10.0 Chlorine Dioxide

10.1 Introduction

Chlorine dioxide is used for disinfection, taste and odor control, and iron and manganese removal. Chlorine dioxide is effective for inactivation of bacteria, viruses, and protozoa, including *Cryptosporidium* while forming fewer halogenated byproducts than chlorine. It is stable only in dilute aqueous solutions and must be generated on-site. It can be generated using a variety of starting materials including chloride, chlorite, or chlorate.

The Surface Water Treatment Rule (SWTR) and subsequent Stage 1 Disinfection Byproducts Rule (Stage 1 DBPR) and Interim Enhanced Surface Water Treatment Rule (IESWTR) all recognize the ability of chlorine dioxide to inactivate pathogens. As a result, there is much information and guidance available on the application of chlorine dioxide for disinfection, particularly in the following two guidance manuals:

- *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources* (USEPA 1991) (commonly referred to as the Surface Water Treatment Rule Guidance Manual).
  - Describes how to calculate the CT value (CT is described in the next sub-section) for a given disinfectant, including methodologies for determining the residual concentration (C) and contact time (T).
  - Includes CT values for log-inactivation of *Giardia* and viruses.
- *Alternative Disinfectants and Oxidants Guidance Manual* (USEPA 1999).
  - Provides full descriptions of:
    - chlorine dioxide chemistry
    - on-site generation
    - primary uses and points of applications
    - pathogen inactivation and disinfection efficiency
    - byproduct production
    - analytical methods
    - operational considerations

The SWTR and Alternative Disinfectants and Oxidants Guidance Manuals are available on EPA's website, http://www.epa.gov/safewater/mdbp/implement.html.

The purpose of this chapter is to (1) describe what systems need to do to achieve *Cryptosporidium* inactivation treatment credit for disinfecting with chlorine dioxide, (2) discuss design and operational considerations that will assist water systems in deciding whether this toolbox option is a practical option for them, and (3) discuss key issues associated with using chlorine dioxide as a disinfectant. This chapter is organized as follows:

10.2 Log Inactivation Requirements - describes the concentration and time variables of the CT parameter, presents the chlorine dioxide CT table for *Cryptosporidium*, and provides a sample CT calculation.

10.3 Monitoring Requirements - describes monitoring requirements of both LT2ESWTR and Stage 1 DBPR.

10.4 Unfiltered Systems LT2ESWTR Requirements - describes the level of *Cryptosporidium* inactivation unfiltered systems must provide, and monitoring requirements that must be met.

10.5 Disinfection with Chlorine Dioxide - describes chlorine dioxide chemistry and disinfection with chlorine dioxide.

10.6 Toolbox Selection Considerations - discusses the advantages and disadvantages of disinfection with chlorine dioxide.

10.7 Design Considerations - discusses effects of temperature and the point of chlorine dioxide addition on achieving the required CT value.

10.8 Operational Considerations - discusses water quality parameters that affect the disinfection ability of chlorine dioxide.

10.9 Safety Issues - describes considerations for chemical storage and discusses the acute health risks of chlorine dioxide.

10.2 Log Inactivation Requirements

Systems can achieve anywhere from 0.5 to 3.0 log *Cryptosporidium* inactivation with the addition of chlorine dioxide. The amount of *Cryptosporidium* inactivation credit a system may receive is determined by the CT provided in the treatment process (40 CFR 141.729(b)). This methodology provides a conservative characterization of the dose of chlorine dioxide necessary to achieve a specified inactivation level of *Cryptosporidium*. CT is the product of the disinfectant concentration and disinfectant contact time and is defined in the LT2ESWTR (40 CFR 141.729(a)):

CT = Disinfectant (mg/L) x Contact Time (minutes)

- "**T**" is the time (in minutes) it takes the water, during peak hourly flow, to move from the point of disinfectant application to a point where, C, residual concentration is measured prior to the first customer, or between points of residual measurement.

- "**C**" is the concentration of chlorine dioxide present in the system, expressed in mg/L.

