

DISINFECTION

Disinfection is the destruction of pathogenic microorganisms in a water. The water is not necessarily sterilized. The protection of the public health from waterborne disease transmission by disinfection of water has been recognized since the turn of the century. The eradication of waterborne pathogens is the most important treatment of water. Disinfection is also applied to wastewater effluents to reduce the risk of disease for recreational users of surface waters and to minimize the contamination to downstream drawers of water.

Pathogen kill efficiency is not the only consideration in selecting a disinfectant. The characteristics of a good disinfectant are:

1. Effective kill of pathogenic microorganisms.
2. Nontoxic to humans or domestic animals.
3. Nontoxic to fish and other aquatic species.
4. Easy and safe to store, transport, and dispense.
5. Low cost.
6. Easy and reliable analysis in water.
7. Provides residual protection in drinking water.

Boiling water for 15 to 20 min eradicates pathogenic microorganisms but it is too energy intensive to be used for water or wastewater disinfection. It was used for a short time in only one municipality, Pathermay, France around the turn of the century (Baker, 1981). However, when municipal water treatment works fail to produce water of suitable microbiological quality, boil water orders are immediately issued to the public.

Currently, disease outbreaks in surface water systems occur primarily because of inadequate or interrupted disinfection, especially in systems that provide disinfection as the only treatment (Craun, 1988). There are many agents that effect disinfection, including chemical oxidants, irradiation, thermal treatment, and electrochemical treatment (Patermarakis and Fountoukidis, 1990). But the history of water and wastewater disinfection is the history of chlorination (White, 1992, 1978). The first continuous application of chlorine for disinfection of a municipal water supply in the United States was in 1908 for the city of Jersey City, NJ (Craun, 1988).

Chlorine satisfies the characteristics of a good disinfectant to a large degree. Developments in disinfection technology have produced many alternatives to chlorination, including other oxidizing agents such as chloramines, chlorine dioxide, permanganate, and ozone. Bromine, bromine chloride, and iodine are feasible alternatives. Ultraviolet (UV) and gamma irradiation may also be used. Silver is also a bactericide.

Chlorine is the least cost disinfection agent but recent research has identified byproducts of chlorination, some of which have been proved to be carcinogenic. In particular there has been much research and concern over trihalomethanes (THMs)

which are produced with chlorine. The hazards associated with these and other byproducts are small at the concentrations produced in a typical operation and modern chlorination practice has been modified to further minimize their formation. Even without the improvements in chlorination practice, it has been stated by many that the benefits of chlorination have far outweighed the risks.

The issue is not solely confined to weighing the benefits and disadvantages of chlorine. Other disinfection agents may produce less risk, although at an elevated cost. Using the Ames test (Section 8.2.2) for comparison among disinfectants for the amount of mutagenic (mutagenic compounds are often carcinogenic) material produced, the ranking of disinfectants generally follows the order of ozone < chlorine dioxide < chloramine < chlorine for the primary disinfectant for a given treatment system (Noot et al., 1989). Ozone can sometimes produce risk values as high as those for chlorine. There is a considerable amount of controversy and ongoing research being devoted to quantifying the risks associated with all disinfection technologies.

Once mutagenic compounds have been formed they can be partially removed by coagulation–flocculation–filtration processes but granular activated carbon treatment is very effective.

In a review of epidemiological studies (Craun, 1988), it was noted that there was an increased risk of certain types of cancer in populations using chlorinated water; however, no direct evidence was obtained to show that THMs were responsible. Other chlorination byproducts may contribute to the risk. The problem of assessing causal relationships between chlorination and cancer is confounded by many factors. Preliminary data from animals also indicate that there may be an association between chlorination and cardiovascular disease (Craun, 1988).

An intense research effort is underway to identify and quantify the risks of chlorination. These must be weighed against the well-established benefits of chlorination. Data used in most studies were obtained for chlorination practices that are not current. Modern chlorination practice reduces the formation of chlorine byproducts. There is even less information available on the risks associated with the use of alternative disinfectants compared to chlorine, which further clouds the decision on the most appropriate disinfectant. For instance, one study has shown that subchronic toxicity of chlorine dioxide > monochloramine > chlorine when administered at the same doses (mg/L basis) to rats for 90 days (Daniel et al., 1990). More studies of this nature are required.

At the moment, the general feeling is that chlorination does not elevate risk levels significantly to eliminate it as a primary alternative. However, increasingly severe regulations on THMs will favor the change to other disinfectants, particularly ozone.

