respiratory diseases	Viral invasion of parenchymiatous of respiratory tracts and secondary inflammatory responses	Respiratory tracts and lungs
					Gastrointestinal tract
			Diarrhea	intestinal infections	Respiratory tract and gastrointestinal tract
			Epidemic myalgia	Not well known	
			Pericarditis and myocarditis	Viral invasion of cells with secondary inflammatory responses	Pericardial and myocardial tissue
			Hepatitis	Invasion of parenchyma cells	Liver
	Coxsackie-virus	>24	Herpangina[2]	Viral invasion of mucosa with secondary inflammation	Mouth
	A		Acute lymphatic pharyngitis	Sore throat, pharyngeal lesions	Lymph nodes and pharynx
			Aseptic meningitis	Inflammation of meninges from virus	Meninges
			Muscular paralysis	Destruction of motor neurons	Intestinal mucosa, spinal cord, brain stem
			Hand-foot-mouth disease[3]	Viral invasion of skin cells of hands-feet-mouth	Skin of hands-feet, and much of mouth
			Respiratory disease	Viral invasion of parenchymiatous of respiratory tracts and secondary inflammatory responses	Respiratory tracts and lungs
			Infantile diarrhea	Viral invasion of cells of mucosa	Intestinal mucosa
			Hepatitis	Invasion of parenchyma cells	Liver
			Pericarditis and myocarditis	Viral invasion of cells with secondary inflammatory responses	Pericardial and myocardial tissue

[1] Ascending type of muscular paralysis
[2] Febrile episode with sores in mouth
[3] Rash and blister on hand-foot-mouth with fever

Table 2-2. Waterborne Diseases from Human Enteric Viruses (Continued)

Group	Subgroup	No. of Types or Subtypes	Disease Entities Associated with These Viruses	Pathological Changes in Patients	Organs Where Virus Multiplies
Enterovirus (continued)	B	6	Pleurodynia[4]	Viral invasion of muscle cells	Intercostal muscles
			Aseptic meningitis	Inflammation of meninges from virus	Meninges
			Muscular paralysis	Destruction of motor neurons	Intestinal mucosa, spinal cord, brain stem
			Meningoencephalitis	Viral invasion of cells	Meninges and brains
			Pericarditis, endocarditis, myocarditis	Viral invasion of cells with secondary inflammatory responses	Pericardial and myocardial tissue
			Respiratory disease	Viral invasion of parenchymiatous of respiratory tracts and secondary inflammatory responses	Respiratory tracts and lungs
			Hepatitis or Rash	Invasion of parenchyma cells	Liver
			Spontaneous abortion	Viral invasion of vascular cells	Placenta
			Insulin-dependent diabetes	Viral invasion of insulin-producing cells	Langerhan's cells of pancreases
			Congenital heart anomalies	Viral invasion of muscle cells	Developing heart
Reovirus		6	Not well known	Not well known	
Adenovirus		31	Respiratory diseases	Viral invasion of parenchymiatous of respiratory tracts and secondary inflammatory responses	Respiratory tracts and lungs
			Acute conjunctivitis	Viral invasion of cells and secondary inflammatory responses	Conjunctival cells and blood vessels
			Acute appendicitis	Viral invasion of mucosa cells	Appendia and lymph nodes
			Intussusception	Viral invasion of lymph nodes	Intestinal lymph nodes
			Subacute thyroiditis	Viral invasion of parenchyma cells	Thyroid
			Sarcoma in hamsters	Sarcoma in hamsters	Muscle cells
Hepatitis		>2	Infectious hepatitis	Invasion of parenchyma cells	Liver
			Serum hepatitis	Invasion of parenchyma cells	Liver
			Down's Syndrome	Invasion of cells	Frontal lobe of brain, muscle, bones

[4] Pleuritis type of pain with fever

Source: Taylor, 1974; Beneson, 1981.

Table 2-3. Waterborne Diseases from Parasites

Causative Agent	Disease	Symptoms
Ascario lumbricoides (round worm)	Ascariasis	Vomiting, live worms in feces
Cryptosporidium muris and *parvum*	Cryptosporidiosis	Acute diarrhea, abdominal pain, vomiting, 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	Amoebic meningoecephalitis	Death
Schistosoma mansoni	Schistosomiasis	Liver and bladder infection
Taenia saginata (beef tapeworm)	Taeniasis	Abdominal pain, digestive disturbances, loss of weight

Source: Geldreich, 1972; Beneson, 1981.

2.1.1.2 Viruses

Viruses are microorganisms composed of the genetic material deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) and a protective protein coat (either 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 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).

2.1.1.3 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 2-5.

Table 2-4. 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

Table 2-5. Human Parasitic Protozoans

Protozoan	Host(s)	Disease	Transmission	Occurrence
Acanathamoeba castellannii	Fresh water, sewage, humans, and soil	Amoebic meningoencephalitis	Gains entry through abrasions, ulcers, and as secondary invader during other infections	North America
Balantidium coli	Pigs, humans	Balantidiasis (dysentery)	Contaminated water	Micronesia has been the only known site of an outbreak
Cryptosporidium parvum	Animals, humans	Cryptosporidiosis	Person-to-person or animal-to-person contact, ingestion of fecally contaminated water or food, or contact with fecally contaminated environmental surfaces.	Canada, England, and the United States
Entamoeba histolytica	Humans	Amoebic dysentery	Contaminated water	Last United States outbreak, 1953
Giardia lamblia	Animals, humans	Giardiasis (gastroenteritis)	Contaminated water	Mexico, United States, USSR
Naegleria fowleri	Soil, water, humans and decaying vegetation	Primary amoebic meningoencephalitis	Nasal inhalation with subsequent penetration of nasopharynx; exposure from swimming in freshwater lakes	North America

Source: Montgomery, 1985; AWWA, 1995.

2.1.2 Recent Waterborne Outbreaks

Within the past 40 years, several pathogenic agents never before associated with documented waterborne outbreaks have appeared in the United States. Enteropathogenic *E. coli* and *Giardia lamblia* were first identified to be the etiological agent 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*.

2.1.2.1 E. coli

The first documented case of waterborne disease outbreaks in the United States associated with enteropathogenic *E. coli* occurred in the 1960s. 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).

2.1.2.2 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 and low temperatures.

2.1.2.3 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 a deterioration in 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 inadequate removal of *Cryptosporidium* oocysts.

2.1.2.4 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 to 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. Altogether, 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 person-to-person. Epidemiological studies have shown that the disease enters the body through the respiratory system. *Legionella* can be inhaled in water particles less than 5μm in size from facilities such as cooling towers, hospital hot water systems, and recreational whirlpools (Witherell et al., 1988).

2.1.3 Mechanism 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; and

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

2.2 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 oxidants in drinking water treatment for several other functions:

- Minimization of DBP formation;
- Control of nuisance Asiatic clams and zebra mussels;
- Oxidation of iron and manganese;
- Prevention of regrowth in the distribution system and maintenance of biological stability;
- Removal of taste and odors through chemical oxidation;
- Improvement of coagulation and filtration efficiency;
- Prevention of algal growth in sedimentation basins and filters;
- Removal of color.

A brief discussion of these additional oxidant uses follows.

2.2.1 Minimization of DBP Formation

Strong oxidants may play a role in disinfection and DBP control strategies in water treatment. Several strong oxidants, including potassium permanganate and ozone, may be used to control DBP precursors.

Potassium permanganate can be used to oxidize organic precursors at the head of the treatment plant, thus minimizing the formation of byproducts at the downstream disinfection stage of the plant. The use of potassium permanganate as an oxidant and disinfectant is discussed in Chapter 5 of this guidance manual.

The use of ozone for oxidation of DBP precursors is currently being studied. Early work has shown that the effects of ozonation, prior to chlorination, were highly site-specific and unpredictable. The key variables that seem to determine the effect of ozone are dose, pH, alkalinity, and the nature of the organic material. Ozone has been shown to be effective for DBP precursor reduction at low pHs. However, at higher pHs (i.e., above 7.5), ozone may actually increase the amount of chlorination byproduct precursors. The use of ozone as an oxidant and disinfectant is addressed in detail in Chapter 3 of this document.

2.2.2 Control of Nuisance Asiatic Clams and Zebra Mussels

The Asiatic clam (*Corbicula fluminea)* was introduced to the United States from Southeast Asia in 1938 and now inhabits almost every major river system south of 40° latitude (Britton and Morton, 1982; Counts, 1986). Asiatic clams have been found in the Trinity River, TX; the Ohio River at Evansville, IN; New River at Narrows and Glen Lyn, VA; and the Catawba River in Rock Hill, SC (Belanger et al., 1991; Cameron et al., 1989a; Matisoff et al., 1996). This animal has invaded many water utilities, clogging source water transmission systems and valves, screens, and meters; damaging centrifugal pumps; and causing taste and odor problems (Sinclair, 1964; Evans et al., 1979; Smith, 1979).

Cameron et al. (1989a) investigated the effectiveness of several oxidants to control the Asiatic clam in both the juvenile and adult phases. As expected, the adult clam was found to be much more resistant to oxidants than the juvenile form. In many cases, the traditional method of control, free chlorination, cannot be used because of the formation of excessive amounts of THMs. As shown in Table 2-6, Cameron et al. (1989a) compared the effectiveness of four oxidants for controlling the juvenile Asiatic clam in terms of the LT50 (time required for 50 percent mortality). Monochloramine was found to be the best for controlling the juvenile clams without forming THMs. Further research showed that the effectiveness of monochloramine increased greatly as the temperature increased (Cameron et al., 1989b). Note that the temperatures in this study reflect conditions in the Lynchburg Reservoir, Houston, Texas. Clams can tolerate temperatures between 2 and 35°C (Cameron et al. 1989a).

Table 2-6. The Effects of Various Oxidants on Mortality of the Asiatic Clam (*Corbicula fluminea*)

Chemical	Residual (mg/L)	Temperature (°C)	pH	Life Stage	LT50 (days)
Free chlorine	0.5	23	8.0	A	8.7
	4.8	21	7.9	A	5.9
	4.7	16	7.8	J	4.8
Potassium Permanganate	1.1	17	7.6	J	7.9
	4.8	17	7.6	J	8.6
Monochloramine	2.6	28	7.9	J	0.6
	10.7	17	7.9	J	0.5
Chlorine dioxide	1.2	24	6.9	J	0.7
	4.7	22	6.6	J	0.6

A=Adult; J=Juvenile
Source: Cameron et al., 1989a.