The concept of regulating surface water treatment disinfection processes through CT was first introduced in the SWTR. Tables of *Giardia* and virus log inactivations correlated to CT values, commonly referred to as CT tables, were presented in the SWTR Guidance Manual. For the LT2ESWTR, EPA developed CT tables for the inactivation of *Cryptosporidium*. Alternatively, a system may conduct a site-specific study to determine the CT values necessary to meet a specified log inactivation, using State approval (40 CFR 141.729(b)(4)). Appendix A provides guidance for conducting a site-specific study.

10.2.1 CT Calculation

The methodology and calculations for determining CT have not changed from the SWTR to the LT2ESWTR requirements. This section briefly reviews how CT is used to determine log-inactivation for the SWTR and presents the chlorine dioxide CT table for *Cryptosporidium* inactivation. Refer to the SWTR Guidance Manual for descriptions of measuring C and determining T.

Summary of CT Determination and Corresponding Log-inactivation as Presented in the SWTR Guidance Manual

CT can be calculated for an entire treatment process or broken into segments and summed for a total CT value. C is measured at the end of a given segment. T is generally estimated by methods involving established criteria (flow, volume, and contactor geometry) or tracer studies. The following steps describe the CT calculation from measured C and T values for a segment of the entire treatment process:

1) Calculate CT_{calc} by multiplying the measured C and T values.

2) From the CT tables, find the CT value for the log inactivation desired, this is CT_{table}.

3) Calculate the ratio of CT_{calc}/CT_{table} for each segment.

4) If a system has multiple segments, sum the CT_{calc}/CT_{table} ratios for a total inactivation ratio.

5) If the ratio of CT_{calc}/CT_{table} is at least 1, then the treatment process provides the log inactivation that the CT_{table} represents (log inactivation desired from step #2).

Table 10.1 CT Values (mg-min/l) for *Cryptosporidium* Inactivation by ClO_2

Log credit	Water Temperature, °C[1]									
	<=0.5	1	2	3	5	7	10	15	20	25
0.5	319	305	279	256	214	180	138	89	58	38
1.0	637	610	558	511	429	360	277	179	116	75
1.5	956	915	838	767	643	539	415	268	174	113
2.0	1275	1220	1117	1023	858	719	553	357	232	150
2.5	1594	1525	1396	1278	1072	899	691	447	289	188
3.0	1912	1830	1675	1534	1286	1079	830	536	347	226

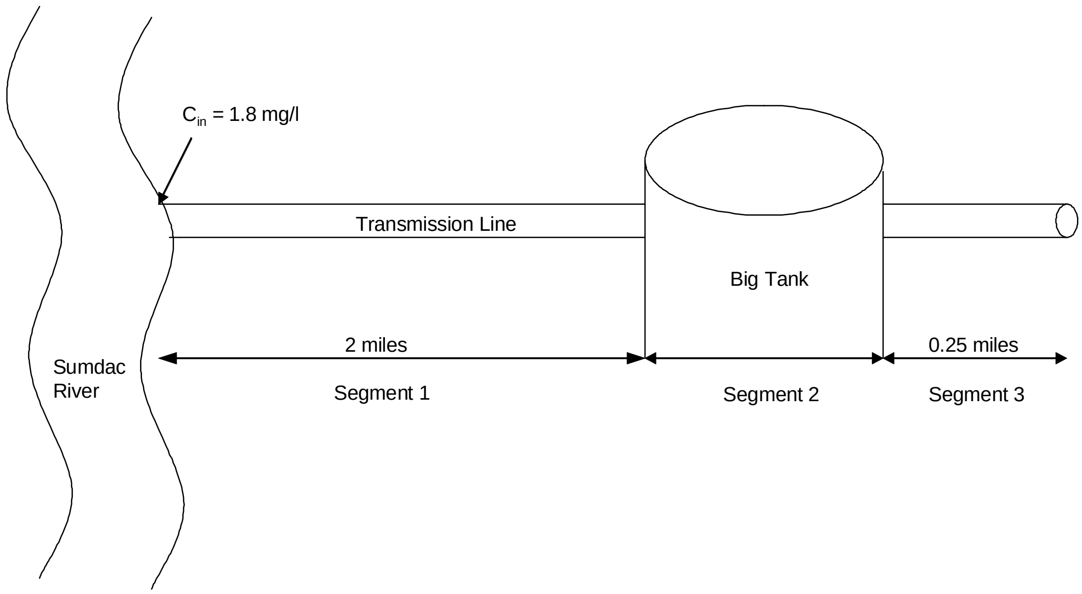
[1] CT values between the indicated temperatures may be determined by interpolation