The focus of this chapter is on the disinfectants and practices for pathogen removal in waters. Beyond the disinfectants discussed in this chapter there are many synthetic biocides used for general control of microorganism growth in pipelines, cooling towers, and other industrial applications. These agents will be present in wastewaters with potential to affect biological treatment processes and to contribute toxicity in the effluent.

16.1 KINETICS OF DISINFECTION

The kinetics of disinfection is described by a first-order law from studies by Chick (1908).

$$\frac{dN}{dt} = -kN \quad (16.1)$$

where

N is the number of microorganisms

t is time

k is the dieoff coefficient

The dieoff coefficient is a function of disinfectant dose, type of microorganism, and conditions in the water. Watson (1908) refined the rate coefficient to explicitly include the concentration of disinfectant and another term related to disinfection power of the disinfectant.

$$k = \alpha C^n \quad (16.2)$$

where

C is the concentration of disinfectant

n is termed a constant of dilution

α is an inactivation constant

In Eq. (16.2) the exponent n is commonly assumed to be 1, although this should be experimentally verified. Combining the above two equations and integrating, the Chick–Watson disinfection model (Eq. 16.3) is obtained.

$$\ln \frac{N}{N_0} = -\alpha C^n t \quad (16.3)$$

where

N_0 is the actual number of microorganisms

The inactivation constant is specific to the microorganism and disinfectant being used and is also sensitive to environmental conditions in the water. Furthermore, disinfectants undergo chemical reactions that diminish their disinfection power but do not destroy it. Therefore, deviations from the Chick–Watson law are common. The general principle embodied in the law is that as concentration or contact time (Ct) is increased, inactivation of microorganisms is increased. Practically, $C \times t$ plots are prepared for in situ conditions to arrive at the dose and contact times required to attain the desired removal.

The bactericidal action of a disinfectant is, of course, not limited to pathogens. Fortunately waterborne disease-causing microorganisms are removed to levels generally considered safe at lower doses of disinfectant than required for complete sterilization of the water. Protozoans and viruses require higher doses of disinfectant than bacteria. Another common use for disinfecting agents is to control microbial growth in treatment units, pipes, and other appurtenances in the operation. Slime growth, which is primarily bacteria, can result in the addition of taste- and odor-causing compounds to a water. Microbial buildup increases headloss in conveyance systems, where the additional energy costs must be weighed against the costs of disinfectant addition. Many disinfectants increase the corrosiveness of a water, which is another cost consideration.

16.2 CHLORINATION

Chlorine participates in a number of reactions that affect its disinfecting capability.

16.2.1 Chemistry of Chlorine

Chlorine is a gas and dissolved chlorine has a tendency to escape to the atmosphere. Henry's law describes the equilibrium relation.

(16.1)

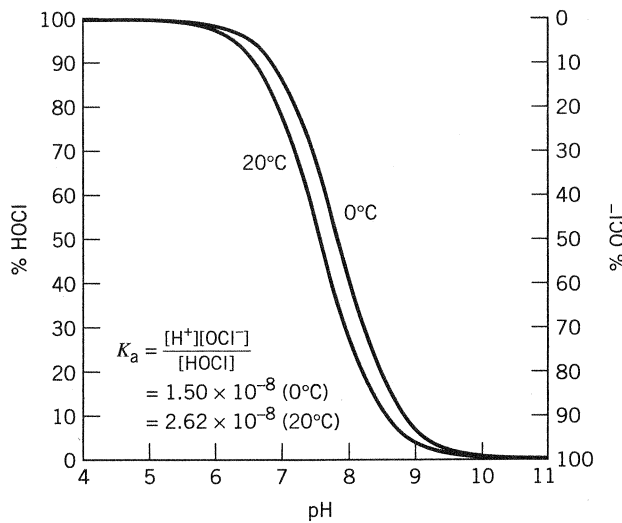
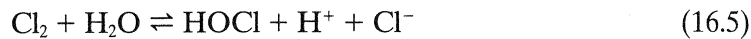


Figure 16.1 Distribution of HOCl and OCl⁻.



However the loss of chlorine by volatilization is minimal because chlorine rapidly hydrolyzes in water according to the following reactions. The reaction in Eq. (16.5) occurs in a fraction of a second at 20°C and takes only a few seconds at 0°C (White, 1992).



Hypochlorous acid (HOCl) is also volatile but it is on the order of 1.28×10^5 less volatile than Cl₂ (i.e., its Henry's law constant is 1.28×10^5 larger than that for Cl₂) (Blatchley et al., 1992).