In a similar study, Belanger et al. (1991) studied the biocidal potential of total residual chlorine, monochloramine, monochloramine plus excess ammonia, bromine, and copper for controlling the Asiatic clam. Belanger et al. (1991) showed that monochloramine with excess ammonia was the most effective for controlling the clams at 30°C. Chlorination at 0.25 to 0.40 mg/L total residual chlorine at 20 to 25°C controlled clams of all sizes (LT50 below 28 days) but had minimal effect at 12 to 15°C (as low as zero mortality). As in other studies, the toxicity of all the biocides was highly dependent on temperature and clam size.

The zebra mussel (*Dreissena polymorpha*) is a recent addition to the fauna of the Great Lakes. It was first found in Lake St. Clair in 1988, though it is believed that this native of the Black and Caspian seas, was brought over from Europe in ballast water around 1985 (Herbert et al., 1989). The zebra mussel population in the Great Lakes has expanded very rapidly, both in size and geographical distribution (Roberts, 1990). Lang (1994) reported that zebra mussels have been found in the Ohio River, Cumberland River, Arkansas River, Tennessee River, and the Mississippi River south to New Orleans.

Klerks and Fraleigh (1991) evaluated the effectiveness of hypochlorite, permanganate, and hydrogen peroxide with iron for their effectiveness controlling adult zebra mussels. Both continuous and intermittent 28-day static renewal tests were conducted to determine the impact of intermittent dosing. Intermittent treatment proved to be much less effective than continuous dosing.

The hydrogen peroxide-iron combination (1–5 mg/L with 25 percent iron) was less effective in controlling the zebra mussel than either permanganate or hypochlorite. Permanganate (0.5–2.5 mg $KMnO_4$/L) was usually less effective than hypochlorite (0.5–10 mg Cl_2/L).

Van Benschoten et al. (1995) developed a kinetic model to predict the rate of mortality of the zebra mussel in response to chlorine. The model shows the relationship between chlorine residual and temperature on the exposure time required to achieve 50 and 95 percent mortality. Data were

collected for chlorine residuals between 0.5 and 3.0 mg Cl_2/L and temperatures from 0.3 to 24°C. The results show a strong dependence on temperature and required contact times ranging from two days to more than a month, depending on environmental factors and mortality required.

Brady et al. (1996) compared the efficiency of chlorine to control growth of zebra mussel and quagga mussel (*Dreissena bugensis*). The quagga mussel is a newly identified mollusk within the Great Lakes that is similar in appearance to the zebra mussel. Full-scale chlorination treatment found a significantly higher mortality for the quagga mussel. The required contact time for 100 percent mortality for quagga and zebra mussels was 23 days and 37 days, respectively, suggesting that chlorination programs designed to control zebra mussels should also be effective for controlling populations of quagga mussels.

Matisoff et al. (1996) evaluated chlorine dioxide (ClO_2) to control adult zebra mussels using single, intermittent, and continuous exposures. A single 30-minute exposure to 20 mg/L chlorine dioxide or higher concentration induced at least 50 percent mortality, while sodium hypochlorite produced only 26 percent mortality, and permanganate and hydrogen peroxide were totally ineffective when dosed at 30 mg/L for 30 minutes under the same conditions. These high dosages, even though only used for a short period, may not allow application directly in water for certain applications due to byproducts that remain in the water. Continuous exposure to chlorine dioxide for four days was effective at concentrations above 0.5 mg/L (LC50 = 0.35 mg/L), and 100 percent mortality was achieved at chlorine dioxide concentrations above 1 mg/L.

These experiences all show that the dose required to induce mortality to these nuisance organisms is extremely high, both in terms of chemical dose and contact time. The potential impact on DBPs is significant, especially when the water is high in organic content with a high propensity to form THMs and other DBPs.

2.2.3 Oxidation of Iron and Manganese

Iron and manganese occur frequently in ground waters but are less problematic in surface waters. Although not harmful to human health at the low concentrations typically found in water, these compounds can cause staining and taste problems. These compounds are readily treated by oxidation to produce a precipitant that is removed in subsequent sedimentation and filtration processes.

Almost all the common oxidants except chloramines will convert ferrous (2+) iron to the ferric (3+) state and manganese (2+) to the (4+) state, which will precipitate as ferric hydroxide and manganese dioxide, respectively (AWWA, 1990). The precise chemical composition of the precipitate will depend on the nature of the water, temperature, and pH.

Table 2-7 shows that oxidant doses for iron and manganese control are relatively low. In addition, the reactions are relatively rapid, on the order of seconds while DBP formation occurs over hours. Therefore, with proper dosing, residual chlorine during iron and manganese oxidation is therefore relatively low and short lived. These factors reduce the potential for DBP formation as a result of oxidation for iron and manganese removal.

Table 2-7. Oxidant Doses Required for Oxidation of Iron and Manganese

Oxidant	Iron (II) (mg/mg Fe)	Manganese (II) (mg/mg Mn)
Chlorine, Cl_2	0.62	0.77
Chlorine dioxide, ClO_2	1.21	2.45
Ozone, O_3	0.43	0.88*
Oxygen, O_2	0.14	0.29
Potassium permanganate, $KMnO_4$	0.94	1.92

Source: Culp/Wesner/Culp, 1986; Langlais et al., 1991.
* Optimum pH for manganese oxidation using ozone is 8-8.5 Source: Reckhow et al., 1991.

2.2.4 Prevention of Regrowth in the Distribution System and Maintenance of Biological Stability

Biodegradable organic compounds and ammonia in treated water can cause microbial growth in the distribution system. "Biological stability" refers to a condition wherein the treated water quality does not enhance biological growth in the distribution system. Biological stability can be accomplished in several ways:

- Removing nutrients from the water prior to distribution;
- Maintaining a disinfectant residual in the treated water; and
- Combining nutrient removal and disinfectant residual maintenance.

To maintain biological stability in the distribution system, the Total Coliform Rule (TCR) requires that treated water have a residual disinfectant of 0.2 mg/L when entering the distribution system. A measurable disinfectant residual must be maintained in the distribution system, or the utility must show through monitoring that the heterotrophic plate count (HPC) remains less than 500/100 mL. A system remains in compliance as long as 95 percent of samples meet these criteria. Chlorine, monochloramine, and chlorine dioxide are typically used to maintain a disinfectant residual in the distribution system. Filtration can also be used to enhance biological stability by reducing the nutrients in the treated water.

The level of secondary disinfectant residual maintained is low, typically in the range of 0.1-0.3 mg/L, depending on the distribution system and water quality. However, because the contact times in the system are quite long, it is possible to generate significant amounts of DBPs in the distribution system, even at low disinfectant doses.

Distribution system problems associated with the use of combined chlorine residual (chloramines), or no residual, have been documented in several instances. The use of combined chlorine is characterized by an initial satisfactory phase in which chloramine residuals are easily maintained throughout the system and bacterial counts are very low. However, problems may develop over a

period of years including increased bacterial counts, reduced combined chlorine residual, increased taste and odor complaints, and reduced transmission main carrying capacity. Conversion of the system to free-chlorine residual produces an initial increase in consumer complaints of taste and odors resulting from oxidation of accumulated organic material. Also, it is difficult to maintain a free-chlorine concentration at the ends of the distribution system (AWWA, 1990).

2.2.5 Removal of Taste and Odors Through Chemical Oxidation

Tastes and odors in drinking water are caused by several sources, including microorganisms, decaying vegetation, hydrogen sulfide, and specific compounds of municipal, industrial, or agricultural origin. Disinfectants themselves can also create taste and odor problems. In addition to a specific taste-and odor-causing compound, the sensory impact is often accentuated by a combination of compounds. More recently, significant attention has been given to tastes and odors from specific compounds such as geosmin, 2-methylisoborneol (MIB), and chlorinated inorganic and organic compounds (AWWARF, 1987).

Oxidation is commonly used to remove taste and odor causing compounds. Because many of these compounds are very resistant to oxidation, advanced oxidation processes (ozone/hydrogen peroxide, ozone/UV, etc.) and ozone by itself are often used to address taste and odor problems. The effectiveness of various chemicals to control taste and odors can be site-specific. Suffet et al. (1986) found that ozone is generally the most effective oxidant for use in taste and odor treatment. They found ozone doses of 2.5 to 2.7 mg/L and 10 minutes of contact time (residual 0.2 mg/L) significantly reduce levels of taste and odors. Lalezary et al. (1986) used chlorine, chlorine dioxide, ozone, and permanganate to treat earthy-musty smelling compounds. In that study, chlorine dioxide was found most effective, although none of the oxidants were able to remove geosmin and MIB by more than 40 to 60 percent. Potassium permanganate has been used in doses of 0.25 to 20 mg/L. Studies at the Metropolitan Water District of Southern California demonstrated the effectiveness of peroxone (ozone plus hydrogen peroxide) to remove geosmin and MIB in water treatment (Ferguson et al., 1990; Ferguson et al., 1991; Huck et al., 1995).

Prior experiences with taste and odor treatment indicate that oxidant doses are dependent on the source of the water and causative compounds. In general, small doses can be effective for many taste and odor compounds, but some of the difficult-to-treat compounds require strong oxidants such as ozone and/or advanced oxidation processes or alternative technologies such as granular activated carbon (GAC) adsorption.

2.2.6 Improvement of Coagulation and Filtration Efficiency

Oxidants, specifically ozone, have been reported to improve coagulation and filtration efficiency (Gurol and Pidatella, 1983; Farvardin and Collins, 1990; Reckhow et al., 1993; Masschelein, 1992). Others, however, have found no improvement in effluent turbidity from oxidation (Tobiason et al., 1992; Hiltebrand et al., 1986). Prendiville (1986) collected data from a large treatment plant showing that preozonation was more effective than prechlorination to reduce filter effluent turbidities. The cause of

the improved coagulation is not clear, but several possibilities have been offered (Reckhow et al., 1986), including:

- Oxidation of organics into more polar forms;
- Oxidation of metal ions to yield insoluble complexes such as ferric iron complexes; and
- Change in the structure and size of suspended particles.

2.2.7 Prevention of Algal Growth in Sedimentation Basins and Filters

Prechlorination is often used to minimize operational problems associated with biological growth in water treatment plants (AWWA, 1990; Culp/Wesner/Culp, 1986). Prechlorination will prevent slime formation on filters, pipes, and tanks, and reduce potential taste and odor problems associated with such slimes. Many sedimentation and filtration facilities operate with a small chlorine residual to prevent growth of algae and bacteria in the launders and on the filter surfaces. This practice has increased in recent years as utilities take advantage of additional contact time in the treatment units to meet disinfection requirements under the SWTR.