Example CT Calculation

A plant draws 1.5 MGD of 5 degrees Celsius water from a stream, adding 1.8 mg/l of chlorine dioxide at the intake. The water travels through 2 miles of 12 inch pipe to a settling tank. The detention time in the tank, as determined by a tracer study, is 150 minutes. After the tank, it travels through another 12-inch pipe to the plant. Figure 10.1 provides a schematic of an intake, piping, and tank. The concentration of chlorine dioxide at each point is measured as follows:

$C_{initial}$ = 1.8 mg/l
$C_{entering\ tank}$ = 1.6 mg/l
$C_{leaving\ tank}$ = 0.8 mg/l
$C_{leaving\ 2nd\ pipe}$ = 0.2 mg/l

Figure 10.1 CT Calculation Example Schematic



The residence times of the two sections of pipe are determined assuming plug flow. Therefore the time for each section is calculated as follows:

$$T_1 = (A_1 * L_1 / Q_1) = (\pi r^2 L_1 / Q_1) * (7.48 \text{ gal.}/1 \text{ ft.}^3) * (\text{MG}/1{,}000{,}000 \text{ gal.}) * (1{,}440 \text{ min./day})$$

where:

- A is the cross-sectional area of the pipe in square feet
- Q is the volumetric flow rate in MGD
- L is the length of pipe in feet
- r is the radius of the pipe in feet.

Therefore the times for the two sections of the pipe are as follows:

$$T_1 = 2 \text{ mi.} * (5{,}280 \text{ ft./mi.}) * \pi * (0.5 \text{ ft.})^2 * (0.0108 \text{ MG*sec/ft.}^3 \text{*day}) / (1.5 \text{ MGD}) = 59.7 \text{ min.}$$
$$T_3 = 0.25 \text{ mi.} * (5{,}280 \text{ ft./mi.}) * \pi * (0.5 \text{ ft.})^2 * (0.0108 \text{ MG*sec/ft.}^3 \text{*day}) / (1.5 \text{ MGD}) = 7.4 \text{ min.}$$

The T_{10}, or time for 90 percent of a tracer to pass through the section for the tank is as follows:

$$T_2 = 150 \text{ minutes}$$

CT Calculation:

Step 1. Calculate CT for each segment.

The concentrations and times for each segment are known. The T's are calculated above and the C is the concentration measured at the end of each segment. The CT for each segment is calculated as follows:

$CT_1 = (1.6 \text{ mg/l}) \times (59.5 \text{ min.}) = 95.2 \text{ mg} \times \text{min./l}$
$CT_2 = (0.8 \text{ mg/l}) \times (150 \text{ min.}) = 120 \text{ mg} \times \text{min./l}$
$CT_3 = (0.2 \text{ mg/l}) \times (7.4 \text{ min.}) = 1.5 \text{ mg} \times \text{min./l}$

Step 2. Look up CT_{table} in Table 10.1. For 5ºC and 0.5 log inactivation,

$CT_{table} = 214 \text{ mg}\times\text{min./l.}$

Step 3. Calculate the ratio of CT_{calc}/CT_{table} for each segment.

$(CT_{calc}/CT_{table})_1 = 95.2/214 = 0.44$
$(CT_{calc}/CT_{table})_2 = 120 /214 = 0.56$
$(CT_{calc}/CT_{table})_3 = 1.5/214 = 0.01$

Step 4. Sum the CT_{calc}/CT_{table} for each segment.