The equilibrium expressions for reactions (16.5) and (16.6) are

$$K = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} = 4 \times 10^{-4} \text{ (at 25}^\circ\text{C)} \tag{16.7}$$

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} \tag{16.8}$$

From Eq. (16.7), it can be seen that Cl₂ is much less than 1% of the total moles of chlorine species (Cl₂, HOCl, and OCl⁻) in the pH range 6–9 of treated waters. Free available chlorine is chlorine in the form of Cl₂, HOCl, or OCl⁻ (hypochlorite ion). The dissociation of HOCl (Eq. 16.8) is also temperature and pH dependent as shown in Fig. 16.1 and Table 16.1. The variation of pK_a in Eq. (16.8) as a function of temperature was studied by Morris (1966), who found the following equation:

$$\text{p}K_a = \frac{3\,000.00}{T} - 10.068\,6 + (0.025\,3)T \tag{16.9}$$

where

T is in °K

TABLE 16
with pH at

pH	% OCl ⁻
0	0
4	10
5	9
6	9
7	8
7.5	6

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TABLE 16.1 Dissociation of Hypochlorous Acid with pH and Temperature

pH	% HOCl		pH	% HOCl	
	0°C	20°C		0°C	20°C
4	100	100	8	40.1	27.6
5	99.9	99.7	8.5	17.4	10.8
6	98.5	97.4	9	6.3	3.7
7	86.9	79.2	10	0.7	0.4
7.5	67.9	54.7	11	0.07	0.04

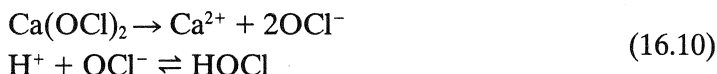
The following observations are made from Fig. 16.1 and Table 16.1.

At pH 5.0 and below, almost all chlorine is in the form of HOCl.

At pH 10.0 and above, almost all chlorine is in the form of OCl⁻.

HOCl is a very strong disinfectant, about 80–200 times as strong as OCl⁻; therefore, pH exerts a strong influence on the effectiveness of chlorine. HOCl reacts with the enzymes essential to the metabolic processes of living cells. If hypochlorite salts are used, the following reactions occur.

(16.4)



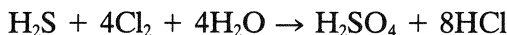
Chlorine reacts with the following substances:

- a. Reducing agents such as S²⁻, Fe²⁺, Mn²⁺, and NO₂⁻

Using Table 1.3, the overall reaction between chlorine and a reducing agent may be formed. An example reaction is

(16.5)

(16.6)

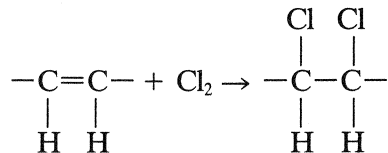


- b. Organic matter

Chlorine is able to react in a variety of ways with functional groups and other reaction sites on organic molecules. As an example, the electrophilic addition of Cl₂ to a double bond of an alkene is shown below.

(16.7)

(16.8)



- c. Ammonia

Hypochlorous acid reacts with ammonia to produce chloramines.



(16.9)

The distribution of the three types of chloramines is a function of pH. Chloramines are combined chlorine residuals. The electron uptake capability of a chloramine is directly dependent on the number of hypochlorous acid molecules used to form it. Ammonia and chloride are released by the reaction of a chloramine with a

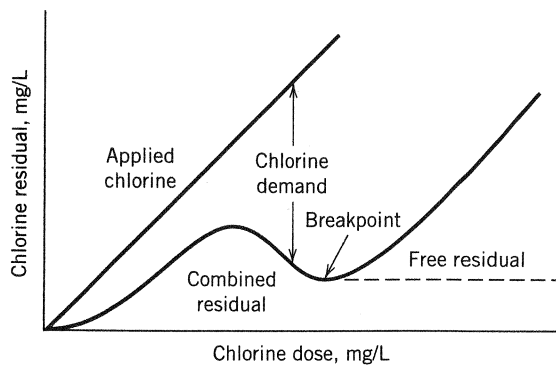
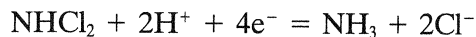


Figure 16.2 Chlorine demand curve.

reducing agent. For instance, the balanced half-reaction for dichloramine is



There were two HOCl molecules required to form NHCl_2 and each HOCl molecule can take up two electrons.

