Ozone in Drinking Water Treatment

Process Design, Operation, and Optimization

Kerwin L. Rakness

First Edition

American Water Works Association

Science and Technology

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Preface

Ozone treatment of drinking water is well established in Europe but relatively new in North America. Ozone was implemented in Quebec, Canada, in the early 1980s and is now gaining popularity in other provinces. Less than 15 plants in the United States used ozone in 1985. The number of installations now exceeds 400. About 50% of the known ozone installations are at larger plants (>1 mgd), possibly because the large plants have resources available to study and test the application and benefits of ozone at their plants, resources that might be unavailable to small plants. However, this does not mean that the technology is limited to large-plant installations, as ozone is equally applicable in smaller plants.

This book serves as a resource for all drinking water treatment plants to gain insight into application, design, operation, control, and optimization of ozone facilities. These aspects are discussed in chapters 1 through 8. Appendix A discusses ozone calculations and conversion factors, which are fairly involved because ozone is delivered to the treated water as a gas. Appendix B presents conversion factors between English units and metric units.

This book is written primarily from an operations perspective, based on operating experiences. It explains the current place and placement of ozone facilities in drinking water treatment plants in North America. It describes why and where ozone is used and how ozone systems are designed, operated, and optimized. It is intended for use in several ways by various disciplines, including:

1. Large and small water agencies that currently use ozone. The book is a resource for ideas concerning achieving or maintaining optimized performance of ozone facilities. The book contains discussions concerning instrumentation quality control and quality assurance guidelines.
2. Large and small water agencies that are considering including ozone as a treatment process option. The book explains why and how ozone is currently being used and precautions for implementation.
3. Design engineers that are involved with ozone system planning and design. The book presents information concerning how ozone has been helpful at plants in North America that are currently using ozone, limitations for selecting and/or using ozone, and important design, operation, and maintenance considerations.
4. Laboratory and research agencies that are involved with bench or pilot testing. The book describes how ozone is used in full-scale installations and also describes scale-up issues and considerations.

5. Regulatory agency staff responsible for enforcement, design review, and inspections of plants that use ozone. The book explains the theory and practice of ozone operation and how ozone disinfection performance is measured, calculated, reported, and optimized.

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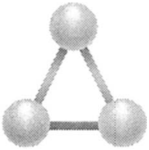

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Introduction

HISTORY AND APPLICATION

Ozone is a strong oxidant and a powerful disinfectant. It has been used continuously in drinking water treatment for close to 100 years, beginning in Nice, France, in 1906 and thereafter at water treatment plants throughout the world. Since 1960 thousands of European water treatment plants have used ozone to achieve disinfection and/or plant-specific oxidation needs. European ozone treatment plants, designed initially to meet disinfection standards, have been operated recently to meet European Union regulations for disinfection by-products (DBPs) and pesticides (Hill and Rice, 1982; Rice, 1999).

Ozone was first used in the United States in 1908, with minimal growth until 1985 (LePage, 1996). In 1980 there were less than 10 known operating ozone treatment plants. However, within the past two decades more than 300 ozone treatment plants have been designed, constructed, and operated to address disinfection, DBPs, taste and odor, color, microcoagulation (also known as microflocculation), hydrogen sulfide, and other drinking water treatment needs (see chapter 2).

PHYSICAL AND CHEMICAL PROPERTIES

Ozone, an unstable gas molecule, has formed the ozone layer surrounding Earth's upper atmosphere since the Earth's formation. However, it was not until 1840 that Schöenbein reported the odor from this gas as being a new substance, to which he gave the name *ozone* (from the Greek word *ozein* meaning to smell) (Rice, 1999). Ozone also exists naturally in the lower atmosphere after lightning storms and as the result of human activities, including photocopying and ambient air-pollution

Table 1-1 Selected Physical Properties of Ozone

	US Units	SI Units
Molecular weight	48.00	48.00
Specific gravity of gas (air = 1.0)	1.66	1.66
Boiling point at 1 atm	–169.4°F	–111.9°C
Melting point at 1 atm	–314.5°F	–192.5°C
Critical temperature	10.2°F	–12.1°C
Critical pressure	791.9 psia	5,460 kPa (abs)
Critical density	33.7 lb/ft^3	540 kg/m^3
Latent heat of gas at boiling point and 1 atm	127 Btu/lb	297 kJ/kg
Specific heat of gas at 32°F (0°C) and 1 atm	0.183 Btu/lb (°F)	0.767 kJ/kg (°C)
Solubility in water, vol/vol at 32°F (0°C)	0.64	0.64
Weight of liquid at boiling point	84.4 lb/ft^3	1,352 kg/m^3

Source: Compressed Gas Association, Inc. Publication CGA P-34, 2001.

events. It can be produced commercially under controlled electric discharge conditions and subsequently used to effectively treat drinking water. The physical characteristics of ozone are listed in Table 1-1.

OZONE GENERATION THEORY AND CONVENTIONAL PROCESS SCHEMATIC

Ozone Generation Theory

Electrical energy flowing across a narrow gap that is filled with oxygen splits the oxygen molecules into oxygen atoms (O). These atoms combine with other oxygen molecules (O_2) to form ozone (O_3), as illustrated in Figure 1-1. The unstable ozone gas quickly reverts back to molecular oxygen; thus, it cannot be stored in a container. The theoretical specific energy requirement to split oxygen molecules to form ozone is:

$$\text{specific energy requirement} = 0.820\ \text{kWh/kg}_{O_3} \text{ or } 0.372\ \text{kWh/lb}_{O_3}$$

The actual specific energy requirement is much higher (10× to 20×) due to generation inefficiencies. On-site ozone production from a commercially available ozone generation system is controlled by adjusting the source oxygen-containing gas flow rate and the applied power in the generator.

Oxygen-containing gas flows through a small “discharge gap” that is located inside the ozone generator (Figure 1-2). The gap might be as large as 3 mm in low-frequency air-fed ozone systems (21 percent-by-volume: %vol oxygen) or as small as 0.3 mm in medium-frequency, high-purity oxygen-fed (>90 %vol oxygen) ozone generators. The gap has a glass or ceramic dielectric on one side and a stainless-steel ground electrode on the other side. Single-phase, high-voltage alternating current

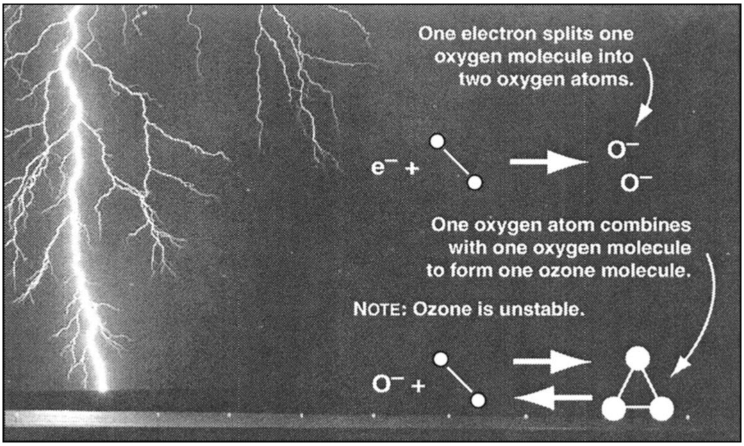


Figure 1-1 Electrical energy splits oxygen molecules to form ozone

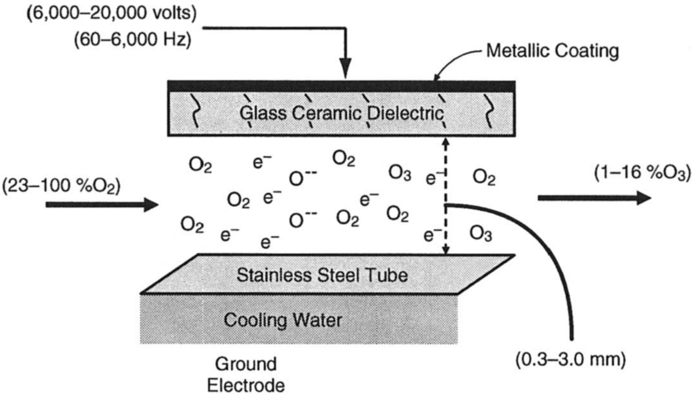


Figure 1-2 Features of commercially available electric-discharge ozone generator

electrical power is applied to the dielectric to distribute the electron flow (called a corona discharge) evenly across the gap. The electrical frequency typically is 60 Hz in low-frequency air-fed ozone generators and 350 Hz to 6,000 Hz in medium-frequency oxygen-fed (also some air-fed) ozone generators. The ozone concentration in the generator product-gas ranges from 1 %wt to 4 %wt (typically 1–2.5 %wt) for air-fed and 6 %wt to 16 %wt (typically 8–12 %wt) for oxygen-fed ozone systems.

The oxygen-containing feed gas must be free from particles, very dry, and low in hydrocarbon concentration. Air-fed ozone systems are quite complex because they use pressure (compressors), temperature (refrigerant dryers), and adsorption (desiccant dryers) equipment to dry the feed gas sufficiently, as shown in Figure 1-3.

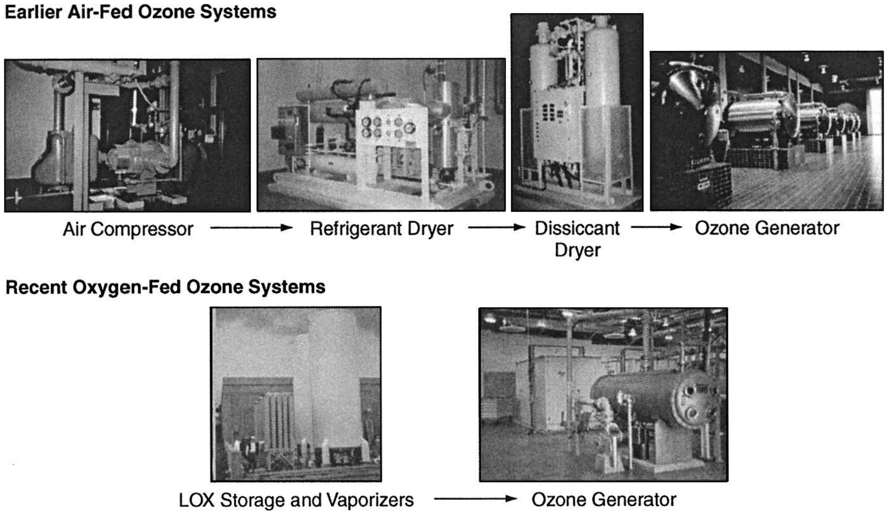


Figure 1-3 Ozone system cost and complexity is reduced using LOX as the feed-gas

Liquid oxygen (LOX)-fed ozone systems are less complicated. The LOX is vaporized to gaseous oxygen in ambient or water-bath vaporizers, which develop operating pressure during vaporization. Economics has favored LOX-fed ozone systems since the late 1980s, when medium-frequency ozone generators, which produce ozone efficiently at high concentrations, were commercialized. Oxygen-containing feed gas can also be produced using pressure swing adsorption or vacuum-pressure swing adsorption (also called vacuum swing adsorption) technology to increase the oxygen concentration in the feed gas from ambient air levels (21 %vol) to greater than 90 %vol.

More cost-effective ozone systems have arisen since the advent of reliable, medium-frequency ozone generators. The biggest advantage is that ozone can be produced from oxygen at higher ozone concentrations while consuming low to moderate specific energy (kWh/lb$_{O_3}$). This combination of low specific energy and reduced oxygen usage (i.e., high ozone concentration operation) has lowered operating costs significantly. Also, the number and size of ozone system equipment components have been reduced, lowering capital and maintenance costs. This reduction in maintenance, operating, and capital costs of ozone systems has greatly benefited water utilities in their application of ozone.