$(CT_{calc}/CT_{table})_{total} = 0.44 + 0.56 + 0.01 = 1.01$

Determine Log Inactivation:

If the result of Step 4 is greater than 1, the log inactivation associated with the CT_{table} values is achieved. If the result is less than 1, that level of log inactivation is not achieved (if the log inactivation was less than 1.0, the calculations should be repeated at a lower log inactivation). In this example, the sum of the CT_{calc}/CT_{table} for all the segments is greater than 1, so the system qualifies for a 0.5 log *Cryptosporidium* inactivation.

10.3 Monitoring Requirements

10.3.1 LT2ESWTR

The LT2ESWTR requires **daily CT monitoring** (40 CFR 141.730), which must be done **during peak hourly flow**. Since systems may not know when the peak hourly flow will occur, EPA recommends monitoring on an hourly basis. Contact time does not have to be determined on a daily basis, only concentration does. Contact time is determined using the peak hourly flow. Systems should reevaluate contact time whenever they modify a process and the hydraulics are affected (e.g., add a pump for increased flow, reconfigure piping).

The chlorine dioxide concentration should be measured using approved analytical methods, either DPD, (Standard Method 4500-ClO_2 D) or Amperometric Method II, (Standard Method 4500-ClO_2 E). Details on these methods can be found in *Standard Methods for the Examination of Water and Wastewater*, 20th edition, American Public Health Association, 1998.

Note, if a system is required to develop a disinfection profile under the LT2ESWTR and changes its disinfection process, the LT2ESWTR requires the system to calculate a disinfection profile and benchmark (40 CFR 141.714(a)) (see Chapter 1, section 1.6 for details).

10.3.2 Stage 1 DBPR

The Stage 1 DBPR requires all systems using chlorine dioxide for disinfection or oxidation to monitor daily for chlorine dioxide and chlorite at the distribution system entry point. In addition, systems must take monthly chlorite samples at three locations in the distribution system. Table 10.2 lists the chlorine dioxide and chlorite distribution system monitoring requirements.

Table 10.2 Distribution System Monitoring Requirements at Each Plant

Location	**Frequency**
Chlorite	
Distribution System Entry Point	Daily
Distribution System Sample Set of 3: 1 Near First Customer 1 In Middle of the Distribution System 1 At Maximum Residence Time	Monthly
Chlorine Dioxide	
Distribution System Entry Point	Daily

If the chlorine dioxide maximum residual disinfectant level (MRDL) of 0.8 mg/L or the chlorite maximum contaminant level (MCL) of 1.0 mg/L is exceeded in any of the samples, additional monitoring is required (see the Stage 1 DBPR, 40 CFR141.132(b) for further information). The monthly monitoring requirements for chlorite may be reduced if all chlorite samples are below the MCL for a 1-year period.

10.4 Unfiltered System LT2ESWTR Requirements

The LT2ESWTR requires unfiltered systems to provide at least 2.0 log *Cryptosporidium* inactivation (40 CFR 141.721(b)). If their source water *Cryptosporidium* concentration is greater than 0.01 oocyst/liter, then systems must provide 3.0 log *Cryptosporidium* inactivation (40 CFR 141.721(b)). The requirements of the previous SWTR regulations still apply— achieve 3 log inactivation of *Giardia* and 4 log inactivation of viruses and maintain a disinfectant residual in the distribution system (e.g., free chlorine or chloramines). LT2ESWTR also requires that a minimum of two disinfectants be used to meet overall disinfection requirements.

The monitoring requirements described in section 10.3 apply to unfiltered systems. Additionally, the LT2ESWTR requires unfiltered systems to meet the *Cryptosporidium* log-inactivation requirements determined by the daily CT value every day the system serves water to the public, except one day per calendar month (40 CFR 141.721(c)). Therefore, if an unfiltered system fails to meet *Cryptosporidium* log-inactivation two days in a month, it is in violation of the treatment technique requirement.

10.5 Disinfection With Chlorine Dioxide

Chlorine dioxide (ClO_2) is an uncharged compound of chlorine in the +IV oxidation state. It is a relatively small, volatile, and highly energetic molecule, and a free radical even in dilute aqueous solutions. At high concentrations, it reacts violently with reducing agents. However, it is stable in dilute solution in a closed container in the absence of light. When an aqueous solution is open to the atmosphere, chlorine dioxide readily comes out of solution. Aqueous solutions of chlorine dioxide are also susceptible to photolytic decomposition, depending on the time of exposure and intensity of UV light.