Dichloramine produces a disagreeable odor and taste whereas monochloramine does not. Trichloramine is not stable and it breaks down to N_2 with a loss of oxidation power. Ammonia and chlorine are both biocides; chloramines are disinfectants but their strength is significantly less than HOCl or OCl^- . However, chloramines are much longer lasting in the water and provide a degree of residual protection. It was found in one study that the combined disinfection effect of free chlorine and monochloramine was greater than the additive effects of each agent; i.e., there was synergism for inactivation of *E. coli* (Kouame and Haas, 1991).

As a result of ammonia and other impurities in a water, there is a chlorine demand. The chlorine demand is assessed by adding known amounts of chlorine to a water and measuring the residual chlorine concentrations after a specified contact time. A typical chlorine demand curve is shown in Fig. 16.2.

The chlorine demand curve shape results from the reactions of chlorine. The curve changes its location as the contact time at which residuals are measured is changed. The first amount of chlorine is consumed by inorganic reducing substances that convert the chlorine into chloride, which has no residual oxidizing power. Excess chlorine after this point is converted into chloramines and chloroorganics but the former usually outweighs the latter. The dominant chloramine formed depends on the molar ratio of chlorine added to ammonia nitrogen present. When the molar ratio exceeds 1, reaction (16.12) begins to dominate; when the ratio exceeds 2, reaction (16.13) begins to dominate. There is some formation of NCl_3 even when the ratio of chlorine to nitrogen is less than 1, even though monochloramine is by far predominant.

The unstable nitrogen trichloride is formed when the molar ratio of chlorine to nitrogen exceeds 2:1 to 3:1 and a large amount of it begins to break down to N_2 . There are also many other inorganic forms of nitrogen with various oxidation states such as nitrate that may be formed from oxidation of ammonia nitrogen as more chlorine is added. Formation of these inorganic species reduces the combined residual. The reactions that occur after the hump in the curve are not well understood. Monochloramines dominate the combined residual up to the hump in the curve. After the dip in the curve, the ammonia reactions are finished and further addition of chlorine

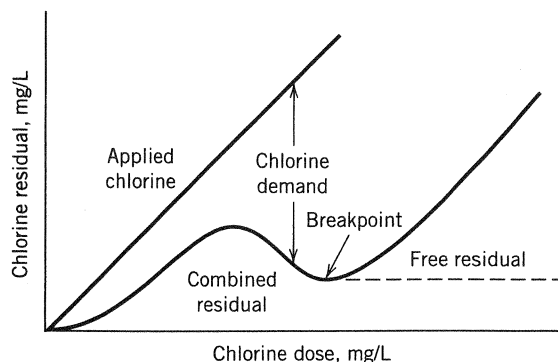
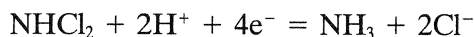


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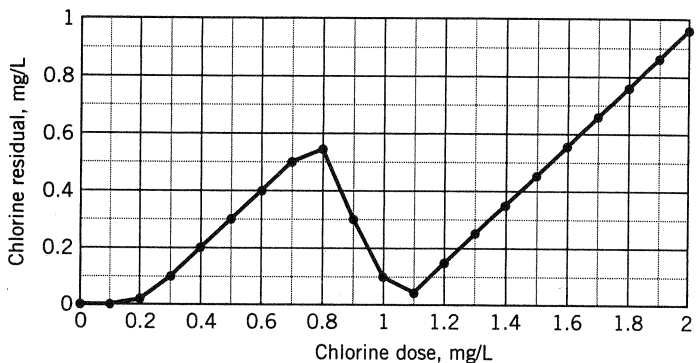
will result in a free chlorine residual (HOCl and OCl⁻). The dip in the curve is known as the breakpoint and addition of chlorine beyond this point is called breakpoint chlorination. There will be a relatively small residual amount of chloramines (all three of them) remaining after the breakpoint that contribute to the total chlorine residual.

Reactions of chlorine with organic matter will occur coincidentally with the chloramine and other reactions. Some organic compounds will completely oxidize chlorine but other chloroorganics formed will have some oxidizing power. Reactions of chlorine with organic matter for the formation of combined chlorine residuals are usually not significant compared to the ammonia reactions. The chlorine demand curve will shift as time progresses and the more slowly occurring reactions consume or convert chlorine to other forms.

It is not desirable to be in the region immediately after the hump in the curve. The rapid change in the curve is an instable region. Dichloramines exist in this region, which are malodorous as noted above, and although they are more powerful disinfectants than monochloramine, they are more unstable. Also NCl₃ is being formed, which is the most unstable chloramine.