Conventional Process Schematic

The four primary components of an ozonation system used in water treatment are shown in Figure 1-4. They include feed-gas supply, ozone generator (includes

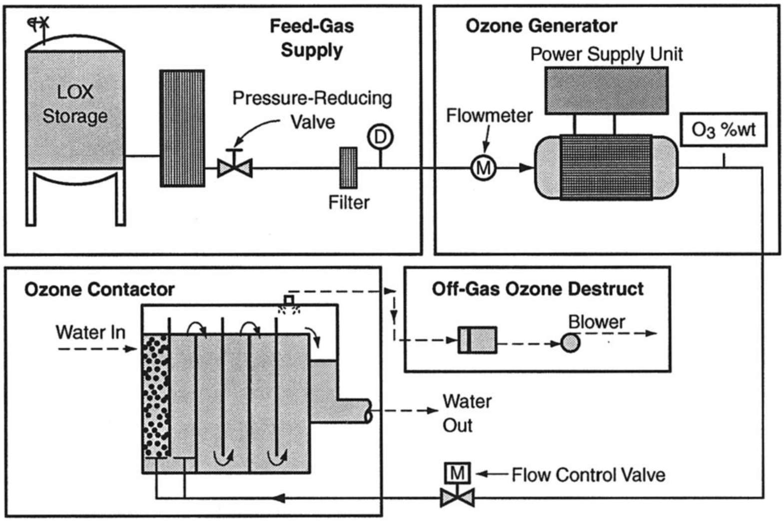


Figure 1-4 Four main components of an ozone system: feed-gas, ozone generator, ozone contactor, and off-gas ozone destruct

generator vessel and power supply unit [PSU]), ozone contactor, and off-gas ozone destruct. The ozone system supplier uniquely designs the ozone generator vessel and associated PSU. Ozone generator sizing, operation, and maintenance considerations are discussed in chapters 3 and 4. The feed-gas supply, ozone contactor, and ozone destruct subsystems are relatively generic. The example feed-gas subsystem shown in Figure 1-4 is LOX with an ambient oxygen vaporizer. Design considerations for other ozone system components, plus alternative feed-gas options, are discussed in chapter 4. Details concerning operation and maintenance of the feed-gas supply equipment are discussed in chapters 4 and 5.

Ozone in the gas phase is only partially soluble in water and, therefore, requires special gas/liquid contacting techniques to ensure that all water is exposed to the required levels of dissolved ozone. The most common ozone contactor is a sealed concrete basin approximately 20 ft deep with vertical baffle walls that create an up-and-down water flow pattern. Ozone usually is dispersed into the first one or two transfer cells through fine-bubble diffusers. Technology for injector ozone dissolution systems is readily available, especially for small and now for larger treatment plants (e.g., 50 mgd and larger). Contactor size, shape, flexibility, and alternative ozone-contacting options are discussed in chapters 3 and 4. Because 5% to 10% of the applied ozone is discharged in the contactor off-gas, an off-gas ozone destruct unit is required. Off-gas ozone destruct system design, operation, and maintenance considerations are presented in chapter 4.

OXYGEN AND OZONE SAFETY

Safety considerations for operating an ozone system include potential for ozone exposure, oxygen exposure when high-purity oxygen is the feed gas, electrical danger, and mechanical hazards. Mechanical safety, such as confined-space entry, is discussed in the ozone contactor subsection in chapter 4. Mechanical safety for ozone system equipment is similar to general mechanical equipment safety for a water treatment plant. Although not discussed in this book, mechanical safety is extremely important. Electrical safety involves carefully accessing the PSU, cautiously opening the end plate of the ozone generator, and properly grounding the dielectrics and other components before touching them. Refer to the ozone system supplier's operation and maintenance manual concerning electrical and other safety precautions for the specific equipment supplied. Specific oxygen and ozone safety issues are discussed in the following paragraphs.

Oxygen Safety

Physical and chemical characteristics of oxygen are listed in Table 1-2. Oxygen is colorless, odorless, and tasteless. It is slightly heavier than air; therefore, locations for sampling are near ground level. Oxygen is nonflammable by itself but vigorously supports combustion in the presence of a fuel source (almost anything) and an ignition source (almost anything). An atmosphere is considered oxygen-enriched

Table 1-2 Selected Physical Properties of Oxygen

	US Units	SI Units
Molecular weight	31.9988	31.9988
Specific gravity of gas (air = 1.0)	1.10	1.10
Boiling point at 1 atm	–297.3°F	–182.9°C
Freezing point at 1 atm	–361.1°F	–218.4°C
Critical temperature	–181.4°F	–118.6°C
Critical pressure	731.4 psia	5,043 kPa
Critical density	27.23 lb/ft^3	436.1 kg/m^3
Latent heat of vaporization at boiling point and 1 atm	91.7 Btu/lb	213 kJ/kg
Specific heat of gas at 70°F (21.1°C) and 1 atm		
C_p	0.220 Btu/lb-°F	0.917 kJ/kg-°C
C_v	0.157 Btu/lb-°F	0.653 kJ/kg-°C
Solubility in water, vol/vol at 32°F (0°C)	0.0489	0.0489
Weight of liquid at boiling point	9.52 lb/gal	1,141 kg/m^3

Source: Compressed Gas Association, Inc. Publication CGA G-4, 1996.

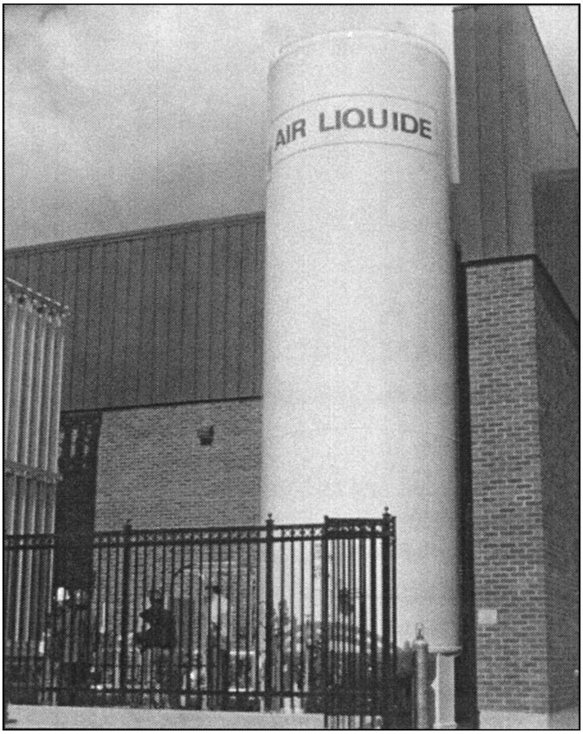


Figure 1-5 LOX storage tanks may be located in urban settings

when the oxygen concentration is >23 %vol. Non-oxygen–enriched ambient air contains ~21 %vol of oxygen. The Compressed Gas Association provides printed resources concerning oxygen installation and safety (CGA, 1996).

Oxygen safety considerations are put into practice when the ozone generation system feed-gas supply is high-purity oxygen from LOX storage vessels or on-site oxygen concentration facilities (see chapter 4). LOX storage (with no relation to ozone) is common in urban settings such as at hospitals, industrial plants, wastewater treatment plants, or drinking water treatment plants (Figure 1-5). A LOX storage tank and vaporizers are often located near buildings and are covered by setback requirements, as outlined by the National Fire Protection Association (NFPA, 2001). The primary safety consideration is combustion or fire, which occurs when the combustion limit is lowered due to an oxygen-enriched atmosphere (Figure 1-6).

Freezing hazards associated with handling cryogenic (extremely cold) LOX (–297°F at 1 atm) are a concern with LOX-fed ozone systems. However, water treatment plant staff typically does not deal directly with cryogenic LOX. The

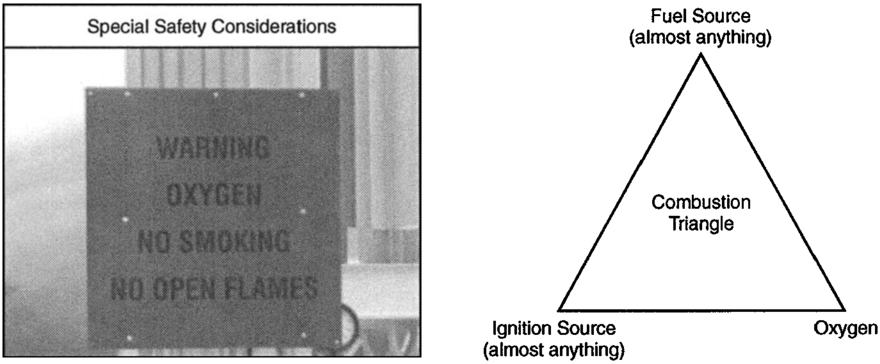


Figure 1-6 LOX is safe when handled with respect

supplier's contract for LOX delivery and price can include both the cost of oxygen and the cost of maintaining the cryogenic system components, including shutoff valve inspection, pressure relief valves inspection, tank vacuum checks, and other tasks. A maintenance contract can be obtained regardless of whether the LOX tank is leased or owned by the water utility. Because special training is required for these maintenance activities, water utilities normally include supplier-provided cryogenic system maintenance as part of the contract price for oxygen.

Ozone Safety

Ozone is beneficial or harmful, depending on its location. Ozone in the upper atmosphere is beneficial because it absorbs ultraviolet (UV) radiation from the sun and thereby reduces risks of skin cancer. Ozone that is controlled and contained within pipes is beneficial when it is used as an oxidant (or disinfectant) at drinking water treatment plants, bottled water plants, food-processing plants, pulp-bleaching plants, and in other industrial applications. Uncontrolled creation or discharge of ozone, however, is detrimental at ground level because of ozone's potential effects on human health and the immediate surroundings.

Ozone Exposure Limits

The maximum ozone concentration in the ambient atmosphere is regulated by air-pollution control agencies. The Occupational Safety and Health Administration regulates in-plant ozone levels in the United States. Suggested personal exposure limits (CGA, 2001) are listed in Table 1-3. Exposure limits (Workers Compensation Board of British Columbia, 1991) in Canada are listed in Table 1-4. Both sources indicate that humans detect (smell) ozone at low levels of 0.01 to 0.04 ppm_V, which is less than the maximum 8-hour recommended exposure limit of 0.1 ppm_V. A value of 0.1 ppm_V is usually used to set the first-alert sound and visual alarm point.

Table 1-3 Personal Exposure Effects and Limits for Ozone—United States

Observed Effects	Concentration, ppm$_V$
Threshold odor detection, normal person	0.01–0.04
Maximum 8-hour average personal exposure limit	0.1
Minor eye, nose, and throat irritation; headache, shortness of breath	>0.1
Breathing disorders, reduction in oxygen consumption, lung irritation, severe fatigue, chest pain, dry cough	0.5–1.0
Headache, respiratory irritation, and possible coma; possibility of severe pneumonia at higher levels of exposure	1–10
Lethal to small animals within 2 hours	15–20
Lethal in a few minutes	>1,700

Source: Compressed Gas Association, Inc. Publication CGA P-34, 2001.

Table 1-4 Personal Exposure Effects and Limits for Ozone—Canada

Observed Effects	Concentration, ppm$_V$
Detectable odor	0.01–0.04
TLV-TWA (threshold limit value–time weighted average) 8-hour limit	0.1
Headache, shortness of breath	>0.1
TLV-STEL (threshold limit value–short-term exposure limit) 15-minute limit	0.3
Chest pain, dry cough, lung irritation, severe fatigue	0.6–1.0 (1–2 hours)
Immediately dangerous to life and health	5
Expected to be fatal	50 (30 minutes)

Source: Workers Compensation Board of British Columbia. 1992. Ozone Manual of Standard Practice.

Olfactory senses, however, become desensitized during continuous and prolonged exposure to ozone. Consequently, once detected, appropriate safety actions should be taken. Olfactory senses will regain their initial sensitivity in the absence of ozone. At water treatment plants located in urban settings with high levels of ambient ozone due to air pollution, the first-alert sound and visual alarm point is often higher than 0.1 ppm$_V$, e.g., 0.2 ppm$_V$. A higher setting is used because, if the alarm sounds when an air pollution event occurs, staff may ignore the warning when an ozone leak occurs. The 15-min exposure limit of 0.3 ppm$_V$ (see Table 1-4) normally is used as the alarm condition for an ozone generator power shutdown. Feed-gas flow continues in order to flush ozone from the pipes.