Disinfection of protozoa is believed to occur by oxidation reactions disrupting the permeability of the cell wall (Aieta and Berg 1986). Chlorine dioxide functions as a highly selective oxidant due to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-) (Hoehn et al. 1996).

In drinking water, chlorite (ClO_2^-) is the predominant reaction end product, with approximately 50 to 70 percent of the chlorine dioxide converted to chlorite and 30 percent to chlorate (ClO_3^-) and chloride (Cl-) (Werdehoff and Singer 1987). This has a significant impact on disinfection capabilities for drinking water, since chlorite is a regulated drinking water contaminant with an MCL of 1.0 mg/L. Based on a 50 to 70 percent conversion of chlorine dioxide to chlorite, the maximum dose is limited to 1.4 to 2.0 mg/l unless the chlorite is removed through subsequent treatment processes.

10.6 Toolbox Selection Considerations

10.6.1 Advantages

There are several advantages to using chlorine dioxide as a primary disinfectant. Chlorine dioxide is approximately four times as effective as chlorine for the inactivation of *Giardia* and is a stronger disinfectant than chlorine for bacteria (White 1999). However, free chlorine is more effective for the inactivation of viruses. Other advantages of disinfection with chlorine dioxide include:

- A high oxidizing potential allows it to oxidize other compounds such as manganese and some taste and odor compounds.
- Chlorine dioxide does not form regulated halogenated organic byproducts.
- The effect of pH on the disinfection ability of chlorine dioxide is much smaller than for other disinfectants.
- Chlorine dioxide has shown a synergistic effect when combined with other disinfectants such as ozone, chlorine, and chloramines that leads to greater inactivation with the disinfectants added in series than by either disinfectant individually.

10.6.2 Disadvantages

A major disadvantage of chlorine dioxide is the byproduct formation of chlorite and chlorate. Section 10.6 describes the dose limits of chlorine dioxide due to the formation of chlorite. Other disadvantages of disinfection with chlorine dioxide include:

- Difficulty in maintaining an effective residual. Additionally, residual will be lost in the filters.
- It decomposes upon exposure to sunlight, flourescent light bulbs, and UV disinfection systems.
- Ability to disinfect is reduced under colder temperatures.
- If the ratio of reactants in the chlorine dioxide generator is incorrect, excess aqueous chlorine can remain, which can form halogenated disinfection byproducts.
- Chlorine dioxide must be generated on-site.

- There may be a need for three-phase power which may not be compatible with some water systems.
- Chlorine dioxide can be explosive at high temperatures or pressures.
- Storage of sodium chlorite solution can be problematic due to crystallization at low temperatures or high concentrations and stratification at temperatures below 40°F (or 4°C).
- High cost of chemicals.
- Dialysis patients are sensitive to higher chlorite levels and should be notified if chlorine dioxide is going to be added where it has not routinely been used.
- Training, sampling, and analysis costs are high.

Systems considering using chlorine dioxide as a disinfectant should perform chlorine dioxide demand/decay tests on the water being considered for disinfection (raw water or filter effluent) under normal and poor water quality conditions. If chlorine dioxide is added where the demand is 1.4 mg/l or greater, the system may have difficulty complying with the chlorite MCL. If the raw water has a chlorine dioxide requirement greater than 1.4 mg/l, chlorine dioxide might still be able to be used for post disinfection since the oxidant demand will be less after the filters.

10.7 Design Considerations

10.7.1 Designing to Lowest Temperature

As the water temperature declines, chlorine dioxide becomes less effective as a disinfectant. LeChevallier et al. (1997) found that reducing the temperature from 20 degrees Celsius to 10 degrees Celsius reduced disinfection effectiveness by 40 percent. Since the treatment achieved for chlorine dioxide addition is temperature dependent, systems need to consider the variability in water temperature to ensure they meet the CT level for the minimum treatment needed for compliance. For example, if a system is required to provide an additional 1 log *Cryptosporidium* treatment and plans to achieve that with chlorine dioxide alone, then it should determine the CT required for the lowest water temperature experienced and ensure it can meet those CT requirements.