In drinking water supplies the dose of chlorine is determined by the amount of chlorine demand and the desired residual concentration, which may be up to 0.5–1.0 mg/L. Significant concentrations of chloramines in water are toxic to pet fish and measures must be taken to remove the chloramines before using the water in aquariums.

■ Example 16.1 Chlorine Demand



The chlorine demand curve on the graph was obtained for a drinking water for a 1-h contact time. Determine the daily amount of NaOCl to be applied to this water to produce a combined residual of 0.4 mg/L and a free residual of 0.5 mg/L after a contact time of 1 h in a flow of 24 000 m³/d (6.34 Mgal/d).

From the graph the chlorine dose to achieve a combined residual of 0.4 mg/L is 0.60 mg/L.

The combined residual remaining after the breakpoint is approximately 0.08 mg/L. The chlorine dose to reach the breakpoint is 1.1 mg/L. After the breakpoint, the curve shows a linear increase in chlorine residual with chlorine dose. The dose of chlorine required to obtain a free residual of 0.5 mg/L is 1.1 mg/L + 0.50 mg/L = 1.60 mg/L. The total residual is 0.58 mg/L at this dose.

NaOCl is a salt that dissociates to



The MW of NaOCl is $23 + 16 + 35.5 = 74.5$ g. One mole of OCl^- is equivalent to 1 mole of Cl_2 from reactions (16.5) and (16.6). The amount of NaOCl that must be added each day for a combined residual of 0.4 mg/L after a 1-h contact time is

$$QC = \left(24\,000 \frac{\text{m}^3}{\text{d}}\right) \left(0.60 \frac{\text{mg Cl}_2}{\text{L}}\right) \left(\frac{74.5 \text{ mg NaOCl}}{71 \text{ mg Cl}_2}\right) \left(\frac{1\,000 \text{ L}}{\text{m}^3}\right) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right) = 15.1 \text{ kg/d}$$

In U.S. units:

$$QC = \left(6.34 \times 10^6 \frac{\text{gal}}{\text{d}}\right) \left(0.60 \frac{\text{mg Cl}_2}{\text{L}}\right) \left(\frac{74.5 \text{ mg NaOCl}}{71 \text{ mg Cl}_2}\right) \left(\frac{3.79 \text{ L}}{\text{gal}}\right) \left(\frac{1 \text{ lb}}{454 \times 10^3 \text{ mg}}\right) \\ = 33.3 \text{ lb/d}$$

Similarly, the daily amount of NaOCl to be added to achieve a free residual of 0.5 mg/L is

$$QC = \left(\frac{1.60 \text{ mg/L}}{0.60 \text{ mg/L}}\right) (15.1 \text{ kg/d}) = 40.3 \text{ kg/d}$$

$$\text{U.S. units: } QC = \left(\frac{1.60 \text{ mg/L}}{0.60 \text{ mg/L}}\right) (33.3 \text{ lb/d}) = 88.8 \text{ lb/d}$$

The chlorine demand of wastewaters will be much higher than the demand for water treated for consumption. The major factor controlling chlorine demand in wastewaters is the concentration of ammonia. Secondary biological treatment processes are often not designed to remove ammonia from the effluent. The amount of chlorine required to achieve a free residual in this case will be excessively high.

16.2.2 Chlorine Decay

Chlorine demand is not exerted immediately upon addition of chlorine to the water. First-order kinetics are assumed to describe the rate of reaction between chlorine and chlorine demand substances. The nature of chlorine demanding substances and flow patterns affects the amount of chlorine decay between the influent and the effluent in a reactor to which chlorine has been added. Teehy and Singer (1990) found first-order rate constants for free chlorine of 0.162 and 0.0624 h^{-1} at two water treatment plants. Lawler and Singer (1993) suggest that 0.2 h^{-1} is a reasonable value for water treatment plants based on other studies.

Abdel-Gawad and Bewtra (1988) studied the decay of total residual chlorine from chlorination of physical-chemical treatment effluent in natural river water. They found a first-order decay model to be suitable with the rate constant influenced by turbulence, evaporation, photolysis, and temperature. The rate constant was formulated as

$$k_T = F_{\text{TB}}(k_{\text{ev}} + k_{\text{S}} + k_{\text{ox}})\theta^{(T-20)} \quad (16.14)$$

where

k_T is overall decay coefficient at temperature T

k_{ev} is rate constant for evaporation

k_{S} is rate constant for photooxidation

k_{ox} is rate of free radical oxidation by chlorine

F_{TB} is a turbulence factor

θ is the Arrhenius constant

T is temperature ($^{\circ}\text{C}$)

The values of constants in the above equation were: $F_{TB} = 2.05$ for turbulent conditions, $F_{TB} = 1.0$ for quiescent conditions; $k_{cv} = 0.013/H \text{ d}^{-1}$ (H is depth of the flow in m); $k_s = 0.03 \text{ d}^{-1}$; $k_{ox} = 0.065 \text{ d}^{-1}$; and $\theta = 1.08$.