In summary, workers do not routinely smell ozone while working at ozone facilities. However, they often will be able to identify minor leaks via the odor of

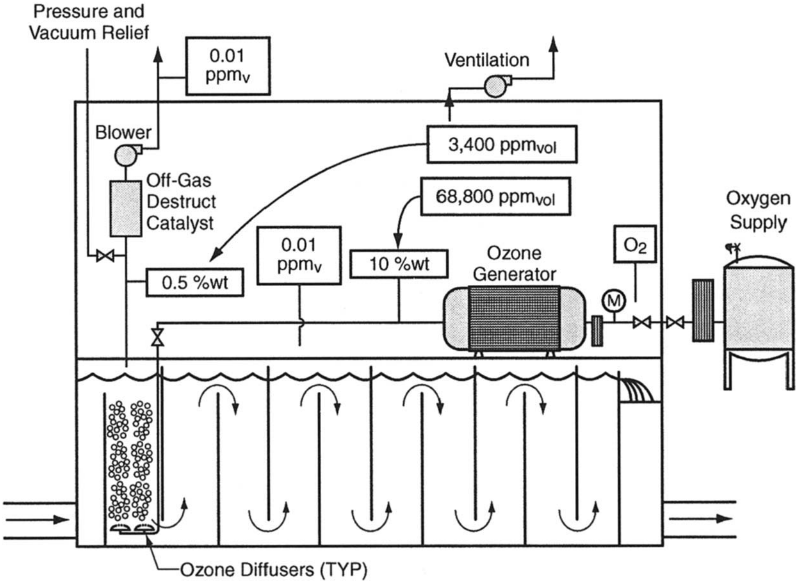


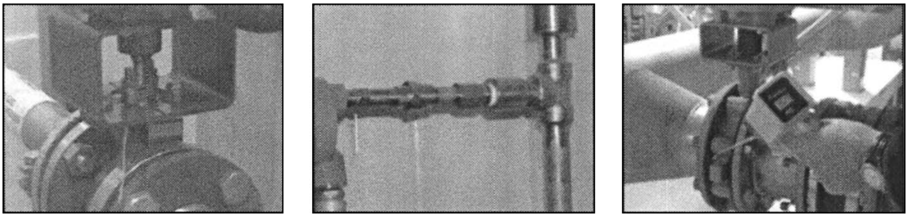
Figure 1-7 Ozone system layout showing important oxygen and ozone safety features

low concentration ozone, which is low enough that it would not cause a shutdown of the ozone facilities. When these low concentration leaks occur, they should be located and repaired as soon as practical.

Ozone Safety Features

Figure 1-7 illustrates important safety features of an ozone system. The ozone generator is normally located in an enclosed building and might be located above the ozone contactor (Figure 1-7). The LOX storage tank and vaporizers are located outside the building. Ambient oxygen meters are located close to the oxygen piping (see previous discussion concerning oxygen safety monitoring and alarms). And ambient ozone monitors are located close to the ozone piping and in low spots (e.g., stairwells) where ozone is likely to accumulate.

In this setup, the dried and clean oxygen feed gas flows into the ozone generator. The product gas ozone concentration is generally 10 %wt, which is 68,800 ppm$_V$ (see appendix A for discussion of ozone conversion factors). The ambient ozone monitor next to the ozone generator shows a typical reading of 0.01 ppm$_V$. If the reading were to rise above 0.1 ppm$_V$ (i.e., assumed normal set point value), a slight ozone leak likely exists. The ventilation fan should be programmed to activate automatically when a leak occurs and discharge 10 or more air changes per hour instead of the normal building design air-change criterion, e.g., 6 air changes per hour. If the ambient ozone reading reaches 0.3 ppm$_V$ (i.e., assumed



Valve Stems Threaded Fittings Flanges

Figure 1-8 Possible locations for ozone leaks

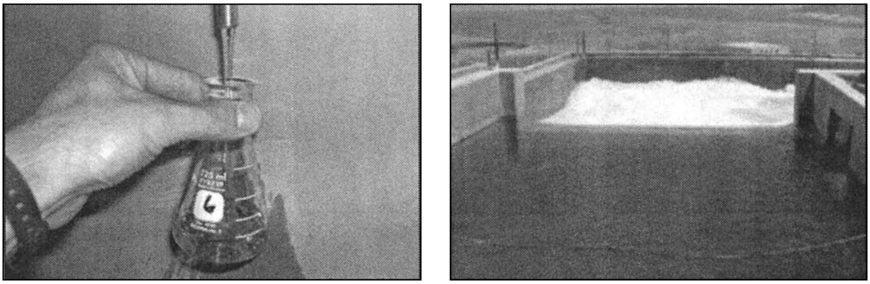
normal set point value that might be elevated in urban settings), the safety interlock should be designed to shut off the power to the ozone generators. The oxygen gas flow should continue in order to flush any remaining ozone from the piping.

The large differential concentration of ozone between the inside of the ozone piping (68,800 ppm$_V$) and the ambient environment (<0.1 ppm$_V$) indicates that even very small ozone leaks are problematic. Ozone systems are expected to occasionally develop ozone leaks, e.g., a few leaks per year. Probable leak locations are illustrated in Figure 1-8. Ambient ozone monitors will detect an elevated ozone concentration due to large ozone leaks and will shut down ozone production by automatically stopping the applied power to the generator. Because stopping the power to the ozone generator immediately stops disinfection treatment, some water utilities program their supervisory control and data acquisition alarm system so that two ozone monitors must display alarm readings before a shutdown occurs. This approach reduces nuisance alarms, without adversely affecting staff safety.

Large ozone leaks can be quickly detected using two ambient ozone monitors. Fortunately, large ozone leaks are uncommon. It is more common for plant staff to notice an ozone odor when walking through the treatment area. These leaks can be located in one of the following three ways and should be repaired as soon as practical. Leaks can be located using:

- A portable ozone detector (see Figure 1-8)
- A weak soap solution sprayed onto the potential leak area (bubbles will form as the gas escapes) (NOTE: Some treatment plants use simple deionized water to reduce cleanup issues due to dried soap.)
- Chemical detection, whereby potassium iodide (2% KI) solution soaked on a white rag or white paper towel turns a brownish color in the presence of ozone

Figure 1-7 shows that the ozone concentration in the off-gas from the contactor is 0.5 %wt (3,400 ppm$_V$), which indicates ozone transfer efficiency of 95%. This off-gas ozone concentration is unsafe for direct discharge; even at 99%



Sample Stations

Contactor Outlet, Rapid Mix, or Filters

Figure 1-9 Possible locations for ozone exposure due to off-gassing

transfer efficiency (i.e., 680 ppm_V), the ozone off-gas is unsafe for direct discharge. An off-gas ozone destruct unit is required to maintain a safe working environment. Design features of ozone destruct units are discussed in chapter 4.

Other locations of ozone exposure are shown in Figure 1-9, including ozone residual sampling stations and mixing locations following ozone contactors where there is high ozone residual in the contactor outlet. Routine sampling does not expose an individual to harmful ozone because samples are collected within a few minutes. However, ozone levels in the plant environment will increase if the sample water is allowed to flow (i.e., splash) for a long time (several minutes to hours), thus allowing ozone gas to be released from the sample and build up in the ambient environment.

The exhaust-gas ozone concentration from the destruct unit, as indicated in Figure 1-7, is 0.01 ppm_V, but typically this concentration is <0.01 ppm_V. If the exhaust-gas concentration is consistently higher than 0.1 ppm_V (i.e., not a spike), the preheater and/or destruct catalyst might need to be replaced. Off-gas destruct design and operating considerations are discussed in chapter 4.

Ozone contactors are enclosed tanks that are operated under a vacuum to prevent ozone leaks. A pressure-vacuum relief valve is located on the contactor roof or on the contactor off-gas line to prevent over-pressure or excess-vacuum damage to the contactor roof. The discharge/intake of the pressure-vacuum relief unit(s) should be placed in a remote location away from worker traffic patterns, such as on the roof of a building or at the far end of the ozone contactor (Figure 1-10). Contactor operation and process control features that help minimize pressure-vacuum relief are discussed in chapter 4.

OZONE APPLICATIONS AND REGULATORY COMPLIANCE

Regulations for drinking water treatment enacted by the US Environmental Protection Agency (USEPA) have directly affected the use of ozone. These enacted

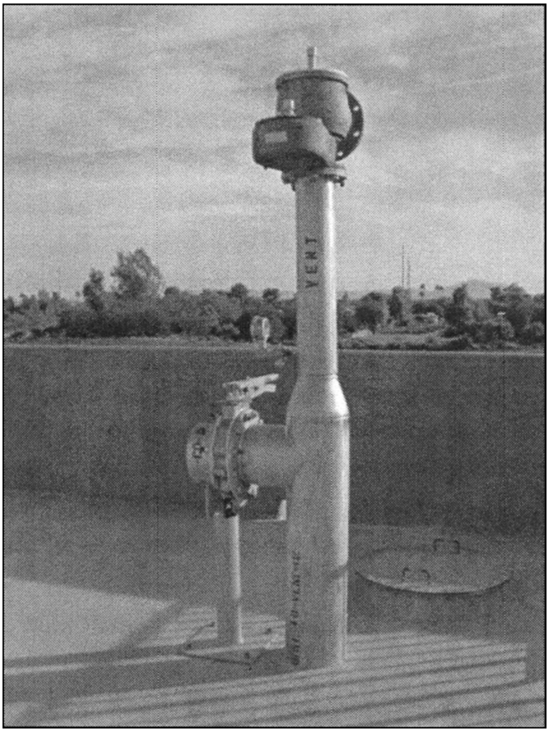


Figure 1-10 Pressure-vacuum relief valve with remote vent location

or proposed regulations are summarized below. Following the list of regulations is a discussion of ozone treatment applications that have been implemented by various water utilities in response to these regulations.

1. The Surface Water Treatment Rule (SWTR) (USEPA 1991), which was promulgated on June 29, 1989, and made effective on December 31, 1990, includes criteria for *Giardia lamblia* and virus removal using sedimentation and filtration and inactivation by disinfection using chlorine, chloramines, chlorine dioxide, or ozone. The guidance manual for the SWTR, particularly Appendix O, discusses ozone CT values for inactivation of *Giardia* and viruses. *Ozone CT* is defined as ozone residual times contact time, which is similar in concept to chlorine CT. More information on ozone CT-value calculations for *Giardia* and viruses is presented in chapter 2.
2. The Interim Enhanced Surface Water Treatment Rule (USEPA 1998a) and Stage 1 Disinfection By-Product Rule (USEPA 1998b) were both

promulgated on December 16, 1998, and made effective on February 16, 1999. The rules:

   a. Lowered filtered water turbidity requirements and introduced *Cryptosporidium parvum* oocysts as a pathogen of public health concern;
   b. Lowered the total trihalomethanes (TTHMs) maximum contaminant level (MCL) to <80 μg/L;
   c. Set the total concentration of five haloacetic acids (HAA5) at a limit of <60 μg/L. HAA5 are a regulated by-product of chlorine oxidation;
   d. Set the concentration of bromate, which is a regulated by-product of ozone (and sodium hypochlorite) oxidation, at a limit of <10 μg/L. Bromate can be formed via ozone addition when bromide is present. Bromate also exists in hypochlorite solutions as a by-product of hypochlorite generation; and
   e. Mandated enhanced coagulation (excess coagulant addition) in specific cases to achieve prescribed removal percentages of total organic carbon (TOC).