2.2.8 Removal of Color

Free chlorine is used for color removal. A low pH is favored. Color is caused by humic compounds, which have a high potential for DBP formation. The chlorine dosage and kinetics for color removal are best determined through bench studies.

2.3 Disinfection Byproducts and Disinfection Residuals

2.3.1 Types of DBPs and Disinfection Residuals

Table 2-8 is a list, compiled by EPA, of DBPs and disinfection residuals that may be of health concern. The table includes both the disinfectant residuals and the specific byproducts produced by the disinfectants of interest in drinking water treatment. These contaminants of concern are grouped into four distinct categories and include disinfectant residuals, inorganic byproducts, organic oxidation byproducts, and halogenated organic byproducts. Tables 1-3 and 1-4 list the disinfection byproducts and disinfectant residuals that are currently regulated.

Table 2-8. List of Disinfection Byproducts and Disinfection Residuals

DISINFECTANT RESIDUALS	**HALOGENATED ORGANIC BYPRODUCTS**
Free Chlorine	Trihalomethanes
Hypochlorous Acid	Chloroform
Hypochlorite Ion	Bromodichloromethane
Chloramines	Dibromochloromethane
Monochloramine	Bromoform
Chlorine Dioxide	Haloacetic Acids
INORGANIC BYPRODUCTS	Monochloroacetic Acid
Chlorate Ion	Dichloroacetic Acid
Chlorite Ion	Trichloroacetic Acid
Bromate Ion	Monobromoacetic Acid
Iodate Ion	Dibromoacetic Acid
Hydrogen Peroxide	Haloacetonitriles
Ammonia	Dichloroacetronitrile
ORGANIC OXIDATION BYPRODUCTS	Bromochloroacetonitrile
Aldehydes	Dibromoacetonitrile
Formaldehyde	Trichloroacetonitrile
Acetaldehyde	Haloketones
Glyoxal	1,1-Dichloropropanone
Hexanal	1,1,1-Trichloropropanone
Heptanal	Chlorophenols
Carboxylic Acids	2-Chlorophenol
Hexanoic Acid	2,4-Dichlorophenol
Heptanoic Acid	2,4,6-Trichlorophenol
Oxalic Acid	Chloropicrin
Assimilable Organic Carbon	Chloral Hydrate
	Cyanogen Chloride
	N-Organochloramines
	MX*

* 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone

The production of DBPs depend on the type of disinfectant, the presence of organic material (e.g., TOC), bromide ion, and other environmental factors as discussed in this manual. By removing DBP precursors, the formation of DBPs can be reduced.

The health effects of DBPs and disinfectants are generally evaluated with epidemiological studies and/or toxicological studies using laboratory animals. Table 2-9 indicates the cancer classifications of both disinfectants and DBPs as of January 1999. The classification scheme used by EPA is shown at the bottom of Table 2-9. The EPA classification scheme for carcinogenicity weighs both animal studies and epidemiologic studies, but places greater weight on evidence of carcinogenicity in humans.

Table 2-9. Status of Health Information for Disinfectants and DBPs

Contaminant	Cancer Classification[1]
Chloroform	B2
Bromodichloromethane	B2
Dibromochloromethane	C
Bromoform	B2
Monochloroacetic Acid	--
Dichloroacetic Acid	B2
Trichloroacetic Acid	C
Dichloroacetonitrile	C
Bromochloroacetonitrile	--
Dibromoacetonitrile	C
Trichloroacetonitrile	--
1,1-Dichloropropanone	--
1,1,1-Trichloropropanone	--
2-Chlorophenol	D
2,4-Dichlorophenol	D
2,4,6-Trichlorophenol	B2
Chloropicrin	--
Chloral Hydrate	C
Cyanogen Chloride	--
Formaldehyde	B1[2]
Chlorate	--
Chlorite	D
Bromate	B2
Ammonia	D
Hypochlorous Acid	--
Hypochlorite	--
Monochloramine	--
Chlorine Dioxide	D

(1) The scheme for categorizing chemicals according to their carcinogenic potential is as follows:*

Group A: Human Carcinogen	Sufficient evidence in epidemiologic studies to support casual association between exposure and cancer.
Group B: Probable Human Carcinogen	Limited evidence in epidemiologic studies (Group B1) and/or sufficient evidence from animal studies (Group B2)
Group C: Possible Human Carcinogen	Limited evidence from animal studies and inadequate or no data in humans
Group D: Not Classifiable	Inadequate or no human and animal evidence of carcinogenicity
Group E: No Evidence of Carcinogenicity for Humans	No evidence of carcinogenicity in at least two adequate animal tests in different species or in adequate epidemiologic and animal studies.

* EPA is in the process of revising the Cancer Guidelines
Source: USEPA, 1996

(2) Based on inhalation exposure.

2.3.2 Disinfection Byproduct Formation

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 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 of the 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.

2.3.2.1 Disinfection Byproduct 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; and
- 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 usually is constant.

DBP concentrations vary seasonally and are typically greatest in the summer and early fall for several reasons:

- The rate of DBP formation increases with increasing temperature (Singer et al., 1992);
- The nature of organic DBP precursors varies with season (Singer et al., 1992); and
- Due to warmer temperatures, chlorine demand may be greater during summer months requiring higher dosages to maintain disinfection.

If the bromide ion is present in source waters, it can be oxidized to hypobromous acid that can react with NOM to form brominated DBPs, such as bromoform. Furthermore, under certain conditions, ozone may react with the hypobromite ion (OBr^-) to form bromate ion (BrO^-_3).

The ratio of bromide ion to the chlorine dose affects THM formation and bromine substitution of chlorine. Increasing the bromide ion to chlorine dose ratio shifts the speciation of THMs to produce more brominated forms (Krasner et al., 1989; Black et al., 1996). In the Krasner et al. study, the chlorine dose was roughly proportional to TOC concentration. As TOC was removed through the treatment train, the chlorine dose decreased and TTHM formation declined. However, at the same time, the bromide ion to chlorine dose increased, thereby shifting TTHM concentrations to the more brominated THMs. Therefore, improving the removal of NOM prior to chlorination can shift the speciation of halogenated byproducts toward more brominated forms.

Chloropicrin is produced by the chlorination of humic materials in the presence of nitrate ion (Duguet et al., 1985; Thibaud et al., 1987). Thibaud et al. (1988) chlorinated humic compounds in the presence of bromide ion to demonstrate the formation of brominated analogs to chloropicrin.

2.3.2.2 Impacts of pH on DBP Formation

The pH of water being chlorinated has an impact on the formation of halogenated byproducts as shown in Table 2-10 (Reckhow and Singer, 1985; Stevens et al., 1989). THM formation increases with increasing pH. Trichloroacetic acid, dichloroacetonitrile, and trichloropropanone formation decrease with increased pH. Overall TOX formation decreases with increasing pH.

Based on chlorination studies of humic material in model systems, high pH tends to favor chloroform formation over the formation of trichloroacetic acid and other organic halides. Accordingly, water treatment plants practicing precipitative softening at pH values greater than 9.5 to 10 are likely to have a higher fraction of TOX attributable to THMs than plants treating surface waters by conventional treatment in pH ranges of 6 to 8 (Singer and Chang, 1989).

Since the application of chlorine dioxide and chloramines may introduce free chlorine into water, chlorination byproducts that may be formed would be influenced by pH as discussed above. Ozone application to bromide ion containing waters at high pH favors the formation of bromate ion, while application at low pH favors the formation of brominated organic byproducts. See discussion under individual disinfectants for a more detailed discussion on pH impacts on DBP formation.

The pH also impacts enhanced coagulation (i.e., for ESWTR compliance) and Lead and Copper Rule Compliance. These issues are addressed in EPA's *Microbial and Disinfection Byproduct Simultaneous Compliance Guidance Manual* (expected to be available in 1999).

2.3.2.3 Organic Oxidation Byproducts

Organic oxidation byproducts are formed by reactions between NOM and all oxidizing agents added during drinking water treatment. Some of these byproducts are halogenated, as discussed in the previous section, while others are not. The types and concentrations of organic oxidation byproducts produced depend on the type and dosage of the oxidant being used, chemical characteristics and concentration of the NOM being oxidized, and other factors such as the pH and temperature.

Specific chemical byproducts belonging to the classification of halogenated organic oxidation products are listed in Table 2-10. As presented in Table 2-10, the formation of DBPs is pH dependent. Comparisons in the table are made to the formation of TTHMs at a pH of 7.0. AOC is not a specific organic contaminant, but a generally used surrogate measure of bacterial regrowth potential in distribution systems. AOC is comprised of many chemical species, including the aldehydes and carboxylic acids listed in Table 2-8. AOC formation studies, primarily performed in the Netherlands, have shown that both ozonation and chlorination can increase concentrations of AOC. This increase in AOC concentration is believed to be the result of oxidizing high molecular weight organics to smaller and more readily bioassimilable molecules. Because AOC is not a specific chemical contaminant, no specific health effects are attributable to AOC.

Table 2-10. Conditions of Formation of DBPs

By-product	Conditions of Formation		
	Chlorination at pH 5.0	Chlorination at pH 7.0	Chlorination at pH 9.4
Total Trihalomethanes	Lower formation		Higher formation
Trichloroacetic Acid	Similar formation to that at pH 7.0	Similar formation to that at pH 5.0	Lower formation
Dichloroacetic Acid	Similar formation to that at pH 5.0 and 9.4 - perhaps slightly higher at pH 7.0	Similar formation to that at pH 5.0 and 9.4- perhaps slightly higher at pH 7.0	Similar formation to that at pH 5.0 and 7.0 - perhaps slightly higher at pH 7.0
Monochloroacetic Acid	At concentrations <5 μg/L, trends not discernible	At concentrations <5 μg/L, trends not discernible	At concentrations <5 μg/L, trends not discernible
Dibromoacetic Acid	At concentrations <1 μg/L, trends not discernible	At concentrations <1 μg/L, trends not discernible	At concentrations <1 μg/L, trends not discernible
Chloral Hydrate	Similar formation to that at pH 7.0	Similar formation to that at pH 5.0	Forms within 4 hours; decays over time to <5 μg/L
Chloropicrin	At concentrations <1 μg/L, trends not discernible	At concentrations <1 μg/L, trends not discernible	At concentrations <1 μg/L, trends not discernible
Dichloroacetonitrile	Higher formation	Forms within 4 hours; decays over time to <5 μg/L	Concentrations <2 μg/L, trends not discernible
Bromochloroacetonitrile	At concentrations <2 μg/L, trends not discernible	At concentrations <2 μg/L, trends not discernible	At concentrations <2 μg/L, trends not discernible
Dibromoacetonitrile	At concentrations <.5 μg/L, trends not discernible	At concentrations <.5 μg/L, trends not discernible	At concentrations <.5 μg/L, trends not discernible
Trichloroacetonitrile	Not detected	Not detected	Not detected
1,1,1-Trichloropropanone	Higher formation	At concentrations <2 μg/L, trends not discernible	Not detected

Source: Stevens et al., 1989.