Nowell and Hoigné (1992) also found that photodegradation of chlorine followed a first-order reaction. Sunlight in the wavelength range 320–340 nm controls photolysis. The hypochlorite ion was more sensitive to sunlight than hypochlorous acid. Covering basins minimizes the dosage of chlorine.

16.2.3 Determination of Chlorine Residuals

Free available chlorine in water is usually measured by either the DPD (*N,N*-diethyl-*p*-phenylenediamine) method or amperometric titration. DPD is a colorimetric redox indicator. In the former method, DPD is mixed along with other agents into a solution containing chlorine. Chlorine oxidizes DPD and the oxidized DPD is measured by titration or spectrophotometrically. Amperometric titration involves titration of chlorine or other halogens with a reducing agent of known normality (usually 0.005 *N* phenylarsine oxide) at a constant applied voltage. These methods are both subject to positive errors, especially in samples high in organic nitrogen and at high temperature, but these methods are currently the best analytical techniques available (Jensen and Johnson, 1989).

Two iodometric methods are also specified in *Standard Methods* (1992). In iodometric method I, iodide is added to a sample and oxidized to iodine, which is then titrated with thiosulfate reducing agent. In iodometric method II, which is suitable only for wastewaters, reducing agent is added to the sample, which is then titrated with iodine or iodate to determine the amount of unreacted reducing agent.

Gordon et al. (1988) have summarized and critiqued the various methods of measuring disinfectant residuals in water. A comparison of recommended techniques for chlorine residuals in wastewaters was performed by Derrigan et al. (1993).

16.3 DISINFECTION PRACTICE

Both drinking water and wastewater effluents are disinfected.

16.3.1 Water Treatment

Current United States practice specified in the Surface Water Treatment Rule¹ (SWTR) for disinfection requires water treatment systems to inactivate 99.9% of *Giardia* cysts and 99.99% of enteric viruses (3 and 4 log reductions, respectively). These organisms were chosen as standards because of their resistance to disinfection.

The SWTR is based on Eq. (16.3), i.e., the *Ct* concept. The appropriate *Ct* value must be satisfied at peak flow conditions through the plant. The concentration of disinfectant is its value measured in the effluent from a reactor. This provides a safety factor considering the decay of chlorine and has been found to be reasonable in a thorough analysis of the effects of mixing (flow pattern) and chlorine decay in reactors by Lawler and Singer (1993).

¹National Primary Drinking Water Regulations: Filtration, Disinfection, Turbidity, *Giardia lamblia*, Viruses, *Legionella* and Heterotrophic Bacteria. Federal Regulation 54:124:27486 (June 29, 1989).

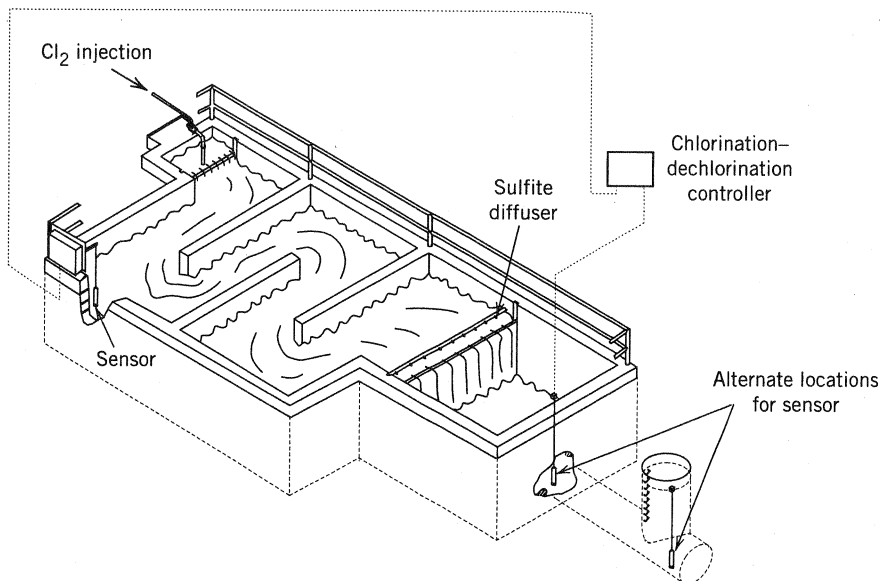


Figure 16.3 Typical contact chamber for chlorination. Baffles are provided to promote plug flow. When chlorine has been applied at elevated concentrations, sulfite is added to reduce chlorine to levels that will not cause consumer reaction to chlorine taste and odor. Sketch courtesy of Stranco.