3. The proposed Stage 2 Disinfectants and Disinfection By-products Rule (USEPA, 2003b) requires:
   a. Source water *Cryptosporidium* oocyst monitoring and, in some cases, enhanced *Cryptosporidium* control; and
   b. More stringent monitoring of TTHMs and HAA5 in the distribution system (i.e., compliance is necessary at the site-specific, likely worst-case, location rather than using a system-wide average of all measurements at all locations).
4. The proposed Long-term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) (USEPA, 2003a) is being enacted to reduce disease incidences associated with *Cryptosporidium* and other pathogenic microorganisms in drinking water. USEPA published the draft *LT2ESWTR Implementation Guidance Manual* and draft *LT2 Toolbox Guidance Manual* on November 11, 2003. The manuals provide guidance concerning ozone (and other disinfectants) CT values for *Cryptosporidium* and CT calculation methods. More information on ozone CT-value calculations for *Cryptosporidium* is presented in chapter 2.

During the past several years, many water utilities have installed ozone to meet one or more of these regulations. Specific ozone applications for regulatory compliance and other reasons are presented in chapter 2.

Ozone applications that focus on regulatory disinfection and DBP considerations also can be designed to provide simultaneous secondary benefits from ozone oxidation, including elimination of undesirable tastes and odors, removal of color, improved filtered water turbidity, and reduced coagulant dosage due to microcoagulation (microflocculation). Meeting regulations and improving customer satisfaction have been instrumental in providing water utilities with an overall satisfaction with their investment in ozone facilities. In all cases, chlorine or chloramine typically is used for secondary disinfection because ozone residual is short lived (minutes).

Ozone used at water treatment plants without filtration systems. Some water utilities with very high-quality raw water supplies meet the combined removal-inactivation disinfection requirements of the SWTR by ozone alone, without filtration. At these water treatment plants, ozone is used to achieve *Giardia* and virus disinfection credits through inactivation. Recently, ozone systems have been designed to meet *Cryptosporidium* inactivation targets. However, ozone, followed by UV irradiation, might be used to meet more stringent *Cryptosporidium* requirements. The combination of ozone followed by UV irradiation provides optimum performance for both treatment subsystems.

Ozone at water treatment plants that exceed TTHM and HAA5 DBP criteria. The Stage 1 and Stage 2 D/DBP Rules contain stringent DBP requirements, in addition to more stringent disinfection criteria. An increased chlorine dosage and higher chlorine residuals might be used to meet disinfection criteria; however, at some water treatment plants DBP problems occur as the result of elevated chlorine residuals and/or longer contact times. Some water utilities reach the chlorine disinfection CT value by increasing chlorine contact time. This is done by moving the chlorine application point to the head of the treatment plant or before filtration. However, this change increases TTHM and HAA5 formation such that many water treatment plants were not able to meet the DBP requirements. Therefore, many water treatment plants install ozone to meet disinfection CT criteria and delay chlorine addition until after filtration, thus reducing TTHM and HAA5 formation. In some cases, enhanced coagulation is avoided either by achieving TOC removal goals through operation of biological filters or by meeting specific water quality criteria conditions provided by the regulations.

Ozone used in water treatment plants to enhance disinfection. Some water utilities install ozone to achieve enhanced disinfection (beyond regulations) for *Giardia*, viruses, and/or *Cryptosporidium*, because chlorine, at drinkable treatment dosages, was ineffective for *Cryptosporidium* inactivation. Some water utilities must increase their disinfection protection due to elevated levels of *Cryptosporidium* oocysts in their source water. Ozone is a candidate treatment process for these water utilities, especially if aesthetic water quality issues, such as off-taste, color, and odor, also need to be addressed.

Ozone use may increase the level of bromate, which is an ozonation by-product. Water utilities that have elevated levels of bromide (e.g., >50 µg/L Br^-)

present in their raw water supply must carefully evaluate their proposed ozone application; otherwise, unacceptable levels (i.e., >10 µg/L) of bromate might be formed during ozonation. Some water utilities adopt bromate control measures when they implement ozonation, e.g., by lowering pH or adding controlled dosages of pre-chlorine and pre-ammonia. Bromate mitigation strategies are discussed further in chapter 2.

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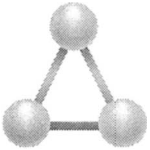


2

Applications in Drinking Water Treatment

Ozone is used at drinking water treatment plants for various reasons. Most treatment plants install ozone for disinfection and operate their ozone systems to meet specific disinfection treatment objectives. For this reason, disinfection with ozone is emphasized in this book, However, multiple secondary benefits are obtained from ozonation, such as color, taste, and odor removal, and these benefits are also discussed. The secondary benefit that is achieved at one plant can be the primary reason ozone is installed at another plant. And, ozone is often applied for one primary reason, but multiple treatment reactions and benefits are typically obtained, all at the same time.

All ozone applications involve oxidative reactions, whether ozone is used for disinfection or oxidation of specific contaminants. Water-related oxidation reactions with common inorganic and organic compounds are outlined in Figure 2-1. Most inorganic reactions are very rapid, except those involving the formation of bromate. In this case, ozone oxidation of bromide to hypobromite ion is moderately fast and in the same order as the oxidation of hypobromite to bromate. Reactions with organic substances can be fast or slow, depending on the organic molecules involved and the water's pH. Advanced oxidation by hydroxyl radicals ($HO^{\bullet}$) is necessary in some cases. A general explanation of ozone reactions is presented later in this chapter. Detailed explanations of ozone reactions are provided in, *Ozone in Water Treatment: Application and Engineering* (Langlais et al., 1991).

Of particular note is that *organic compounds* that are oxidized by ozone or by $HO^{\bullet}$ form shorter-chained organic molecules. Fortunately, many of these shorter-chained organics are readily biodegradable and removed in biological filters. More information on biological filter operation is presented in chapter 5.

Inorganic	**Organic**	
	Pathogens	**Other**
Iron	Bacteria	Solvents, $HO^\bullet$
Manganese	Virus	Pesticides, $HO^\bullet$
Hydrogen sulfide	*Giardia*	Color
Bromide	*Cryptosporidium*	Taste and odor, $HO^\bullet$

$HO^\bullet$ Hydroxyl-free radical formation occurs naturally but may be promoted with high pH (>8.0) or with the addition of hydrogen peroxide.

Figure 2-1 Water-related oxidation reactions with inorganic and organic compounds

Difficult-to-oxidize organics include many solvents, most pesticides, and compounds that cause tastes and odors (2-methylisoborneol [MIB] and geosmin), which are by-products of algal growth and decomposition. These non-double-bonded, or "saturated," organics cannot be oxidized rapidly by ozone alone. However, they can be oxidized by the hydroxyl radical ($HO^\bullet$). In many water treatment plants, the concentration of naturally occurring $HO^\bullet$ will be sufficient for oxidation of moderate levels of off-taste and odor-causing compounds, such as 50 ng/L of MIB and geosmin (Morioka et al., 1993). As a result, most water treatment plants that operate ozone systems to meet disinfection needs (e.g., *Giardia*, virus, or *Cryptosporidium* log-inactivation credit) also eliminate offensive tastes and odors, which greatly improves customer satisfaction with the ozone-treated water. When naturally occurring concentrations of $HO^\bullet$ are insufficient (e.g., high carbonate ion concentrations that quench $HO^\bullet$) or when offensive taste-and-odor compound concentrations are excessive, hydrogen peroxide can be added, along with an increased ozone dose, to create additional $HO^\bullet$. More information is presented later in this chapter concerning the ozone-plus-hydrogen peroxide advanced oxidation process, which is sometimes called the PEROXONE process.

DISINFECTION TREATMENT

The primary purpose of ozonation at many water treatment plants is to achieve disinfection log-inactivation credit for viruses, *Giardia*, and *Cryptosporidium* at regulated or above-regulated levels. *Giardia*, virus, and *Cryptosporidium* regulatory requirements are discussed briefly in chapter 1.

Log-Inactivation Credit Overview

Plant operators calculate disinfection credit, or more specifically log-inactivation credit, for meeting regulatory requirements. The value of 1-log inactivation is the same as 90% inactivation, 2 log is 99%, 3 log is 99.9%, etc. The term *log removal* or *log inactivation*, instead of *percent removal*, is used in regulations for ease in disinfection reporting.

Water treatment processes reduce concentrations of pathogens in water by the actions of both physical removal and chemical inactivation. Removal involves the processes of sedimentation and filtration. Inactivation means that even though the pathogenic organism might physically exist in the finished water supply, it has been rendered dead, inactive, or incapable of reproduction.

Equation 2-1 is the fundamental equation for determining the number of organisms that are still viable after exposure to any disinfectant, including ozone. Equation 2-1 can also be expressed as a natural-log (Ln) base-e value instead of a log base-10 value. Some researchers use the Ln expression. Log base-10 is used exclusively in this book, because this terminology is used in the disinfection regulations promulgated by the US Environmental Protection Agency (USEPA). It is important to know which expression (i.e., Ln or log) is being used for the inactivation value and to always use the correct expression. To convert a Ln base-e inactivation value to a log base-10 value, divide by 2.303, since Ln(10) = 2.303. The log base-10 value is always a lower number (log base-10 value = log base-e value ÷ 2.303).

$$N = N_0 \times 10^{-k_p C^n T^m} \qquad \text{(Eq. 2-1)}$$

Where:

N = number of organisms that remain viable

N_0 = initial number of viable organisms

k_p = pathogen inactivation rate constant, *Giardia*–k_g, virus–k_v, or *Cryptosporidium*–k_c, $\log(N/N_0)/CT$

C = residual-in-water, "concentration" of the disinfectant, mg/L

T = exposure time, min

n = allows the relative impact of C to be adjusted upward or downward

m = allows the relative impact of T to be adjusted upward or downward

Most researchers have found that the values of n and m are equal to 1.0; therefore, Eq. 2-1 becomes Eq. 2-2 (commonly referred to as Chick's law). The USEPA also uses n and m equal to 1.

$$N = N_0 \times 10^{-k_p CT} \qquad \text{(Eq. 2-2)}$$

Equation 2-3 is obtained by rearranging Eq. 2-2.

$$\text{Log}\left(\frac{N}{N_0}\right) = -k_p \times C \times T \qquad \text{(Eq. 2-3)}$$

Equation 2-4 is obtained by inverting N and N_0 in Eq. 2-3. By doing so, the negative sign is eliminated from the equation and the result is a positive value (e.g., 2-log credit). Equation 2-4 is the *primary* equation used by plant operators to calculate disinfection credits. In Eq. 2-4, the log-inactivation credit, Log (N_0/N), is equal to the inactivation rate constant of the pathogen, k_p, multiplied by the CT value ($C \times T$), which is residual concentration times contact time.

$$\text{Log}\left(\frac{N_0}{N}\right) = k_p \times C \times T \qquad \text{(Eq. 2-4)}$$

Where:

Log (N_0/N) = log-inactivation credit

k_p = pathogen log-inactivation rate, which is *Giardia*–k_g, virus–k_v, or *Cryptosporidium*–k_c

$C \times T$ = disinfection "power," or ozone residual (mg/L), times time (min)

Equation 2-5 is obtained by rearranging Eq. 2-4. Equation 2-5 is important because it is necessary for operators to know the inactivation rate constant, k_p, to calculate the log-inactivation credit. The USEPA *Guidelines for Implementing the Surface Water Treatment Rule* contain ozone log-inactivation rates for *Giardia* and viruses, as shown in Table 2-1 (USEPA, 1991). Some water utilities interpolate with Eq. 2-6 to find the inactivation rate constant when temperatures are between the listed temperatures.

$$k_p = \frac{\text{Log}\left(\frac{N_0}{N}\right)}{CT} \qquad \text{(Eq. 2-5)}$$

$$k_{v \text{ or } g} = a_{v \text{ or } g} + b_{v \text{ or } g} \times (T_{\text{measured}} - T_{\text{low}}) \qquad \text{(Eq. 2-6)}$$

Where:

$k_{v \text{ or } g}$ = inactivation rate constant for viruses or *Giardia* (NOTE: Use k_v or k_g at 25°C when $T_{\text{measured}} \geq 25°\text{C}$.)