2.3.2.4 Inorganic Byproducts and Disinfectants

Table 2-11 shows some of the inorganic DBPs that are produced or remain as residual during disinfection. As discussed earlier, bromide ion reacts with strong oxidants to form bromate ion and other organic DBPs. Chlorine dioxide and chloramines leave residuals that are of concern for health considerations, as well as for taste and odor. The significance of these compounds is discussed further in subsequent chapters.

Table 2-11. Inorganic DBPs Produced During Disinfection

Disinfectant	Inorganic Byproduct or Disinfectant Residual Discussed
Chlorine Dioxide	Chlorine Dioxide, Chlorite ion, Chlorate ion, Bromate ion (in presence of light)
Ozone	Bromate ion, Hydrogen Peroxide
Chloramination	Monochloramine, Dichloramine, Trichloramine, Ammonia, Cyanogen Chloride

2.3.3 DBP Control Strategies

In 1983, the EPA identified technologies, treatment techniques, and plant modifications that community water systems could use to comply with the maximum contaminant level for TTHMs. The principal treatment modifications involved moving the point of chlorination downstream in the water treatment plant, improving the coagulation process to enhance the removal of DBP precursors, and using chloramines to supplement or replace the use of free chlorine (Singer, 1993). Moving the point of chlorination downstream in the treatment train often is very effective in reducing DBP formation, because it allows the NOM precursor concentration to be reduced during treatment prior to chlorine addition. Replacing prechlorination by preoxidation with an alternate disinfectant that produces less DBPs is another option for reducing formation of chlorinated byproducts.

Other options to control the formation of DBPs include; source water quality control, DBP precursor removal, and disinfection strategy selection. An overview of each is provided below.

2.3.3.1 Source Water Quality Control

Source water control strategies involve managing the source water to lower the concentrations of NOM and bromide ion in the source water. Research has shown that algal growth leads to the production of DBP precursors (Oliver and Shindler, 1980; Wachter and Andelman, 1984; Karimi and Singer, 1991). Therefore, nutrient and algal management is one method of controlling DBP formation potential of source waters. Control of bromide ion in source waters may be accomplished by preventing brine or salt water intrusion into the water source.

2.3.3.2 DBP Precursor Removal

Raw water can include DBP precursors in both dissolved and particulate forms. For the dissolved precursors to be removed in conventional treatment, they must be converted to particulate form for subsequent removal during settling and filtering. The THM formation potential generally decreases by about 50 percent through conventional coagulation and settling, indicating the importance of moving the point of chlorine application after coagulation and settling (and even filtration) to control TOX as well as TTHM formation (Singer and Chang, 1989). Conventional systems can lower the DBP formation potential of water prior to disinfection by further removing precursors with enhanced coagulation, GAC adsorption, or membrane filtration prior to disinfection. Precursor removal efficiencies are site-specific and vary with different source waters and treatment techniques.

Aluminum (alum) and iron (ferric) salts can remove variable amounts of NOM. For alum, the optimal pH for NOM removal is in the range of 5.5 to 6.0. The addition of alum decreases pH and may allow the optimal pH range to be reached without acid addition. However, waters with very low or very high alkalinities may require the addition of base or acid to reach the optimal NOM coagulation pH (Singer, 1992).

GAC adsorption can be used following filtration to remove additional NOM. For most applications, empty bed contact times in excess of 20 minutes are required, with regeneration frequencies on the order of 2 to 3 months (Singer, 1992). These long contact times and frequent regeneration requirements make GAC an expensive treatment option. In cases where prechlorination is practiced, the chlorine rapidly degrades GAC. Addition of a disinfectant to the GAC bed can result in specific reactions in which previously absorbed compounds leach into the treated water.

Membrane filtration has been shown effective in removing DBP precursors in some instances. In pilot studies, ultrafiltration (UF) with a molecular weight cutoff (MWCO) of 100,000 daltons was ineffective for controlling DBP formation. However, when little or no bromide ion was present in source water, nanofiltration (NF) membranes with MWCOs of 400 to 800 daltons effectively controlled DBP formation (Lâiné et al., 1993). In waters containing bromide ion, higher bromoform concentrations were observed after chlorination of membrane permeate (compared with raw water). This occurs as a result of filtration removing NOM while concentrating bromide ions in the permeate thus providing a higher ratio of bromide ions to NOM than in raw water. This reduction in chlorine demand increases the ratio of bromide to chlorine, resulting in higher bromoform concentrations after chlorination of NF membrane permeate (compared with the raw water). TTHMs were lower in chlorinated permeate than chlorinated raw water. However, due to the shift in speciation of THMs toward more brominated forms, bromoform concentrations were actually greater in chlorinated treated water than in chlorinated raw water. Use of spiral-wound NF membranes (200–300 daltons) more effectively controlled the formation of brominated THMs, but pretreatment of the water was necessary (Lâiné et al., 1993). Significant limitations in the use of membranes are disposal of the waste brine generated, fouling of membranes, cost of membrane replacement, and increasing energy cost.

The promulgated DBPR requires enhanced coagulation as an initial step for removal of DBP precursors. In addition to meeting MCLs and MRDLs, some water suppliers also must meet treatment requirements to control the organic material (DBP precursors) in the raw water that combines with disinfectant residuals to form DBPs. Systems using conventional treatment are required to control precursors (measured as TOC) by using enhanced coagulation or enhanced softening. A system must remove a specified percentage of TOC (based on raw water quality) prior to the point of continuous disinfection (Table 2-12).

Systems using ozone followed by biologically active filtration or chlorine dioxide that meet specific criteria would be required to meet the TOC removal requirements prior to addition of a residual disinfectant. Systems able to reduce TOC by a specified percentage level have met the DBPR treatment technique requirement.

Table 2-12. Required Removal of TOC by Enhanced Coagulation for Surface Water Systems[+] Using Conventional Treatment[++] (percent reduction)

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0-60	>60-120	>120[+++]
>2.0-4.0	35.0	25.0	15.0
>4.0-8.0	45.0	35.0	25.0
>8.0	50.0	40.0	30.0

\+ Also applies to utilities that treat ground water under the influence of surface water.

++ Systems meeting at least one of the conditions in 40 CFR §§ 141.135(a)(1)(I)-(iv) are not required to operate with enhanced coagulation.

+++ Systems practicing precipitative softening must meet the TOC removal requirements in this column.

If the system does not meet the percent reduction, it must determine its alternative minimum TOC removal level. The primacy agency approves the alternative minimum TOC removal possible for the system on the basis of the relationship between coagulant dose and TOC in the system based on results of bench or pilot-scale testing. Enhanced coagulation is determined in part as the coagulant dose where an incremental addition of 10 mg/L of alum (or an equivalent amount of ferric salt) results in a TOC removal below 0.3 mg/L.

2.3.3.3 Disinfection Strategy Selection

In addition to improving the raw or predisinfectant water quality, alternative disinfection strategies can be used to control DBPs. These strategies include the following:

- Use an alternative or supplemental disinfectant or oxidant such as chloramines or chlorine dioxide that will produce fewer DBPs;
- Move the point of chlorination to reduce TTHM formation and, where necessary, substitute chloramines, chlorine dioxide, or potassium permanganate for chlorine as a preoxidant;
- Use two different disinfectants or oxidants at various points in the treatment plant to avoid DBP formation at locations where precursors are still present in high quantities;
- Use of powdered activated carbon for THM precursor or TTHM reduction seasonally or intermittently; and
- Maximize precursor removal.

2.3.4 CT Factor

One of the most important factors for determining or predicting the germicidal efficiency of any disinfectant is the CT factor, a version of the Chick-Watson law (Chick, 1908; Watson, 1908). The CT factor is defined as the product of the residual disinfectant concentration, C, in mg/L, and the contact time, T, in minutes, that residual disinfectant is in contact with the water.

EPA developed CT values for the inactivation of *Giardia* and viruses under the SWTR. Table 2-13 compares the CT values for virus inactivation using chlorine, chlorine dioxide, ozone, chloramine, and ultraviolet light disinfection under specified conditions. Table 2-14 shows the CT values for inactivation of *Giardia* cyst using chlorine, chloramine, chlorine dioxide, and ozone under specified conditions. The CT values shown in Table 2-13 and Table 2-14 are based on water temperatures of 10°C and pH values in the range of 6 to 9. CT values for chlorine disinfection are based on a free chlorine residual. Note that chlorine is less effective as pH increases from 6 to 9. In addition, for a given CT value, a low C and a high T is more effective than the reverse (i.e., a high C and a low T). For all disinfectants, as temperature increases, effectiveness increases.

Table 2-13. CT Values for Inactivation of Viruses

Disinfectant	Units	Inactivation		
		2-log	3-log	4-log
Chlorine[1]	mg · min/L	3	4	6
Chloramine[2]	mg · min/L	643	1,067	1,491
Chlorine Dioxide[3]	mg · min/L	4.2	12.8	25.1
Ozone	mg · min/L	0.5	0.8	1.0
UV	$mW \cdot s/cm^2$	21	36	not available

CT values were obtained from AWWA, 1991.
[1] Values are based on a temperature of 10°C, pH range of 6 to 9, and a free chlorine residual of 0.2 to 0.5 mg/L.
[2] Values are based on a temperature of 10°C and a pH of 8.
[3] Values are based on a temperature of 10°C and a pH range of 6 to 9.