The best disinfection kinetics are realized in a plug flow (PF) basin (Fig. 16.3). The characteristic time specified in the SWTR is the time for 10% of the water that enters the reactor at one instant to leave the reactor, t_{10} . (For the step feed input in Example 10.3, this corresponds to the time at which $C = 0.10C_1$.) In the case of a PF reactor, t_{10} and t_d are the same; however, for complete mixed (CM) reactors t_{10} is approximately $0.105t_d$. For an intermediate mixed reactor t_{10} is between these values. The use of t_{10} does not properly account for the effects of mixing on the rate of disinfection, which can be determined from application of principles developed in Chapter 10 and other advanced theory (Lawler and Singer, 1993). The SWTR approach normally tends to underestimate the amount of disinfection.

Table 16.2 gives Ct values for chlorine and other disinfectants to meet the SWTR standard. Free chlorine hydrolyzes into hypochlorous acid, which then dissociates

TABLE 16.2 SWTR Ct^a Values for Achieving 99.9% Reduction of *Giardia lamblia*

Disinfectant	pH	Temperature, °C					
		≤1	5	10	15	20	25
Free chlorine ^b (2 mg/L)	6	165	116	87	58	44	29
	7	236	165	124	83	62	41
	8	346	243	182	122	91	61
	9	500	353	265	177	132	88
Ozone	6–9	2.9	1.9	1.4	0.95	0.72	0.48
Chlorine dioxide	6–9	63	26	23	19	15	11
Chloramines (preformed)	6–9	3 800	2 200	1 850	1 500	1 100	750

^a C is in mg/L and t is in minutes.

^b Ct values depend on the concentration of free chlorine (see text).

TABLE 16.3 SWTR Ct^a Values for Achieving 90% Reduction of *Giardia lamblia*

Disinfectant	pH	Temperature, °C					
		≤1	5	10	15	20	25
Free chlorine ^b (2 mg/L)	6	55	39	29	19	15	10
	7	79	55	41	28	21	14
	8	115	81	61	41	30	20
	9	167	118	88	59	44	29
Ozone	6–9	0.97	0.63	0.48	0.32	0.24	0.16
Chlorine dioxide	6–9	21	8.7	7.7	6.3	5	3.7
Chloramines (preformed)	6–9	1 270	735	615	500	370	250

^a C is in mg/L and t is in minutes.

^b Ct values depend on the concentration of free chlorine (see text).

(Eqs. 16.5 and 16.6). Because the disinfection powers of hypochlorous acid and hypochlorite ion are different, Ct values for free chlorine in Table 16.2 are variable with pH; furthermore, for the same reason, Ct values for free chlorine are dependent on the total concentration of free chlorine. The SWTR provides tables of Ct values for different free chlorine concentrations. For chlorine, the value of n in Eqs. (16.2) and (16.3) is taken as 0.82 by the USEPA.

If filtration of a water is included in its treatment, the SWTR allows a credit of 2 log reductions of *Giardia* cysts. Ct values for disinfectants are decreased to values given in Table 16.3.

Total chlorine dosages at treatment plants vary from 0.2 to 40 mg/L (White, 1992). Maximum doses rarely exceed 15 mg/L. Water is commonly chlorinated to produce finished water free chlorine residuals near 1.0 mg/L. Prechlorination doses vary considerably depending on raw water quality and treatment objectives.

Concern over disinfection byproducts has substantially modified application of chlorine over recent years. THMs, which are a primary byproduct of chlorination, are regulated in both Canada and the United States (Section 8.6). In addition to chlorination as the final treatment, chlorine may be added near the beginning of the treatment plant (prechlorination) to reduce microbial populations throughout the plant. There may be other purposes for prechlorination such as oxidation of problematic metals to cause their precipitation and removal in sedimentation basins and filters.

The alterations in practice generally reduce the amount of chlorine applied. Elimination of prechlorination or reducing the prechlorination dosage is common (Disinfection Committee, 1992). Organic matter contains the precursors for THM formation. Organic matter concentrations are highest in the raw water and decrease throughout the plant. The potential for THM formation increases as the concentrations of chlorine or organic matter rise; thus, the application of chlorine in the earlier stages of treatment is discouraged. Conventional coagulation and sedimentation processes remove approximately 50% of the total organic carbon and precursors of THMs or total organic halides (TOX) (Singer and Chang, 1989).