$a_{v \text{ or } g}$ = coefficient *a* for viruses or *Giardia* from Table 2-1

$b_{v \text{ or } g}$ = coefficient *b* for viruses or *Giardia* from Table 2-1

T_{measured} = measured water temperature, °C

T_{low} = smaller of the interpolated water temperature value from Table 2-1, °C

An example solution for water with a temperature of 9°C is shown below.

$k_g = 1.58 + [0.100 \times (9 - 5)] = 1.98$ Log/CT

$k_v = 3.33 + [0.134 \times (9 - 5)] = 3.866$ Log/CT

An alternative used by some water utilities is to apply Eq. 2-7, which is a best-fit equation of the data in Table 2-1 as shown in Figure 2-2. The equation can be easily programmed into a computer control system or electronic spreadsheet.

Table 2-1 *Giardia* and Virus Inactivation Rates

Water Temperature °C	Virus Inactivation		*Giardia* Inactivation	
	a_v	b_v	a_g	b_g
0.5	2.22	0.220	1.03	0.122
5	3.33	0.134	1.58	0.100
10	4.00	0.534	2.08	0.208
15	6.67	0.266	3.12	0.210
20	8.00	1.060	4.17	0.416
25	13.30		6.25	

Source: USEPA, *Surface Water Treatment Rule Guidelines,* Appendix O.

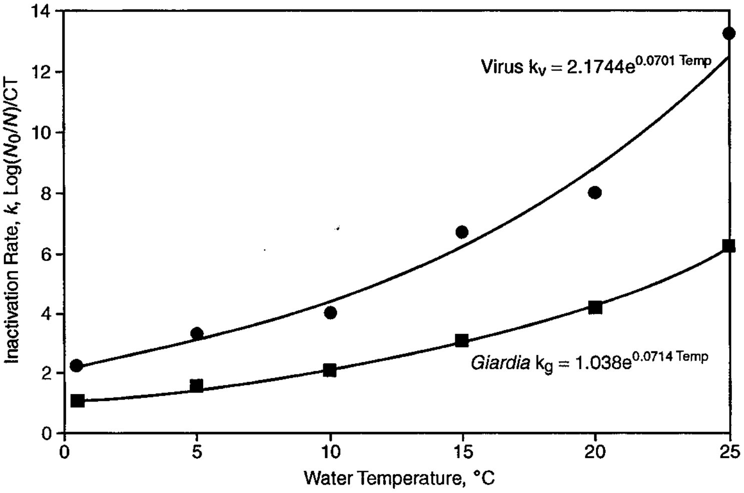


Figure 2-2 *Giardia* and virus log-inactivation rates based on USEPA tables

$$k_{v\ \text{or}\ g} = c \times e^{d \times \text{Temp}} \qquad \text{(Eq. 2-7)}$$

Where:

c = 2.174 for viruses and 1.038 for *Giardia*
d = 0.0701 for viruses and 0.0714 for *Giardia*
Temp = water temperature, °C

The USEPA draft CT values for *Cryptosporidium* log-inactivation credit are published in the *Federal Register* (40 CFR 141.730); these values are listed in Table 2-2. In the *Long-term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) Toolbox Guidance Manual,* the USEPA published a table of

Table 2-2 CT Values for *Cryptosporidium* Inactivation by Ozone

Log Credit	Water Temperature, °C*									
	0.5	**1**	**2**	**3**	**5**	**7**	**10**	**15**	**20**	**25**
0.5	12	12	10	9.5	7.9	6.5	4.9	3.1	2.0	1.2
1.0	24	23	21	19	16	13	9 6	2 3	9 2	2.5
1.5	36	35	31	29	24	20	15	9.3	5.9	3.7
2.0	48	46	42	38	32	26	20	12	7.8	4.9
2.5	60	58	52	48	40	33	25	16	9.8	6.2
3.0	72	69	63	57	47	39	30	19	12	7.4

Source: USEPA, *LT2ESWTR Toolbox Guidance Manual*, Chapter 11 (draft June 2003).

* CT values between the indicated temperatures may be determined by interpolation.

Table 2-3 Inactivation Rate by Ozone, k_C, for *Cryptosporidium*

Water Temperature, °C									
0.5	1	2	3	5	7	10	15	20	25
0.0417	0.043	0.0482	0.0524	0.0629	0.0764	0.101	0.161	0.254	0.407

Source: USEPA, *LT2ESWTR Toolbox Guidance Manual*, Chapter 11 (draft June 2003).

Cryptosporidium inactivation rate constants for variable water temperatures (see Table 2-3), plus an equation that can be used to determine *Cryptosporidium* inactivation rate constant, k_C, as shown in Eq. 2-8 (USEPA, 2003).

$$k_C = g \times h^{\text{Temp}} \qquad \text{(Eq. 2-8)}$$

Where:

g = 0.0397
h = 1.09757
Temp = water temperature, °C

Ozone CT Overview

Various methods are available for calculating CT values (Rakness et al. 2005). The method chosen depends largely on available information concerning ozone residual characteristics and hydrodynamic features of the ozone contactor. Appendix O of the USEPA *Surface Water Treatment Rule Guidance Manual* introduces CT_{10} (i.e., effluent residual × contact time T_{10}, or $C_{\text{Effluent}}T_{10}$) for calculating the ozone CT value for *Giardia* and virus log inactivation (USEPA, 1991). Research studies have demonstrated validity of the $C_{\text{average}}T_{10}$ method, which is a variation of the $C_{effluent}T_{10}$ method (Coffey, 2000). Chapter 11 and Appendix B of the draft *LT2ESWTR Toolbox Guidance Manual* describes the extended completely stirred tank reactor (CSTR) method for calculating *Cryptosporidium* log inactivation, which is applicable for compartmentalized ozone contactors such as over–under or serpentine baffled basins (USEPA, 2003). The extended integrated CT_{10} method is a variation of extended CSTR and T_{10} methodologies and may be suitable for noncompartmentalized ozone contactors such as pipelines or long channels.

The four methods differ in their approach to calculating the extent of disinfection. The $C_{effluent}T_{10}$ method is perhaps most conservative of the four, typically resulting in the highest ozone dose. Nevertheless, the $C_{effluent}T_{10}$ method is widely used for *Giardia* and virus log inactivation, probably because implementation of an alternative method would require justification to the regulatory agency by the water utility (USEPA, 1991). Most water utilities have not pursued justification of a less conservative method, because the incremental increase in ozone dose is somewhat muted (i.e., CT values are quite low for *Giardia* and virus log inactivation). However, some utilities have pursued and received authorization to use the $C_{average}T_{10}$ method, primarily because they are faced with the potential for elevated bromate levels when the ozone dose is increased.

Cryptosporidium log inactivation requires a significantly higher CT value and, as such, the most accurate, albeit least conservative, methodology. The extended CSTR and extended-integrated CT_{10} methods typically generate higher estimates of *Cryptosporidium* log inactivation (also *Giardia* and virus log inactivation). They are considered most accurate because they involve more detailed descriptions concerning ozone residual decay and the hydrodynamic state of the contactor. All four CT calculation methods are described here.

Ozone CT Value and *Giardia* and Virus Log-Inactivation Credit

Giardia and virus removal and inactivation became treatment goals when the Surface Water Treatment Rule (SWTR) was implemented in 1990. All water treatment plants must achieve a minimum of 4-log virus and 3-log *Giardia* removal plus inactivation (Table 2-4). The required credit from inactivation (disinfection) depends on the type of filtration used at the plant. A conventional treatment plant is given 2-log virus and 2.5-log *Giardia* removal credit. Therefore, required virus and *Giardia* credits from disinfection are 2 log and 0.5 log, respectively. A direct filtration plant that does not have sedimentation is given 1-log virus and 2.0-log *Giardia* removal credit. At direct filtration water treatment plants that do not have sedimentation, the required virus and *Giardia* credits from disinfection are higher—at 3 log and 1 log, respectively. At water plants that do not have filtration processes, the full disinfection requirement (3-log *Giardia*, 4-log virus, and 2-log

Table 2-4 ***Giardia*** **and Virus Removal and Inactivation Requirements**

	Giardia Log	Virus Log
Conventional Sedimentation and Filtration		
Required Removal/Inactivation	3	4
Removal, Conventional Treatment	2.5	2
Inactivation From Disinfection	0.5	2
Direct Filtration		
Required Removal/Inactivation	3	4
Removal, Direct Filtration	2	1
Inactivation From Disinfection	1	3

Cryptosporidium) can be obtained using ozone (usually for *Giardia* and virus inactivation) or ozone followed by ultraviolet (UV) light disinfection (usually for *Cryptosporidium* inactivation).

Contactor Shape Considerations

The type and shape of the ozone contactor affect calculations for *Giardia* and virus inactivation credits. Ozone contactors include provision for both ozone dissolution (i.e., dissolving ozone gas into the water) and ozone reaction (i.e., ozone residual and detention time for development of CT value). Two basic ozone contactor configurations are the vertical-baffled, bubble diffuser unit and the side-stream injection-type unit. The bubble diffuser contactor is the most common configuration, but side-stream systems are gaining in popularity with the implementation of high-concentration (low gas flow) ozone generators. In side-stream systems, ozone is dissolved into the water outside of the contactor and is followed by mixing of the concentrated side-stream with the rest of the water to be ozonated (see chapter 4). The ozonated water is then directed to the contactor for oxidation and disinfection reaction. Systems with disinfection reaction zones can vary greatly in size and shape and might include pipeline contactors, horizontal baffled tanks, vertical baffled tanks, or other configurations.

In a bubble-diffuser contactor, the water enters chamber 1 and is directed downward by the vertically constructed baffle located between the chambers, as shown in Figure 2-3. Water flows through the under-baffle of chamber 1 and is diverted back upward in chamber 2, down in chamber 3, etc., through all chambers in the contactor. Bubble-diffuser contactors that are used for disinfection applications typically have 6, 8, 10, or 12 chambers. Fewer chambers and shorter detention times (e.g., 6 to 10 min) are commonly used to meet *Giardia* and virus disinfection objectives, since required CT values are fairly low.

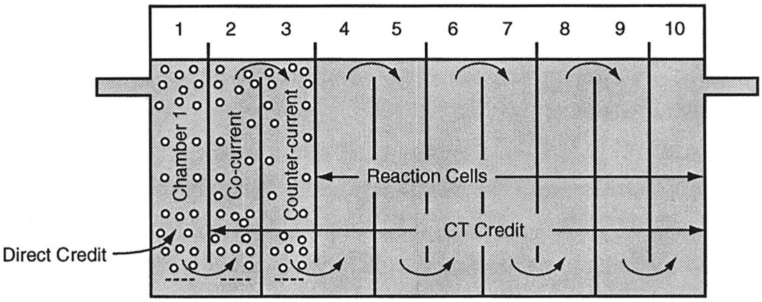


Figure 2-3 Example vertical-baffled bubble-diffuser ozone contactor

Extra chambers and additional detention time (e.g., 20 to 60 min) are used for enhanced disinfection applications (e.g., for *Cryptosporidium*) that have higher CT-value requirements. More information on bubble-diffuser contactor design is presented in chapter 4.

In Figure 2-3, chambers are labeled as chamber 1, co-current, counter-current, and reaction chambers. Ozone is always added in chamber 1. Flexibility to add ozone in co-current chamber 2 usually is provided (gas and water flow up); sometimes ozone is added in counter-current chamber 3 (gas flow up and water flow down). Chambers without ozone addition are called reaction chambers, which include chambers 2 and 3 if ozone is added to chamber 1 only.

The *SWTR Guidance Manual*, Appendix O, provides guidelines for calculating *Giardia* and virus inactivation credits. The guidelines do not allow calculation of CT value (residual concentration, C, × time, T) in chamber 1 but does allow direct credit if the following conditions are met:

- Chamber 1 must be equal in size or larger than the largest downstream chamber.
- *Giardia* direct credit = 0.5 log if the chamber 1 outlet residual is >0.3 mg/L.
- Virus direct credit = 1 log if the chamber 1 outlet residual is >0.1 mg/L.