Table 2-14. CT Values for Inactivation of *Giardia* Cysts

Disinfectant	Inactivation (mg · min/L)					
	0.5-log	1-log	1.5-log	2-log	2.5-log	3-log
Chlorine[1]	17	35	52	69	87	104
Chloramine[2]	310	615	930	1,230	1,540	1,850
Chlorine Dioxide[3]	4	7.7	12	15	19	23
Ozone[3]	0.23	0.48	0.72	0.95	1.2	1.43

CT values were obtained from AWWA, 1991.
[1] Values are based on a free chlorine residual less than or equal to 0.4 mg/L, temperature of 10°C, and a pH of 7.
[2] Values are based on a temperature of 10°C and a pH in the range of 6 to 9.
[3] Values are based on a temperature of 10°C and a pH of 6 to 9.

2.4 Pathogen Inactivation Versus DBP Formation

Table 2-15 presents a summary of disinfection parameter impacts on pathogen inactivation and DBP formation.

Table 2-15. Summary of Disinfection Impacts

Disinfection Parameter	Typical Impact on Pathogen Inactivation	Typical Impact on DBP Formation
Disinfectant Type	Depends on inactivation efficacy	Depends on disinfectant reactivity
Disinfectant Strength	The stronger the disinfectant, the quicker the disinfection process.	The stronger the disinfectant, the greater the amount of DBPs.
Disinfectant Dose	Increasing the disinfectant dose increases the disinfection rate.	Increasing the disinfectant dose typically increases the rate of DBP formation.
Type of Organism	Susceptibility to disinfection varies according to pathogen group. In general, protozoa are more resistant to disinfectants than bacteria and viruses.	None.
Contact Time	Increasing the contact time decreases the disinfectant dose required for a given level of inactivation.	Increasing contact time with an equivalent disinfectant dose increases the formation of DBPs.
pH	pH may affect the disinfectant form and, in-turn, the efficiency of the disinfectant.	The impact of pH varies with DBP. See Section 2.3.2.3 for a brief summary of relationships between pH and DBP formation.
Temperature	Increasing the temperature increases the rate of disinfection.	Increasing temperature is typically associated with faster oxidation kinetics, hence, increased DBP formation.
Turbidity	Particles responsible for turbidity can surround and shield pathogenic microorganisms from disinfectants.	Increased turbidity may be associated with increased NOM, which represents an increased amount of DBP precursors for the formation of DBPs when disinfectant is applied.
Dissolved Organics	Dissolved organics can interfere with disinfection by creating a demand and reducing the amount of disinfectant available for pathogen inactivation.	Increased dissolved organics will represent a larger amount of DBP precursor for the formation of DBPs when disinfectant is applied.

2.5 Disinfectant Residual Regulatory Requirements

One of the most important factors for evaluating the merits of alternative disinfectants is their ability to maintain the microbial quality in the water distribution system. Disinfectant residuals may serve to protect the distribution system against regrowth (Snead et al., 1980). The SWTR requires that filtration and disinfection must be provided to ensure that the total treatment of the system achieves at least a 3-log removal/inactivation of *Giardia* cysts and a 4-log removal/inactivation of viruses. In addition, the disinfection process must demonstrate by continuous monitoring and recording that the disinfectant residual in the water entering the distribution system is never less than 0.2 mg/L for more than 4 hours.

Several of the alternative disinfectants examined in this manual cannot be used to meet the residual requirements stated in the SWTR. For example, if either ozone or ultraviolet light disinfection are used as the primary disinfectant, a secondary disinfectant such as chlorine or chloramines should be utilized to obtain a residual in the distribution system.

DBP formation continues in the distribution system due to reactions between the residual disinfectant and organics in the water. Koch et al. (1991) found that with a chlorine dose of 3-4 mg/L, THM and HAA concentrations increase rapidly during the first 24 hours in the distribution system. After the initial 48 hours, the subsequent increase in THMs is very small. Chloral hydrate concentrations continued to increase after the initial 24 hours, but at a reduced rate. Haloketones actually decreased in the distribution system.

Nieminski et al. (1993) evaluated DBP formation in the simulated distribution systems of treatment plants in Utah. Finished water chlorine residuals ranged from 0.4 to 2.8 mg/L. Generally, THM values in the distribution system studies increased by 50 to 100 percent (range of 30 to 200 percent) of the plant effluent value after 24-hour contact time. The 24-hour THM concentration was essentially the same as the 7-day THM formation potential. HAA concentrations in the simulated distribution system was about 100 percent (range of 30 to 200 percent) of the HAA in the plant effluent. The 7-day HAA formation potential was sometimes higher, or below the distribution system values. If chlorine is used as a secondary disinfectant, one should therefore anticipate a 100-percent increase in the plant effluent THMs, or plan to reach the 7-day THM formation level in the distribution system.

2.6 Summary of Current National Disinfection Practices

Most water treatment plants disinfect water prior to distribution. The 1995 Community Water Systems Survey (USEPA, 1997a) reports 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 ground water as their only water source.

The most commonly used disinfectants/oxidants are chlorine, chlorine dioxide, chloramines, ozone, and potassium permanganate. Table 2-16 shows a breakdown on the chemical usage from the survey. Note that the table shows the percentages of systems using the particular chemical as either disinfectant or some other role. The table shows the predominance of chlorine in surface and ground water disinfection treatment systems with more than 60 percent of the treatment systems using chlorine as disinfectant/oxidant. Potassium permanganate on the other hand, is used by many systems, but its application is primarily for oxidation, rather than for disinfection.

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.

The International Ozone Association conducted a survey of ozone facilities in the United States (IOA, 1997). The survey documented the types of ozone facilities, size, objective of ozone application, and year of operation. Table 2-17 summarizes the findings from the survey. The most common use for ozone is 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 the 158

operating ozone facilities, the survey identified 19 facilities under construction and another 30 under design. The capacity of the systems range from less than 25 gpm to exceeding 500 mgd. Nearly half of the operating facilities have a capacity exceeding 1 mgd. Rice et al. (1998) found that as of May 1998, 264 drinking water plants in the United States are using ozone.

Table 2-16. Disinfection Practices of Water Systems that Include Some Form of Treatment

Treatment	Service Population								
	<100	101-500	501-1,000	1,001-3,300	3,301-10,000	10,001-50,000	50,001-100,000	Over 100,001	Total
Surface Water Systems									
Total Number of Systems	218	432	330	845	679	626	103	104	3,337
Pre-Disinfection, Oxidation/Softening									
Chlorine	59.0%	73.9%	67.3%	66.3%	68.8%	58.6%	47.5%	57.1%	63.8%
Chlorine dioxide	0	0	0	5.0	4.7	13.2	14.2	7.8	6.3
Chloramines	4.6	0	1.1	2.1	0	2.2	15.5	10.8	3.1
Ozone	0	0	0	0	0.3	0	5.4	5.8	0.9
$KMnO_4$	0	4.9	9.6	9.9	15.2	28.3	25.9	28.5	16.0
Predisinfection/oxidation	0	0	2.0	2.9	0.6	9.2	5.1	4.3	3.5
Lime/Soda ash softening	6.8	9.8	20.9	16.2	14.3	11.7	3.5	5.9	12.5
Recarbonation	0	0	0	0	2.1	4.7	0.6	6.3	1.9
Post-Disinfection									
Chlorine	49.7 %	51.6%	80.6%	62.8%	77.9%	71.1%	73.8 %	63.6 %	67.5 %
Chlorine dioxide	0	0	0	0	0.3	4.9	5.9	11.2	1.6
Chloramines	0	0	0	2.9	2.1	15.6	29.4	24.2	8.1
Postdisinfection combinations	0	0	0	2.1	4.0	3.9	1.9	1.6	3.0
Ground Water Systems									
Total Number of Systems	9,042	10,367	4,443	4,422	2,035	1,094	120	56	31,579
Pre-Disinfection, Oxidation/Softening									
Chlorine	64.2 %	69.9 %	56.7 %	73.2 %	60.6 %	57.4 %	36.2 %	38.1 %	63.9 %
Chlorine dioxide	1.3	0	0	0	0	0	3.1	0	0.3
Chloramines	0	0	0	0	0	0.6	1.4	0.7	0.1
Ozone	0	0	0	0	0	0	0	0.6	0
$KMnO_4$	0	0.9	2.2	0.6	5.8	3.2	7.0	0	1.8
Predisinfection/oxidation	0.3	0.5	0	0.7	1.0	2.6	0	0	0.7
Lime/Soda ash softening	2.9	2.9	2.2	3.6	3.5	3.8	5.0	9.1	3.2
Recarbonation	0	0.5	0	0.6	1.4	1.5	2.8	1.1	0.6
Post-Disinfection									
Chlorine	23.0 %	23.4%	32.5%	28.3 %	42.5%	41.9 %	54.5 %	65.8 %	31.0 %
Chlorine dioxide	0	1.0	0	0	0	0.6	0	0	0.4
Chloramines	0	0	0	0	0.1	1.1	3.9	4.3	0.3
Postdisinfection combinations	0	0	0	0	0.1	0.1	0	0	0

Source: USEPA, 1997a.

Table 2-17. Ozone Application in Water Treatment Plants in the United States

Ozone Objective	Number of Plants	% Plants
THM Control	50	32
Disinfection	63	40
Iron/Manganese, Taste and Odor Control	92	58
Total	158	--

Source: IOA, 1997.

2.7 Chlorine

Although chlorine is not a focus of this guidance manual, the following section provides a brief overview of chlorine use in the water treatment industry to compare with the alternative disinfectants discussed in this manual. Since there is a wealth of excellent literature on chlorine's uses and performance capabilities, summarizing this large body of knowledge here is neither practical nor necessary (see, for example: White, 1992; Chlorine Institute, 1996; and Connell, 1996).

One of the recent developments in chlorine disinfection is the use of multiple and interactive disinfectants. In these applications, chlorine is combined with a second disinfectant to achieve improved disinfection efficiency and/or effective DBP control. A detailed discussion on multiple disinfectants, including chlorine combinations, is provided in Chapter 9.

As described earlier, the 1995 Community Water System Survey (USEPA, 1997a), indicated that the majority of all surface water and ground water systems in the United States use chlorine for disinfection.

Chlorine has many attractive features that contribute to its wide use in the industry. Four of the key attributes of chlorine are that it:

- Effectively inactivates a wide range of pathogens commonly found in water;
- Leaves a residual in the water that is easily measured and controlled;
- Is economical; and
- Has an extensive track record of successful use in improving water treatment operations (despite the dangers associated with chlorine application and handling, specifically chlorine gas, it still maintains an excellent safety record).