There are many measures that can be taken to reduce THM formation. Other disinfectant–oxidants can be substituted for chlorine. Chloramines do not form THMs in significant amounts. Preformed chloramines can be added for disinfection purposes or ammonia can be added along with chlorine to form chloramines. Coagulation can be improved by adjusting pH. Activated carbon can be used to remove THM precursors at different stages of treatment.

Current North American practice is to maintain a residual concentration of disinfectant throughout the distribution system to provide protection against leaks and other breakdowns in system integrity. Residuals also retard the growth and regrowth of heterotrophic bacteria in the distribution system. Chloramines are the most commonly chosen agent. Chloramines are more stable and more effective than chlorine for maintaining residual protection throughout the distribution system (Neden et al., 1992). The average chloramine residual in water utilities serving more than 50 000 people in the United States in 1991 was 2.5 mg/L (Kirmeyer et al., 1991).

■ Example 16.2 Disinfection Design According to the Ct Concept

Calculate the quantity of chlorine consumed on a daily basis and the detention time required for 99.9% reduction of *G. lamblia* according to the SWTR rule. The minimum temperature of the water is 5°C, the free chlorine residual in the effluent from the basins is to be 2 mg/L, the decay rate for chlorine is assumed to be 0.2 h⁻¹, and the flow rate is 1.50 × 10⁴ m³/d (3.96 Mgal/d). The pH of the water varies between 7.2 and 8.00. Make the calculations for both a CM and a PF basin.

The highest pH requires the largest Ct value from Table 16.2. At a pH of 8.00 and temperature of 5°C, the Ct value is 243. The effective contact time, $t = 243/2 = 122$ min at these conditions. If the basin is PF, the detention time in the basin is 122 min because $t_d = t_{10}$. Using a first-order decay model with a rate constant of 0.2 h⁻¹ (see Eq. 10.4f),

$$\frac{dC}{dt} = -kt \Rightarrow C = C_0 e^{-kt_d} \quad \text{or} \quad C_0 = C e^{kt_d} = (2.00 \text{ mg/L}) e^{(0.2 \text{ h}^{-1})(122 \text{ min})(1 \text{ h}/60 \text{ min})}$$

$$= 3.00 \text{ mg/L}$$

The quantity of chlorine consumed is

$$QC = \left(1.50 \times 10^4 \frac{\text{m}^3}{\text{d}}\right) \left(1000 \frac{\text{L}}{\text{m}^3}\right) \left(3.00 \frac{\text{mg}}{\text{L}}\right) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right) = 45 \text{ kg/d}$$

$$\text{In U.S. units: } QC = \left(3.96 \times 10^6 \frac{\text{gal}}{\text{d}}\right) \left(3.00 \frac{\text{mg}}{\text{L}}\right) \left(\frac{3.79 \text{ L}}{\text{gal}}\right) \left(\frac{1 \text{ lb}}{454 \times 10^3 \text{ mg}}\right) = 99.2 \text{ lb/d}$$

If the basin is CM, the detention time in the basin must be

$$t_d = t_{10}/0.105 = (122 \text{ min})/0.105 = 1162 \text{ min} = 19.4 \text{ h}$$

Equation (10.21) was derived for first-order decay in a CM basin.

$$C = \frac{C_0}{1 + kt_d} \Rightarrow C_0 = C(1 + kt_d) = (3.00 \text{ mg/L})[1 + (0.2 \text{ h}^{-1})(19.4 \text{ h})] = 14.6 \text{ mg/L}$$

The quantity of chlorine consumed in this case is

$$QC = \left(1.50 \times 10^4 \frac{\text{m}^3}{\text{d}}\right) \left(1000 \frac{\text{L}}{\text{m}^3}\right) \left(14.6 \frac{\text{mg}}{\text{L}}\right) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right) = 219 \text{ kg/d}$$

$$\text{In U.S. units: } QC = \left(3.96 \times 10^6 \frac{\text{gal}}{\text{d}}\right) \left(14.6 \frac{\text{mg}}{\text{L}}\right) \left(\frac{3.79 \text{ L}}{\text{gal}}\right) \left(\frac{1 \text{ lb}}{454 \times 10^3 \text{ mg}}\right) = 482 \text{ lb/d}$$

The benefits of a PF regime are apparent from both the size of the basins and the quantity of chlorine required.