CT value is calculated downstream of chamber 1, whether or not ozone is added to downstream chambers. It is important to note that ozone residual, C, is measured at the outlet of individual chambers and not just at the outlet of the contactor. Refer to chapter 7 for additional information on residual measurement techniques and residual sampling locations.

The operating characteristics within a chamber affect the value of ozone residual, C, that is used in the CT calculation. Adding ozone to chamber 1 only achieves optimum performance most of the time, but not all of the time. Adding ozone to chamber 1 and to chamber 2 (co-current) typically is more effective when ozone demand is high and ozone decay is rapid (e.g., water temperature and/or pH are high). Ozone is infrequently added to downstream counter-current chambers, because the allowable residual for the CT-value calculation is only 50% of the measured value. Following is a summary of allowable ozone residual for different types of contact chambers:

1. Allowable C is 50% of the measured outlet residual ($C_{out}/2$) in a counter-current chamber that is located downstream of chamber 1.
2. Allowable C is the greater of measured C_{out} or the quotient of $[C_{out} + C_{in}] \div 2$ in a co-current chamber that is located downstream of chamber 1.
3. Allowable C is C_{out} in a reactive chamber, unless an alternative approach such as averaging through integration using C_{in} and C_{out} is authorized by the governing regulatory agency (Coffey, 2000).

The CT-calculated disinfection credit is determined using Eq. 2-4. This credit is added to the direct credit to determine the total log-inactivation credit that is achieved using ozone. Required CT values at variable water temperatures are shown in Figure 2-4 for different *Giardia* and virus log-inactivation values. For example, a conventional filtration plant is required to achieve 0.5-log *Giardia* and 2-log virus log-inactivation credit with ozone. If the chamber 1 outlet residual is 0.29 mg/L, the allowable direct credit is 1-log virus and 0-log *Giardia*. Therefore, the *Giardia* and virus log-inactivation credit that must be obtained from CT disinfection is 1-log virus and 0.5-log *Giardia*, which is the required credit minus direct credit. At a water temperature of 10°C the required CT value is 0.21 mg-min/L, from Figure 2-4.

Example Calculations

An example ozone residual profile is shown in Figure 2-5 for a conventional filtration plant that is pursuing 0.5-log *Giardia* and 2-log virus-inactivation credit using both direct credit and CT-calculated credit. Table 2-5 displays the data that is used to calculate CT value and log-inactivation credit and also shows calculation results. The CT calculations in this example are developed using the "effluent" method. Alternative calculation methods are discussed later.

Water temperature influences the virus (k_v) and *Giardia* (k_g) inactivation rate constants, as indicated in Table 2-1 and Eq. 2-7. The T_{10}/T ratio affects the value for T that can be used in the CT calculation, because T must be the T_{10}-time. The T_{10}-time is the product of the T_{10}/T ratio times the hydraulic detention time in the chamber. Hydraulic detention time, in minutes, is the quotient of the chamber volume (gallons) divided by water flow rate (gpm). Total log-inactivation credit is the sum of CT-value credit and direct credit. The log-inactivation ratio (IR) is the measured total credit divided by the target credit. The target is achieved when the IR is greater than 1.0.

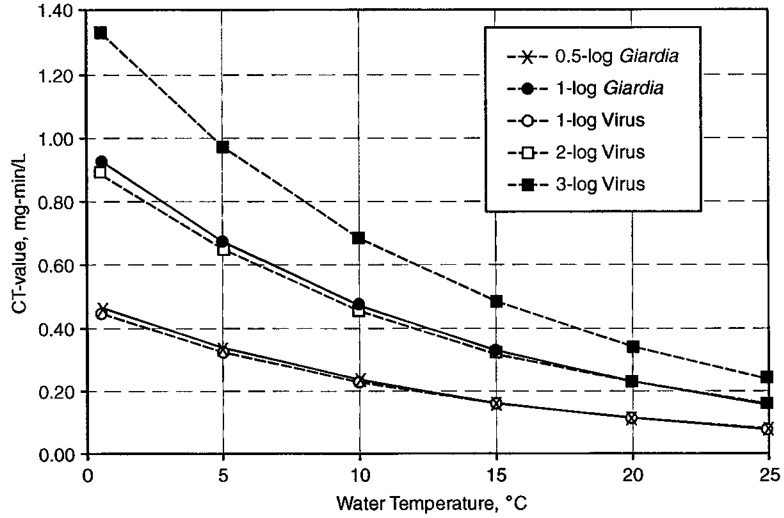


Figure 2-4 CT value for variable water temperature and *Giardia* and virus log-inactivation targets using best-fit equations from Figure 2-2

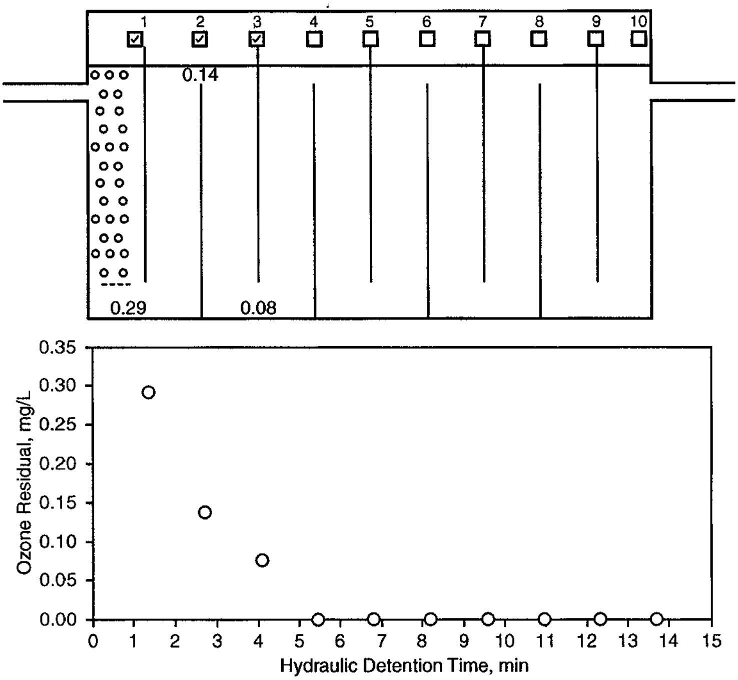


Figure 2-5 Example ozone residual profile for 2-log virus and 0.5-log *Giardia* log-inactivation credit at a water temperature of 17°C

Table 2-5 ***Giardia*** **and Virus Disinfection Data and Calculation Results for a Conventional Treatment Plant at Water Temperature of 17°C**

T_{10}/T Ratio is	0.60	Typical range is 0.5 to 0.7.				
Water Temperature	17.0	C				
	Gas Added	Measured C	HDT	C for CT	T for CT	CT
	Y or N	mg/L	min	mg/L	min	mg/L × min
Chamber 1	Y	0.29				
Chamber 2	N	0.14	1.41	0.14	0.85	0.117
Chamber 3	N	0.08	1.41	0.08	0.85	0.065
Chamber 4			1.41		0.85	
Chamber 5			1.41		0.85	
Chamber 6			1.41		0.85	
Chamber 7			1.41		0.85	
Chamber 8			1.41		0.85	
Chamber 9			1.41		0.85	
Chamber 10			1.41		0.85	
			SUBTOTAL FOR MEASURED CT			0.182
				Virus Inactivation Credits		
	Inact. Rate	From CT	Direct	Total	Required	Virus IR
	k_v	Log I	Log I	Log I	Log I	—
	7.16	1.30	1.00	2.30	2.0	1.15
				Giardia Inactivation Credits		
	Inact. Rate	From CT	Direct	Total	Required	*Giardia* IR
	k_g	Log I	Log I	Log I	Log I	—
	3.49	0.64	0.00	0.64	0.5	1.28

The following items from Table 2-5 are noted:

- The water temperature is 17°C and the associated virus and *Giardia* inactivation rate constants are 7.16 and 3.49 Log/CT (i.e., Log per CT value = 1), respectively, when calculated using best-fit Eq. 2-7, which was developed in Figure 2-2.
- The T_{10}/T ratio is 0.60, which was obtained from tracer tests.
- The subtotal for measured CT value is 0.182 mg-min/L. Ozone is added to chamber 1 only. The measured residual values from the outlet of chambers 2 and 3 are used to calculate CT value for the respective chamber.

- The direct credit for viruses is 1 log, because the chamber 1 outlet residual is >0.1 mg/L.
- The direct credit for *Giardia* is 0 log, because the chamber 1 outlet residual is <0.3 mg/L.
- The CT-calculated credits for viruses and *Giardia* are 1.30 log and 0.64 log, respectively, which were obtained using Eq. 2-4.
- The direct plus CT-calculated log-inactivation credits (i.e., total credits) for viruses and *Giardia* are 2.30 log and 0.64 log, respectively.
- In a conventional plant, the targets for virus and *Giardia* credits are 2 log and 0.5 log, respectively. IR is calculated as measured credit divided by target credit. The IR_v is 1.15 and IR_g is 1.28. Disinfection log-inactivation performance objectives were achieved because the IR was >1.0.
- Disinfection objectives in this example were achieved within 5 min of ozone contact time using results from three ozone readings.

Required virus and *Giardia* log-inactivation credits are greater for a direct filtration plant, at 1-log *Giardia* and 3-log virus disinfection credit. Also, the inactivation rate constants (k_p) are lower at colder water temperatures. These two variables were incorporated into the example ozone residual profile in Figure 2-6. Table 2-6 displays the data used to calculate CT value and log-inactivation credit for the Figure 2-6 residual profile and also shows calculation results. The following items from Table 2-6 are noted:

- The water temperature is 1°C and the associated virus and *Giardia* inactivation rate constants are 2.33 and 1.11 Log/CT, respectively, when calculated using Eq. 2-7, which was developed in Figure 2-2.
- The T_{10}/T ratio is 0.60, which was obtained from tracer tests.
- The subtotal for measured CT value is 1.005 mg-min/L. Ozone is added to chamber 1 only. The measured residual values from the outlet of chambers 2, 3, 4, 5, and 6 are used to calculate CT value for the respective chamber.
- The direct credit for viruses is 1 log, because the chamber 1 outlet residual is >0.1 mg/L.
- The direct credit for *Giardia* is 0.5 log, because the chamber 1 outlet residual is >0.3 mg/L.
- The CT-calculated credits for viruses and *Giardia* are 2.34 log and 1.12 log, respectively, which were obtained using Eq. 2-4.
- The direct plus CT-calculated log-inactivation credits (i.e., total credits) for viruses and *Giardia* are 3.34 log and 1.62 log, respectively.

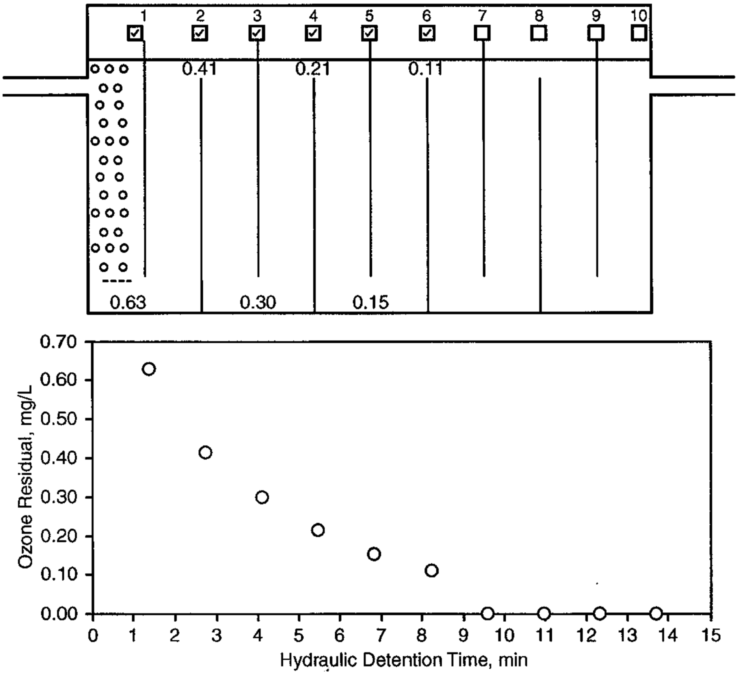


Figure 2-6 Example ozone residual profile for 3-log virus and 1-log *Giardia* log-inactivation credit at a water temperature of 1°C

- In a direct filtration plant, targets for virus and *Giardia* credits are 3 log and 1 log, respectively. IR is calculated as measured credit divided by target credit. The IR_V is 1.11 and IR_g is 1.62. Disinfection log-inactivation performance objectives were achieved because the IR was >1.0.
- Disinfection objectives in this example were achieved within 9 min of ozone contact time when using results from six ozone residual readings. Methods to reduce the number of residual readings are discussed below.