There are, however, some concerns regarding chlorine usage that may impact its uses such as:

- Chlorine reacts with many naturally occurring organic and inorganic compounds in water to produce undesirable DBPs;
- Hazards associated with using chlorine, specifically chlorine gas, require special treatment and response programs; and
- High chlorine doses can cause taste and odor problems.

Chlorination is used in water treatment facilities primarily for disinfection. Because of chlorine's oxidizing powers, it has been found to serve other useful purposes in water treatment, such as (White, 1992):

- Taste and odor control;
- Prevention of algal growths;
- Maintenance of clear filter media;
- Removal of iron and manganese;
- Destruction of hydrogen sulfide;
- Bleaching of certain organic colors;
- Maintenance of distribution system water quality by controlling slime growth;
- Restoration and preservation of pipeline capacity;
- Restoration of well capacity, water main sterilization; and
- Improved coagulation by activated silica.

2.7.1 Chlorine Chemistry

Chlorine for disinfection typically is used in one of three forms: chlorine gas, sodium hypochlorite, or calcium hypochlorite. A brief description of the chemistry of these three chemicals is provided below.

2.7.1.1 Chlorine Gas

Chlorine gas hydrolyzes rapidly in water to form hypochlorous acid (HOCl). The following equation presents the hydrolysis reaction:

$$Cl_{2(g)} + H_2O \Rightarrow HOCl + H^+ Cl^- \qquad \textit{Equation 1}$$

Note that the addition of chlorine gas to water reduces the pH of the water due to the production of hydrogen ion.

Hypochlorous acid is a weak acid (pK_a of about 7.5), meaning it dissociates slightly into hydrogen and hypochlorite ions as noted in Equation 2:

$$HOCl \; \hat{U} \; H^+ + O\,Cl^- \qquad \textit{Equation 2}$$

Between a pH of 6.5 and 8.5 this dissociation is incomplete and both HOCl and OCl^- species are present to some extent (White, 1992). Below a pH of 6.5, no dissociation of HOCl occurs, while above a pH of 8.5, complete dissociation to OCl^- occurs. As the germicidal effects of HOCl is much higher than that of OCl^-, chlorination at a lower pH is preferred.

2.7.1.2 Hypochlorite

In addition to chlorine gas, chlorine is also available in hypochlorite form as both aqueous solutions and dry solids. The most common aqueous hypochlorite solution is sodium hypochlorite. The most common form of dry solid hypochlorite is calcium hypochlorite (White, 1992).

Sodium Hypochlorite. Sodium hypochlorite is produced when chlorine gas is dissolved in a sodium hydroxide solution. Sodium hypochlorite solution typically contains 12.5 percent available chlorine (White, 1992). One gallon of 12.5 percent sodium hypochlorite solution typically contains the equivalent of one pound of chlorine.

The reaction between sodium hypochlorite and water is shown in the following reaction:

$$NaOCl + H_2O \Rightarrow HOCl + Na^+ + OH^- \qquad \textit{Equation 3}$$

Equation 3 shows that the application of sodium hypochlorite to water produces hypochlorous acid, similar to chlorine gas hydrolysis (Equation 1). However, unlike chlorine hydrolysis, the addition of sodium hypochlorite to water yields a hydroxyl ion that will increase the pH of the water. In addition, excess sodium hydroxide is used to manufacture sodium hypochlorite, which will further increase the pH of the water.

Calcium Hypochlorite. Calcium hypochlorite is formed from the precipitate that results from dissolving chlorine gas in a solution of calcium oxide (lime) and sodium hydroxide. Granular calcium hypochlorite commercially available typically contains 65 percent available chlorine. This means that 1.5 pounds of calcium hypochlorite contains the equivalent of one pound of chlorine. The reaction between calcium hypochlorite and water is shown in the following reaction:

$$Ca(OCl)_2 + 2H_2O \Rightarrow 2HOCl + Ca^{++} + 2OH^- \qquad \textit{Equation 4}$$

Equation 4 shows that the application of calcium hypochlorite to water also produces hypochlorous acid, similar to chlorine gas hydrolysis (Equation 1). Similar to sodium hypochlorite solution, the addition of calcium hypochlorite to water yields hydroxyl ions that will increase the pH of the water.

2.7.2 Chlorine Generation

Onsite generation of chlorine has recently become practical. These generation systems, using only salt and electric power, can be designed to meet disinfection and residual standards and to operate unattended at remote sites. Considerations for chlorine generation include cost, concentration of the brine produced, availability of raw materials, and the reliability of the process (AWWA and ASCE, 1997).

2.7.2.1 Chlorine

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. About 70 percent of the chlorine produced in the United States is manufactured from the electrolysis of salt brine and caustic solutions in a diaphragm cell (White, 1992). Since chlorine is a stable compound, it is typically produced off-site by a chemical manufacturer. Once produced, chlorine is packaged as a liquefied gas under pressure for delivery to the site in railcars, tanker trucks, or cylinders.

2.7.2.2 Sodium Hypochlorite

Dilute sodium hypochlorite solutions (less than 1 percent) can be generated electrochemically on-site from salt brine solution. Typically, sodium hypochlorite solutions are referred to as liquid bleach or Javelle water. Generally, the commercial or industrial grade solutions produced have hypochlorite strengths of 10 to 16 percent. The stability of sodium hypochlorite solution depends on the hypochlorite concentration, the storage temperature, the length of storage (time), the impurities of the solution, and exposure to light. Decomposition of hypochlorite over time can affect the feed rate and dosage, as well as produce undesirable byproducts such as chlorite ions or chlorate (Gordon et al., 1995). Because of the storage problems, many systems are investigating onsite generation of hypochlorite in lieu of its purchase from a manufacturer or vendor (USEPA, 1998b).

2.7.2.3 Calcium Hypochlorite

To produce calcium hypochlorite, hypochlorous acid is made by adding chlorine monoxide to water and then neutralizing it with a lime slurry to create a solution of calcium hypochlorite. The water is removed from the solution, leaving granulated calcium hypochlorite. Generally, the final product contains up to 70 percent available chlorine and 4 to 6 percent lime. Storage of calcium hypochlorite is a major safety consideration. It should never be stored where it is subject to heat or allowed to contact any organic material of an easily oxidized nature (USEPA, 1998b).

2.7.3 Primary Uses and Points of Application of Chlorine

2.7.3.1 Uses

The main usage of chlorine in drinking water treatment is for disinfection. However, chlorine has also found application for a variety of other water treatment objectives such as, the control of nuisance organisms, oxidation of taste and odor compounds, oxidation of iron and manganese, color removal, and as a general treatment aid to filtration and sedimentation processes (White, 1992; Connell, 1996; Culp/Wesner/Culp, 1986). Table 2-18 presents a summary of chlorine uses and doses.

Table 2-18. Chlorine Uses and Doses

Application	Typical Dose	Optimal pH	Reaction Time	Effectiveness	Other Considerations
Iron	0.62 mg/mg Fe	7.0	less than 1 hour	Good	
Manganese	0.77 mg/mg Mn	7–8 9.5	1–3 hour minutes	Slow kinetics	Reaction time increases at lower pH
Biological growth	1–2 mg/L	6–8	NA	Good	DBP formation
Taste/odor	Varies	6–8	Varies	Varies	Effectiveness depends on compound
Color removal	Varies	4.0–6.8	Minutes	Good	DBP formation
Zebra mussels	2–5 mg/L 0.2–0.5 mg/L[(a)]		Shock level Maintenance level	Good	DBP formation
Asiatic clams	0.3–0.5 mg/L[(a)]		Continuous	Good	DBP formation

Notes:
[(a)] Residual, not dose

Sources: Adapted in part from White, 1992; Connell, 1996; Culp/Wesner/Culp, 1986.

2.7.3.2 Points of Application

At conventional surface water treatment plants, chlorine is typically added for prechlorination at either the raw water intake or flash mixer, for intermediate chlorination ahead of the filters, for postchlorination at the filter clearwell, or for rechlorination of the distribution system (Connell, 1996). Table 2-19 summarizes the typical uses for each point of application.

Table 2-19. Typical Chlorine Points of Application and Uses

Point of Application	Typical Uses
Raw Water Intake	Zebra mussel and Asiatic clam control, control biological growth
Flash Mixer (prior to sedimentation)	Disinfection, iron and manganese oxidation, taste and odor control, oxidation of hydrogen sulfide
Filter Influent	Disinfection, control biological growth in filter, iron and manganese oxidation, taste and odor control, algae control, color removal
Filter Clearwell	Disinfection
Distribution System	Maintain disinfectant residual

Sources: Connell, 1996; White, 1992; AWWA, 1990.

2.7.3.3 Typical Doses

Table 2-20 shows the typical dosages for the various forms of chlorine. The wide range of chlorine gas dosages most likely represents its use as both an oxidant and a disinfectant. While sodium hypochlorite and calcium hypochlorite can also serve as both an oxidant and a disinfectant, their higher cost may limit their use.

Table 2-20. Typical Chlorine Dosages at Water Treatment Plants

Chlorine Compound	Range of Doses
Calcium hypochlorite	0.5–5 mg/L
Sodium hypochlorite	0.2–2 mg/L
Chlorine gas	1–16 mg/L

Source: SAIC, 1998, as adapted from EPA's review of public water systems' Initial Sampling Plans which were required by EPA's Information Collection Rule (ICR)

2.7.4 Pathogen Inactivation and Disinfection Efficacy

2.7.4.1 Inactivation Mechanisms

Research has shown that chlorine is capable of producing lethal events at or near the cell membrane as well as affecting DNA. In bacteria, chlorine was found to adversely affect cell respiration, transport, and possibly DNA activity (Haas and Engelbrecht, 1980). Chlorination was found to cause an immediate decrease in oxygen utilization in both *Escherichia coli* and *Candida parapsilosis* studies. The results also found that chlorine damages the cell wall membrane, promotes leakage through the cell membrane, and produces lower levels of DNA synthesis for *Escherichia coli, Candida parapsilosis*, and *Mycobacterium fortuitum* bacteria. This study also showed that chlorine inactivation is rapid and does not require bacteria reproduction (Haas and Engelbrecht, 1980). These observations rule out mutation or lesions as the principal inactivation mechanisms since these mechanisms require at least one generation of replication for inactivation to occur.