10.7.2 Point of Addition

There are two main considerations for determining locations of chlorine dioxide addition for the purpose of *Cryptosporidium* inactivation—contact time and chlorine dioxide demand. Additionally, systems using ozone should consider that ozone will degrade chlorine dioxide. The application point for chlorine dioxide should be well upstream of the ozone process or just after the ozone process.

Contact Time

There must be substantial contact time with a residual concentration. The CT requirements for *Cryptosporidium* are much higher than for *Giardia* and viruses and when designing to the lowest water temperatures, the resulting contact time requirements are relatively high for even the 0.5 and 1.0 log inactivation. Chlorine dioxide readily degrades when exposed to light from flourescent lamps or the sun, therefore all the available concentration in open basins will most likely not be utilized for disinfection. For most systems, the point of application will be either at the raw water intake or after the filters, whichever can provide the necessary contact time.

Oxidant Demand

The oxidant demand of the water affects chlorite and chlorate byproduct formation (section 10.6). If the chlorine dioxide requirement of the raw water is greater than 1.4 mg/L then chlorite concentration will likely exceed the MCL. However, chlorine dioxide could be added after the filters where the oxidant demand is frequently lower and, therefore, a lower dose of chlorine dioxide would result in a lower byproduct concentration of chlorite.

10.8 Operational Considerations

Of all the water quality parameters, water temperature has the strongest effect on the disinfection ability of chlorine dioxide. The concentration of suspended matter and pH also have an effect, but to a lesser extent than temperature. Although the disinfection potential of chlorine dioxide is not strongly affected by pH, studies have shown that chlorine dioxide disinfection is better under higher pH (LeChevallier et al. 1997).

Suspended matter and pathogen aggregation affect the disinfection efficiency of chlorine dioxide. Protection from chlorine dioxide inactivation due to bentonite was determined to be approximately 11 percent for water with turbidity values less than or equal to 5 NTU and 25 percent for turbidity between 5 and 17 NTUs (Chen et al. 1984).

Based on the research discussed above, the optimal conditions for *Cryptosporidium* disinfection with chlorine dioxide are low turbidity, high pH, and high temperature.

10.9 Safety Issues

Because chlorine dioxide can be explosive and pose acute health risks to those exposed to gaseous chlorine dioxide, a safety plan should be developed that includes precautions for generation, handling, storage, and emergency response.

Airborne concentrations greater than 10 percent may cause explosions.

10.9.1 Chemical Storage

Most chlorine dioxide generators use sodium chlorite solutions as a raw material. If sodium chlorite solutions are accidently acidified or exposed to a reducing agent, uncontrolled production and release of gaseous chlorine dioxide can result. In addition to being toxic, if the gaseous chlorine dioxide reaches concentrations greater than 10 percent, it can spontaneously explode.

Sodium chlorite should be stored away from other chemicals, particularly any acid solutions or chemicals that could act as reducing agents. Construction materials in sodium chlorite storage areas, as well as chlorine dioxide generating areas, should be fire resistant such as concrete. Sodium chlorite fires burn especially hot and produce oxygen as a byproduct, so special fire fighting techniques are required to extinguish the fire. These firefighting techniques should be part of the safety plan and proper equipment and supplies should be stored nearby. Temperatures in storage and generation areas should be kept below 130 degrees Celsius.

10.9.2 Acute Health Risks of Chlorine Dioxide

Exposure to gaseous chlorine dioxide can cause shortness of breath, coughing, respiratory distress, and pulmonary edema. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is 0.1 ppm. Areas where chlorine dioxide is generated and stored should have appropriate monitoring to detect leaks of chlorine dioxide or other chlorine containing chemicals into the air. Proper ventilation and scrubbing systems should be installed. First aid kits and respirators should also be accessible outside the building. Operators should be trained to use the respirators.

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