Collecting six residual readings to report ozone log-inactivation performance might become an operational burden, even if on-line analyzers, which must be calibrated routinely (e.g., weekly or bi-weekly), are used. The previous example for 1°C illustrates a case in which six ozone residual readings were used, whereas three readings were necessary at 17°C. The direct filtration plant example for operation at 1°C could also use three readings, as shown in Figure 2-7 and Tables 2-7 and 2-8.

The ozone residual readings in Table 2-7 are shown in Figure 2-7, but residual values are indicated for chambers 2, 4, and 6 only. Residual values from these locations are used to calculate CT value and log-inactivation credit in two different

Table 2-6 *Giardia* and Virus Disinfection Data and Calculation: Results for a Direct-Filtration Treatment Plant at Water Temperature of 1°C

T_{10}/T Ratio is	0.60	Typical range is 0.5 to 0.7.				
Water Temperature	1.0	C				
	Gas Added Y or N	Measured C mg/L	HDT min	C for CT mg/L	T for CT min	CT mg/L × min
Chamber 1	Y	0.63				
Chamber 2	N	0.41	1.41	0.41	0.85	0.350
Chamber 3	N	0.30	1.41	0.30	0.85	0.251
Chamber 4		0.21	1.41	0.21	0.85	0.181
Chamber 5		0.15	1.41	0.15	0.85	0.130
Chamber 6		0.11	1.41	0.11	0.85	0.093
Chamber 7			1.41		0.85	
Chamber 8			1.41		0.85	
Chamber 9			1.41		0.85	
Chamber 10			1.41		0.85	
			SUBTOTAL FOR MEASURED CT			1.005
				Virus Inactivation Credits		
	Inact. Rate k_V	From CT Log I	Direct Log I	Total Log I	Required Log I	Virus IR —
	2.33	2.34	1.00	3.34	3.0	1.11
				Giardia Inactivation Credits		
	Inact. Rate k_g	From CT Log I	Direct Log I	Total Log I	Required Log I	*Giardia* IR —
	1.11	1.12	0.50	1.62	1.0	1.62

ways, as shown in Tables 2-7 and 2-8. In Table 2-7 the $C_{effluent}$ method, which means that the value for C in the CT-calculated result is the outlet residual from the subject reactive-flow segment, is used. An alternative integrated average or "$C_{average}$" method is displayed in Table 2-8. The integrated-average method (Coffey, 2000) is implemented by some water utilities after obtaining authorization from their governing regulatory agency.

In Figure 2-7, chamber 2 is the first residual sampling point. When ozone is added to chamber 1 only, residual from chamber 2 is used to assess direct credit from chamber 1, because residual in chamber 1 will always be higher than in chamber 2. One less residual reading is required when using this approach.

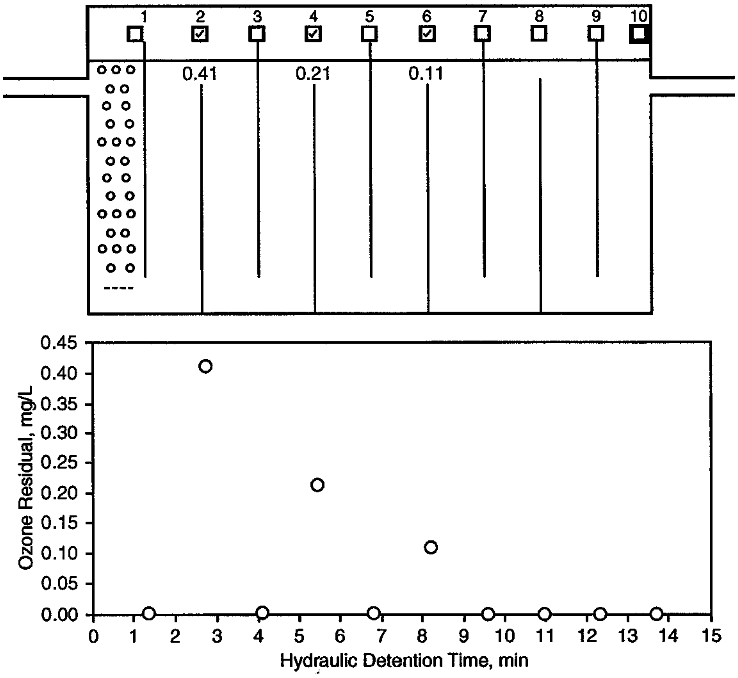


Figure 2-7 Alternative ozone residual profile for 3-log virus and 1-log *Giardia* log-inactivation credit at a water temperature of 1°C (see also Figure 2-6)

The log-inactivation ratio is the most important comparative result for the six-residual and three-residual options presented in Tables 2-6 and 2-7, respectively. The *Giardia* IR values are 1.62 and 1.50, respectively. The virus IR values are 1.11 and 1.03, respectively. Again, disinfection performance objectives were met because the IR value is >1.0. More important, the three-analyzer option, which is favorable for operation and maintenance (O&M), reduces log-inactivation credit only slightly. However, the direct credit cannot be determined when ozone is added to chamber 2 as well as to chamber 1. In this case, water utilities that have implemented the three-residual approach simply ignore direct credit in order to continue operation with three analyzers.

The integrated-average approach shown in Table 2-8 reflects a more accurate, albeit less conservative, value for CT, because the value for C considers that the actual ozone residual within the two chambers has gradually decreased while following a mathematical first-order decay profile. The value for $C_{average}$ is obtained from Eq. 2-9. More information about first-order decay is presented in the next section, in which calculating *Cryptosporidium* log-inactivation credit is discussed.

Table 2-7 Disinfection Results (see also Table 2-6) Using Three Residual Analyzers and C_{Effluent} in the CT Value Calculation

T_{10}/T Ratio is	0.60	Typical range is 0.5 to 0.7.				
Water Temperature	1.0	C				
	Gas Added	Measured C	HDT	C for CT	T for CT	CT
	Y or N	mg/L	min	mg/L	min	mg/L × min
Chamber 1	Y					
Chamber 2	N	0.41	1.41	0.41	0.85	0.350
Chamber 3	N		1.41			
Chamber 4		0.21	1.41	0.21	1.70	0.362
Chamber 5			1.41			
Chamber 6		0.11	1.41	0.11	1.70	0.187
Chamber 7			1.41			
Chamber 8			1.41			
Chamber 9			1.41			
Chamber 10			1.41			
			SUBTOTAL FOR MEASURED CT			0.899
			Virus Inactivation Credits			
	Inact. Rate	From CT	Direct	Total	Required	Virus IR
	k_v	Log I	Log I	Log I	Log I	—
	2.33	2.10	1.00	3.10	3.0	1.03
			Giardia Inactivation Credits			
	Inact. Rate	From CT	Direct	Total	Required	*Giardia* IR
	k_g	Log I	Log I	Log I	Log I	—
	1.11	1.00	0.50	1.50	1.0	1.50

$$C_{\text{average}} = \frac{(C_{\text{out}} - C_{\text{in}})}{\text{Ln}\left[\frac{C_{\text{out}}}{C_{\text{in}}}\right]} \qquad \text{(Eq. 2-9)}$$

Where:

C_{out} = measured residual exiting the reactive zone in question, mg/L
C_{in} = measured residual entering the reactive zone in question, mg/L

The value for C from Table 2-8 is 0.30 mg/L (C_{average}) for the CT calculation between chambers 2 and 4, whereas the value for C from Table 2-7 is 0.21 mg/L (C_{effluent}). The result is that the subtotal CT value and log-inactivation ratios are

Table 2-8 Disinfection Results (see Tables 2-6 and 2-7) Using Three Residual Analyzers and $C_{average}$ in the CT Value Calculation

T_{10}/T Ratio is	0.60	Typical range is 0.5 to 0.7.				
Water Temperature	1.0	C				
	Gas Added	Measured C	HDT	C for CT	T for CT	CT
	Y or N	mg/L	min	mg/L	min	mg/L × min
Chamber 1	Y					
Chamber 2	N	0.41	1.41	0.41	0.85	0.350
Chamber 3	N		1.41			
Chamber 4		0.21	1.41	0.30	1.70	0.512
Chamber 5			1.41			
Chamber 6		0.11	1.41	0.16	1.70	0.265
Chamber 7			1.41			
Chamber 8			1.41			
Chamber 9			1.41			
Chamber 10			1.41			
			SUBTOTAL FOR MEASURED CT			1.127
			Virus Inactivation Credits			
	Inact. Rate	From CT	Direct	Total	Required	Virus IR
	k_v	Log I	Log I	Log I	Log I	—
	2.33	2.63	1.00	3.63	3.0	1.21
			Giardia Inactivation Credits			
	Inact. Rate	From CT	Direct	Total	Required	*Giardia* IR
	k_g	Log I	Log I	Log I	Log I	—
	1.11	1.26	0.50	1.76	1.0	1.76

higher in Table 2-8. The *Giardia* IR increases from 1.50 to 1.76 from Table 2-7 and 2-8, respectively. The virus IR increases from 1.03 to 1.21 from Table 2-7 and 2-8, respectively. The integrated-average approach provides a more accurate estimate of actual virus and *Giardia* log inactivation.

Ozone CT Value and *Cryptosporidium* Log-Inactivation Credit

Cryptosporidium removal and inactivation became treatment considerations at drinking water plants in the early 1990s. Based on research studies, the USEPA allows 2-log credit for *Cryptosporidium* oocyst removal in water treatment plants with filtration, provided the filter effluent quality meets turbidity regulations

(USEPA, 2003). Therefore, filtration alone might be sufficient and remove the need for *Cryptosporidium* disinfection by inactivation. However, if source water quality is poor and the source water contains elevated levels of *Cryptosporidium* oocysts, disinfection by inactivation is required (USEPA, 2003). Research (Rennecker, 2000) indicates that chlorine does not effectively inactivate *Cryptosporidium.* Ozone is effective, but overall CT values, ozone residuals, and contactor detention times are much higher than for *Giardia* and virus inactivation.

Several water utilities installed ozone in the mid to late 1990s to provide disinfection inactivation that is well above regulatory requirements, such as 1-log or 2-log *Cryptosporidium* log-inactivation credit. Design CT values at these utilities were based on CT values that were 5 to 10 times greater than those for *Giardia* (Biswas, 2002). In 2003, the USEPA developed draft *Cryptosporidium* CT values, which are shown in Table 2-2. These values include a factor of safety that is applied to research-reported CT values and show CT values that are 10 to 30 times greater than those for *Giardia* log inactivation (USEPA, 2003).

The higher CT value for *Cryptosporidium* log inactivation has made it necessary to change contactor design and to slightly modify the CT calculation methods used to determine *Cryptosporidium* log inactivation. The modified ozone contactor typically has a longer detention time (e.g., 15 to 40 min or more) and additional baffles (8 to 12 chambers), which maximizes CT value at a given operating ozone dose. The contactor reaction zones are compartmentalized, e.g., over-under or serpentine (i.e., back-and-forth) compartments, or noncompartmentalized with high length–width ratios, e.g., pipeline or long-channel contactors.

In addition to the methods discussed for *Giardia* and viruses, two other methods can be used to calculate *Cryptosporidium* log inactivation. The methods are:

- Extended CSTR and
- Extended integrated-CT_{10}.