2.7.4.2 Environmental Effects

Several environmental factors influence the inactivation efficiency of chlorine, including water temperature, pH, contact time, mixing, turbidity, interfering substances, and the concentration of available chlorine. In general, the highest levels of pathogen inactivation are achieved with high chlorine residuals, long contact times, high water temperature, and good mixing, combined with a low pH, low turbidity, and the absence of interfering substances. Of the environmental factors, pH and temperature have the most impact on pathogen inactivation by chlorine. The effect of pH and temperature on pathogen inactivation are discussed below.

pH. The germicidal efficiency of hypochlorous acid (HOCl) is much higher than that of the hypochlorite ion (OCl^-). The distribution of chlorine species between HOCl and OCl^- is determined by pH, as discussed above. Because HOCl dominates at low pH, chlorination provides more effective disinfection at low pH. At high pH, OCl^- dominates, which causes a decrease in disinfection efficiency.

The inactivation efficiency of gaseous chlorine and hypochlorite is the same at the same pH after chlorine addition. Note, however, that addition of gaseous chlorine will decrease the pH (see Equation 1) while the addition of hypochlorite will increase the pH of the water (see Equation 3 and

Equation 4). Therefore, without pH adjustment to maintain the same treated water pH, gaseous chlorine will have greater disinfection efficiency than hypochlorite.

The impact of pH on chlorine disinfection has been demonstrated in the field. For example, virus inactivation studies have shown that 50 percent more contact time is required at pH 7.0 than at pH 6.0 to achieve comparable levels of inactivation. These studies also demonstrated that a rise in pH from 7.0 to 8.8 or 9.0 requires six times the contact time to achieve the same level of virus inactivation (Culp and Culp, 1974). Although these studies found a decrease in inactivation with increasing pH, some studies have shown the opposite effect. A 1972 study reported that viruses were more sensitive to free chlorine at high pH than at low pH (Scarpino et al., 1972).

Temperature. For typical drinking water treatment temperatures, pathogen inactivation increases with temperature. Virus studies indicate that the contact time should be increased by two to three times to achieve comparable inactivation levels when the water temperature is lowered by 10°C (Clarke et al., 1962).

2.7.4.3 Disinfection Efficacy

Since its introduction, numerous investigations have been made to determine the germicidal efficiency of chlorine. Although there are widespread differences in the susceptibility of various pathogens, the general order of increasing chlorine disinfection difficulty are bacteria, viruses, and then protozoa.

Bacteria Inactivation. Chlorine is an extremely effective disinfectant for inactivating bacteria. A study conducted during the 1940s investigated the inactivation levels as a function of time for *E. coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, and *Shigella dysenteriae* (Butterfield et al., 1943). Study results indicated that HOCl is more effective than OCl^- for inactivation of these bacteria. These results have been confirmed by several researchers that concluded that HOCl is 70 to 80 times more effective than OCl^- for inactivating bacteria. (Culp/Wesner/Culp, 1986).

Virus Inactivation. Chlorine has been shown to be a highly effective viricide. One of the most comprehensive virus studies was conducted in 1971 using treated Potomac estuary water (Liu et al., 1971). The tests were performed to determine the resistance of 20 different enteric viruses to free chlorine under constant conditions of 0.5 mg/L free chlorine and a pH and temperature of 7.8 and 2°C, respectively. In this study, the least resistant virus was found to be reovirus and required 2.7 minutes to achieve 99.99 percent inactivation (4 log removal). The most resistant virus was found to be a poliovirus, which required more than 60 minutes for 99.99 inactivation. The corresponding CT range required to achieve 99.99 percent inactivation for all 20 viruses was between 1.4 to over 30 mg·min/L.

Virus survival studies have also been conducted on a variety of both laboratory and field strains (AWWA, 1979). All of the virus inactivation tests in this study were performed at a free chlorine residual of 0.4 mg/L, a pH of 7.0, a temperature of 5°C, and contact times of either 10, 100, or 1,000 minutes. Test results showed that of the twenty cultures tested only two poliovirus strains reached

99.99 percent inactivation after 10 minutes (CT = 4 mg·min/L), six poliovirus strains reached 99.99 percent inactivation after 100 minutes (CT = 40 mg·min/L), and 11 of the 12 polioviruses plus one *Coxsackievirus* strain (12 out of a total of 20 viruses) reached 99.99 percent inactivation after 1,000 minutes (CT = 400 mg·min/L).

Protozoa Inactivation. Chlorine has been shown to have limited success inactivating protozoa. Data obtained during a 1984 study indicated that the resistance of *Giardia* cysts are two orders of magnitude higher than that of enteroviruses and more than three orders of magnitude higher than the enteric bacteria (Hoff et al., 1984). CT requirements for *Giardia* cysts inactivation when using chlorine as a disinfectant has been determined for various pH and temperature conditions (AWWA, 1991). These CT values increase at low temperatures and high pH (See also Table 2-13).

Chlorine has little impact on the viability of *Cryptosporidium* oocysts when used at the relatively low doses encountered in water treatment (e.g., 5 mg/L). Approximately 40 percent removals (0.2 log) of *Cryptosporidium* were achieved at CT values of both 30 and 3,600 mg·min/L (Finch et al., 1994). Another study determined that "no practical inactivation was observed" when oocysts were exposed to free chlorine concentrations ranging from 5 to 80 mg/L at pH 8, a temperature of 22°C, and contact times of 48 to 245 minutes (Gyürék et al., 1996). CT values ranging from 3,000 to 4,000 mg·min/L were required to achieve 1-log of *Cryptosporidium* inactivation at pH 6.0 and temperature of 22°C. During this study, one trial in which oocysts were exposed to 80 mg/L of free chlorine for 120 minutes was found to produce greater than 3-logs of inactivation.

2.7.4.4 CT Curves

Chlorine is regarded as a strong disinfectant that is effective at inactivating bacteria and viruses, and under certain circumstances, *Giardia*. Because of chlorine's extremely high virus inactivation efficiency, CT values are almost always governed by protozoa inactivation. For example, Figure 2-1 shows the CT values required to achieve between 0.5 and 3-logs of virus and *Giardia* inactivation (AWWA, 1991). As shown, the CT values required to achieve the recommended disinfection efficiency for conventional filtration systems (i.e., 0.5-log *Giardia* cyst and 2-log virus inactivation level) are 23 and 3 mg min/L, respectively.

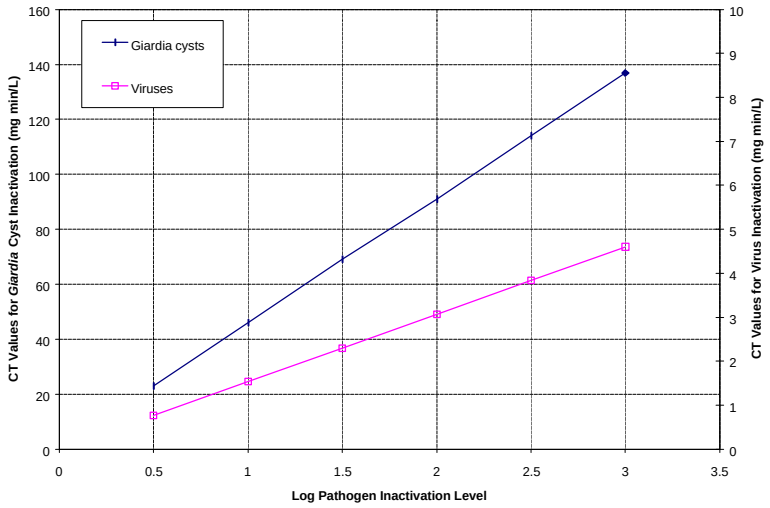

Figure 2-1. Free Chlorine *Giardia* and Virus CT Requirements

CT values for *Giardia* inactivation for various pH values and temperatures at a chlorine dose of 3.0 mg/L are shown in Figures 2-2 and 2-3. As shown, the inactivation efficacy of free chlorine decreases with increasing pH and/or decreasing temperature. CT values shown in Figures 2-2 and 2-3 are based on animal infectivity and excystation studies. CT values ranging from 0.5 to 3-log inactivation at temperatures of 0.5 and 5°C were based on a multiplicative model, and applying first order kinetics to the 99 percent upper confidence interval of the 99.99-percentile CT values. CT values for temperatures above 5°C were estimated by assuming a twofold decrease for every 10°C decrease in temperature.

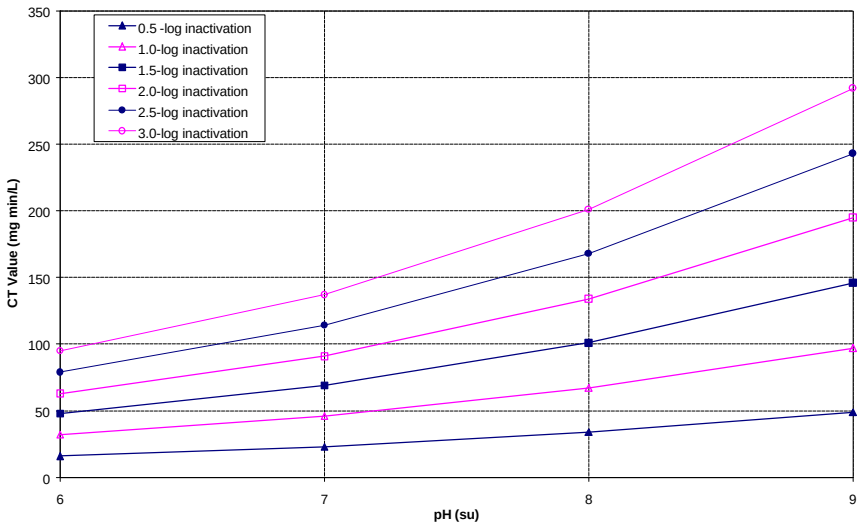

Figure 2-2. CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 10°C (at Cl_2 dose of 3.0 mg/L)

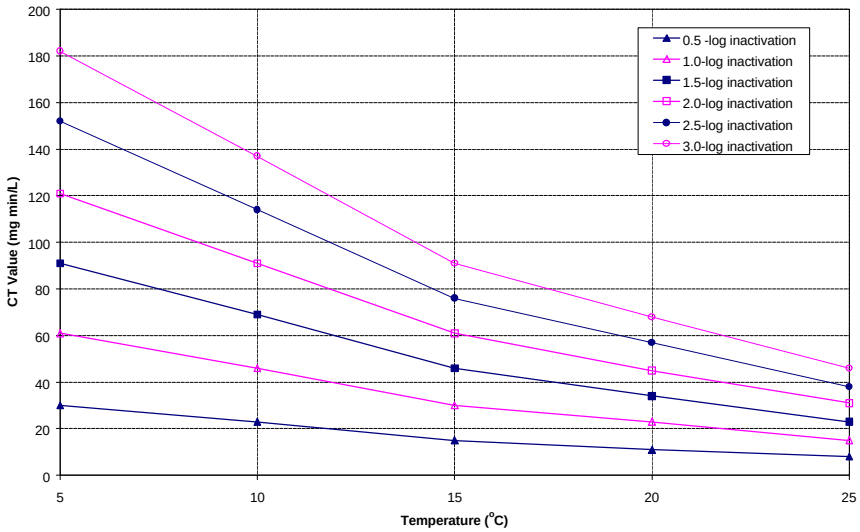

Figure 2-3. CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at pH 7.0 (at Cl_2 dose of 3.0 mg/L)

2.7.5 DBP Formation and Control

2.7.5.1 DBP Formation

Halogenated organics are formed when natural organic matter (NOM) reacts with free chlorine or free bromine. Free chlorine is normally introduced into water directly as a primary or secondary disinfectant. Free bromine results from the oxidation by chlorine of the bromide ion in the source water. Factors affecting the formation of these halogenated DBPs include type and concentration of NOM, chlorine form and dose, time, bromide ion concentration, pH, organic nitrogen concentration, and temperature. Organic nitrogen significantly influenced the formation of nitrogen containing DBPs, including haloacetonitriles, halopicrines, and cyanogen halides (Reckhow et al., 1990; Hoigné and Bader, 1988).

The formation of DBPs is strongly related to TOC at the point of disinfection. DBP formation also correlates with the amount of chlorine consumed (Singer et al., 1995). Stevens et al. (1989) found that higher TTHM formation occurs at high pH (9.4) than at low pH (5.0) while HAA showed no clear trend as a function of pH. A survey of 35 water utilities conducted by MWDSC (Krasner et al., 1989) showed the median TTHM and HAA concentrations measured as 39 and 19 µg/L (i.e. more THMs than HAAs are formed). However, a subsequent study by Singer et al. (1995) found a reversal in dominance, with more HAAs than THMs produced in waters from North Carolina utilities. They postulated that the reason for this change is due to the lower pH levels and differences in TOC and bromide concentrations in the North Carolina waters. Pourmoghaddas et al. (1993) showed that brominated and mixed brominated/chlorinated THMs and HAAs are formed when using chlorine in the presence of bromide.

The occurrence of THMs and HAAs is important because regulatory limits are placed on both groups of compounds. One water utility may therefore find that its chlorination practice is limited by the production of THMs, while another will find that HAAs limit the use of chlorine. This distribution of THMs and HAA is a function of the TOC and bromide concentration in the water, as well as the pH during chlorination.

Of note, Chlorate is produced as a byproduct when hypochlorite degrades during storage.

2.7.5.2 DBP Control

DBPs can be controlled by several means, including removing the DBP precursors, modifying the chlorination strategy, changing disinfectants, or removing the DBP itself. Because DBPs are difficult to remove once they are formed, control strategies typically focus on the first three methods.

Studies have shown that removal of TTHM precursors tends to remove the formation potential for the other DBPs. Generally, aggregate DBP formation will decrease as the removal of TOC increases. Recent research indicates that moving the point of chlorination back into the treatment process can reduce the formation of DBPs.

Summers et al. (1997) recently summarized the results from four studies evaluating the impact of pretreatment on DBP formation. Jar tests were conducted to simulate the water treatment through rapid mix, coagulation, flocculation, and sedimentation. Chlorine was added at various points in the jar testing to simulate the impact of various dose points on production of DBPs. The results clearly demonstrate the benefits of delaying the point of chlorination downstream in the treatment train to take advantage of precursor removal during initial flocculation and sedimentation processes. Table 2-21 summarizes the results from this study.

Table 2-21. Percent Reduction in DBP Formation by Moving Chlorination Point Later In Treatment Train

Chlorination point	TTHM Baseline (%)	TTHM Enhanced (%)	HAA5 Baseline (%)	HAA5 Enhanced (%)
Pre rapid mix	Basis	17	Basis	4.7
Post rapid mix	1.6	21	5.3	21
Mid flocculation	8.7	36	14	36
Post sedimentation	21	48	35	61

Notes: Source: USEPA, 1997b based on Summers et al., 1997.
Baseline = Baseline coagulant (alum) dose for optimal turbidity removal (~30 mg/L)
Enhanced = Enhanced coagulant (alum) dose for optimal TOC removal (~52 mg/L)

Table 2-21 also shows the benefit of enhanced coagulation to reduce DBP production. The THM reduction of 21 percent by moving the chlorination point to post sedimentation is more than doubled to 48 percent by enhanced coagulation. The HAA removal increases from 45 to 61 percent under

enhanced coagulation with post sedimentation chlorination. Therefore, DBP control by selecting the optimal dose location and conditions along with enhanced precursor removal can significantly reduce DBP formation at low added cost.

White (1992) suggested that pretreatment goals should include: 1) maximizing THM precursor removal; 2) reducing ammonia-N concentration to 0.10 mg/L; 3) reducing organic-N concentration to 0.05 mg/L; and 4) limiting 15-minute chlorine demand to 0.5 mg/L. These guidelines should improve raw water quality sufficiently to allow the use of the free chlorine residual process without exceeding the EPA MCLs for TTHMs.

2.7.6 Operational Considerations

2.7.6.1 Application Methods

Different application methods are used, depending upon the form of chlorine used. The following paragraphs describe the typical application methods for chlorine, sodium hypochlorite, and calcium hypochlorite.

Chlorine. Liquefied chlorine gas is typically evaporated to gaseous chlorine prior to metering. The heat required for evaporation can be provided through either a liquid chlorine evaporator or the ambient heat input to the storage container. Once the compressed liquid chlorine is evaporated, chlorine gas is typically fed under vacuum conditions. Either an injector or a vacuum induction mixer usually creates the required vacuum. The injector uses water flowing through a venturi to draw the chlorine gas into a side stream of carrier water to form a concentrated chlorine solution. This solution is then introduced into the process water through a diffuser or mixed with a mechanical mixer. A vacuum induction mixer uses the motive forces of the mixer to create a vacuum and draws the chlorine gas directly into the process water at the mixer.

Sodium Hypochlorite. Sodium hypochlorite solutions degrade over time. For example, a 12.5 percent hypochlorite solution will degrade to 10 percent in 30 days under “best case” conditions (White, 1992). Increased temperature, exposure to light, and contact with metals increase the rate of sodium hypochlorite degradation (Connell, 1996).

Sodium hypochlorite solution is typically fed directly into the process water using a type of metering pump. Similar to chlorine solution, sodium hypochlorite is mixed with the process water with either a mechanical mixer or induction mixer. Sodium hypochlorite solution is typically not diluted prior to mixing to reduce scaling problems.

Calcium Hypochlorite. Commercial high-level calcium hypochlorite contains at least 70% available chlorine (USEPA, 1991). Under normal storage conditions, calcium hypochlorite loses 3 to 5% of its available chlorine in a year (AWWA and ASCE, 1997). Calcium hypochlorite comes in powder, granular, and compressed tablet forms (USEPA, 1991). Typically, calcium hypochlorite solution is prepared by mixing powdered or granular calcium hypochlorite with a small flow. The highly chlorinated solution is then flow paced into drinking water flow.

2.7.6.2 Safety and Handling Considerations

Chlorine. Chlorine gas is a strong oxidizer. The U.S. Department of Transportation classifies chlorine as a poisonous gas (Connell, 1996). Fire codes typically regulate the storage and use of chlorine. In addition, facilities storing more than 2,500 pounds of chlorine are subject to the following two safety programs:

- Process Safety Management standards regulated by the Occupational Safety and Health Administration under 29 CFR 1910.
- The Risk Management Program Rule administered by EPA under Section 112(r) of the Clean Air Act.

All of these regulations (as well as local and state codes and regulations) must be considered during the design and operation of chlorination facilities at a water treatment plant.

Sodium Hypochlorite. Sodium hypochlorite solution is a corrosive liquid with an approximate pH of 12 (AWWA, 1990). Therefore, typical precautions for handling corrosive materials such as avoiding contact with metals, including stainless steel, should be used.

Sodium hypochlorite solutions may contain chlorate. Chlorate is formed during the both the manufacturing and storage of sodium hypochlorite (due to degradation of the product). Chlorate formation can be minimized by reducing the degradation of sodium hypochlorite (Gilbert et al., 1995) by limiting storage time, avoid high temperatures and reduce light exposure.

Spill containment must be provided for the sodium hypochlorite storage tanks. Typical spill containment structures include containment for the entire contents of the largest tank (plus freeboard for rainfall or fire sprinklers), no uncontrolled floor drains, and separate containment areas for each incompatible chemical.

Calcium Hypochlorite. Calcium hypochlorite is an oxidant and as such should be stored separately from organic materials that can be readily oxidized. It should also be stored away from sources of heat. Improperly stored calcium hypochlorite has caused spontaneous combustion fires (White, 1992).

2.8 Summary

2.8.1 Advantages and Disadvantages of Chlorine Use

The following list presents selected advantages and disadvantages of using chlorine as a disinfection method for drinking water (Masschelein, 1992; Process Applications, Inc., 1992). Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

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 the 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 a chlorine residual is not maintained.

- Release of constituents bound in the distribution system (e.g., arsenic) by changing the redox state.

2.8.2 Summary Table

Table 2-22 presents a summary of the considerations for the use of chlorine as a disinfectant.

Table 2-22. Summary of Chlorine Disinfection

Consideration	Description
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, prevention of algal growths, maintaining clear filter media, removal of iron and manganese, destruction of hydrogen sulfide, color removal, 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 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	Raw water storage, precoagulation/post-raw water storage, presedimentation/ postcoagulation, postsedimentation/prefiltration, 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 handling and use of chlorine is an important consideration.

2.8.3 Reference for Additional Information on Chlorine

With the focus of this manual on disinfectants other than chlorine, all of chlorine's uses and capabilities are not described here. For more detailed information regarding the use of chlorine in water treatment, refer to the list of references provided below. For complete references, see the References section at the end of this chapter.

- AWWA (1990)
- Connell (1996)
- DeMers and Renner (1992)
- Hazen and Sawyer (1992)
- Hoigné and Bader (1988)
- Sawyer et al. (1994)
- Singer (1988)
- White (1992)

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