These methods provide an accurate estimate of *Cryptosporidium* log inactivation while minimizing the required ozone dose. A lower operating ozone dose will reduce disinfection by-product formation, such as bromate, and lower operating cost. At the same time, *Cryptosporidium* log-inactivation credit is calculated efficiently and accurately. The type of contactor influences the method selected for calculating *Cryptosporidium* log-inactivation credit. Either extended method can be used with the compartmentalized contactor. The noncompartmentalized contactor must make use of the extended integrated-CT_{10} method.

The extended CSTR method was introduced in the USEPA *LT2ESWTR Toolbox Guidance Manual,* Appendix B (USEPA, 2003). This method has the following important characteristics:

- Only three residual readings are required.
- Log-inactivation credit is calculated using the entire reaction zone detention time, which might extend beyond the location of the third residual reading.
- Calculations take into consideration the fact that the ozone residual follows a mathematical first-order decay profile.

An extended CSTR calculation example for *Cryptosporidium* log-inactivation credit is developed in Figure 2-8 and Table 2-9. The methodology conservatively assumes that every chamber is completely mixed. Equation 2-10 determines the log-inactivation value for each chamber. Calculations based on three residual readings determine the characteristic residual in all chambers. The total contactor log-inactivation credit is the sum of individual chamber credits.

$$\text{Log Inactivation} = \text{Log}[1 + 2.303 \times k_c \times C_{char} \times HDT] \qquad \text{(Eq. 2-10)}$$

Where:

C_{char} = characteristic ozone residual across the CSTR, mg/L
HDT = chamber (CSTR) hydraulic detention time, min
k_c = inactivation rate constant for *Cryptosporidium*, Log/CT

The contactor shown in Figure 2-8 has 12 chambers. Ozone is added to chamber 1 only, which makes the remaining 11 chambers an ozone reaction zone. Residual readings are collected at the outlet of chambers 2, 5, and 7. The following five calculation steps determine residual value for each chamber, *Cryptosporidium* log inactivation for each chamber, and total *Cryptosporidium* log inactivation for the entire contactor:

1. Calculate the ozone decay coefficient, k*.
2. Calculate the residual at the entrance of the reaction zone, C_0.
3. Calculate the characteristic residual for every reaction chamber, C_{char}.
4. Calculate the log inactivation for every chamber, Log (N_0/N).
5. Calculate the total log inactivation for the entire reaction zone as the sum of log inactivation for every chamber, Log (N_0/N).

It might seem logical to use a measured value at the entrance to the reaction zone as the initial ozone residual, but this practice is not recommended. The measured residual entering the reaction zone is usually higher than the residual predicted by the first-order decay profile (Amy et al., 1997; Carlson et al., 1997; Hoigné and Bader, 1994; Rakness and Hunter, 2000; Roustan et al., 1998). This phenomenon is commonly attributed to the more rapid ozone decay rate that occurs immediately after ozone addition (e.g., within 1 min of reaction time), which is followed by a somewhat slower first-order decay profile. Theoretically, the second and third sample points can be in subsequent chambers (e.g., chamber 3

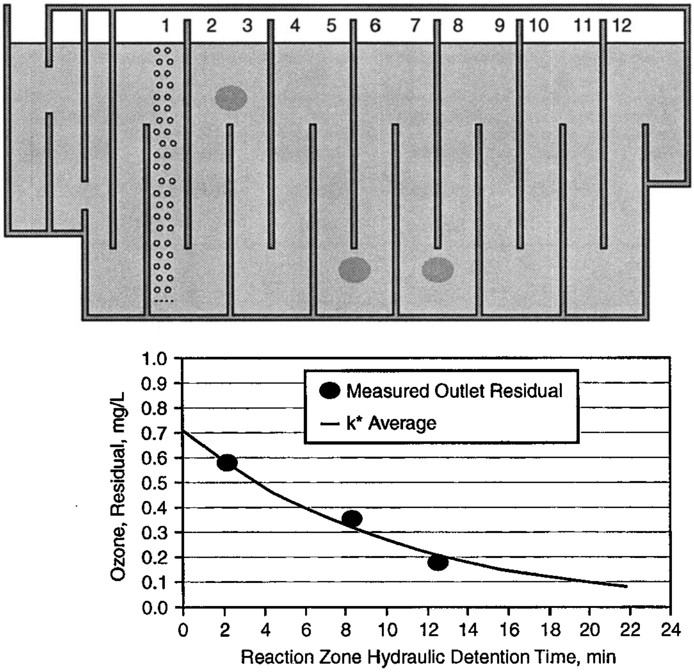


Figure 2-8 Example ozone residual profile for 1.0-log *Cryptosporidium* log-inactivation credit at a water temperature of 18°C

and 4 in the example), but more consistent and more accurate results are obtained when the sample points are further along the ozone residual profile (e.g., chambers 5 and 7 in the example).

The average ozone decay rate, k*, is determined from the decay rate equation (Eq. 2-11) using residual from samples 1 and 2 and decay rate equation (Eq. 2-12) using residual from samples 1 and 3. Theoretically, the decay rates should be equal, but slight sampling error or non-steady-state operation at the time of sampling (e.g., water flow increased) can cause the two decay rates to be dissimilar. In the example calculations shown in Table 2-9, k^*_{1-2} is 0.0893 min^{-1} and k^*_{1-3} is 0.1275 min^{-1}. The $k^*_{average}$ value is 0.1084 min^{-1}. The percent variance is 18% between the individual k* values and $k^*_{average}$. Restrictions on k* variance (i.e., sample variance) are discussed later.

$$k^*_{1-2} = \frac{N_{1-2}}{HDT_{1-2}}\left[\left(\frac{C_1}{C_2}\right)^{\left(\frac{1}{N_{1-2}}\right)} - 1\right] \qquad \text{(Eq. 2-11)}$$

Table 2-9 Extended CSTR *Cryptosporidium* Log-Inactivation Data and Calculation Results Using k^*_{avg}

	A	B	C	D	E	F	G
1	Chamber		Measured	HDT		Calculated	CSTR
2	Volume	Meter	Outlet	Chamber	Chamber	Residual	*Crypto*
3	Gallons	Number	Residual	Outlet	Number	Profile	Credit
4	#	#	mg/L	min	#	mg/L	Log
5	96,576				1	0.71	
6	96,486	1	0.58	2.2	2	0.57	0.20
7	96,576			4.4	3	0.46	0.17
8	96,486			6.5	4	0.37	0.14
9	96,576	2	0.34	8.7	5	0.30	0.12
10	96,486			10.9	6	0.24	0.10
11	96,576	3	0.17	13.1	7	0.20	0.08
12	96,486			15.3	8	0.16	0.07
13	96,576			17.5	9	0.13	0.05
14	96,486			19.6	10	0.10	0.04
15	96,576			21.8	11	0.08	0.04
16	96,486			24.0	12	0.07	0.03
17	**Total Contactor *Crypto* Credit is Subtotal of Individual Chambers**						**1.04**
18	N_{1-2}	3	N_{1-3}	5	HDT_{0-1}	HDT_{0-2}	HDT_{0-3}
19	HDT_{1-2}	6.5	HDT_{1-3}	10.9	2.2	8.7	13.1
20	C_1	0.58	C_1	0.58	N_{0-1}	N_{0-2}	N_{0-3}
21	C_2	0.34	C_3	0.17	1	4	6
22	k^*_{1-2}	0.0893	k^*_{1-3}	0.1275	$C_{0,1}$	$C_{0,2}$	$C_{0,3}$
23	$k^*_{average}$ =	**0.1084**	min^{-1}		0.72	0.79	0.61
24		**k* Variance**	18%		$C_{o,\ average}$ =	**0.71**	mg/L
25	Water Temperature, °C =		18		k_c =	0.2057	Log/CT

$$k^*_{1-3} = \frac{N_{1-3}}{HDT_{1-3}}\left[\left(\frac{C_1}{C_3}\right)^{\left(\frac{1}{N_{1-3}}\right)} - 1\right] \quad \text{(Eq. 2-12)}$$

Where:

k^* = first-order ozone decay coefficient between sampling locations 1 and 2 or locations 1 and 3, min^{-1}

C_1 = measured ozone residual at location 1, which is chamber 2 in the example, mg/L

C_2 = measured ozone residual at location 2, which is chamber 5 in the example, mg/L

C_3 = measured ozone residual at location 3, which is chamber 7 in the example, mg/L

HDT_{1-2} = hydraulic detention time between sample locations 1 and 2, which are chambers 2 and 5 in the example, min

HDT_{1-3} = hydraulic detention time between sample locations 1 and 3, which are chambers 2 and 7 in the example, min

N_{1-2} = number of CSTRs (chambers) between sample locations 1 and 2, which are between chambers 2 and 5 in the example

N_{1-3} = number of CSTRs (chambers) between sample locations 1 and 3, which are between chambers 2 and 7 in the example

The value for the residual entering the reaction zone, C_0, is calculated as the average of three estimated values obtained from Eq. 2-13, 2-14, and 2-15. The three estimates are determined using $k^*_{average}$ and residuals from sample locations 1, 2, and 3 (C_1, C_2, and C_3). In the example calculations shown in Table 2-9, the residual values for $C_{0,1}$, $C_{0,2}$, and $C_{0,3}$ are 0.72, 0.79, and 0.61 mg/L.

$$C_{0,1} = C_1 \times \left[1 + k^*_{avg} \times \frac{HDT_{0-1}}{N_{0-1}}\right]^{N_{0-1}} \qquad \text{(Eq. 2-13)}$$

$$C_{0,2} = C_2 \times \left[1 + k^*_{avg} \times \frac{HDT_{0-2}}{N_{0-2}}\right]^{N_{0-2}} \qquad \text{(Eq. 2-14)}$$

$$C_{0,3} = C_3 \times \left[1 + k^*_{avg} \times \frac{HDT_{0-3}}{N_{0-3}}\right]^{N_{0-3}} \qquad \text{(Eq. 2-15)}$$

Where:

k^*_{avg} = average first-order ozone decay coefficient, min^{-1}

$C_{0,1}$ = calculated reaction-zone initial residual $C_{0,1}$ using measured residual (C_1) at sample location 1 (chamber 2 in the example); hydraulic detention time (HDT) between the inlet to the reaction zone and sample location 1 (chambers 1 and 2 in this example); and number of CSTRs (chambers) between the inlet to the reaction zone and sample location 1 (chambers 1 and 2 in this example)

$C_{0,2}$ = calculated reaction-zone initial residual $C_{0,2}$ using measured residual (C_2) at sample location 2 (chamber 5 in the example); hydraulic detention time (HDT) between the inlet to the reaction zone and sample location 2 (chambers 1 and 5 in this example); and number of CSTRs (chambers) between the inlet to the reaction zone and sample location 2 (chambers 1 and 5 in this example)

$C_{0,3}$ = calculated reaction-zone initial residual $C_{0,3}$ using measured residual (C_3) at sample location 3 (chamber 7 in the example); hydraulic detention time (HDT) between the inlet to the reaction zone and sample location 3 (chambers 1 and 7 in this example); and number of CSTRs (chambers) between the inlet to the reaction zone and sample location 3 (chambers 1 and 7 in this example)

The characteristic residual for each chamber is calculated using Eq. 2-16. Calculated values for the example in Table 2-9 are displayed in column F, rows 5 through 15. In column G, the individual chamber log-inactivation value is calculated using Eq. 2-10. In Eq. 2-10, the *Cryptosporidium* inactivation rate constant at 18°C, k_C, is 0.2057 Log/CT, which is determined using Eq. 2-8. The total contactor log inactivation is the sum of individual chamber values and is 1.04 log.

$$C_x = \frac{C_{0,avg}}{\left[1 + k^*_{avg} \times \frac{HDT_{0-x}}{N_{0-x}}\right]^{N_{0-x}}} \qquad \text{(Eq. 2-16)}$$

Where:

C_x = characteristic residual for chamber x, mg/L

k^* = calculated average first-order ozone decay coefficient, min^{-1}

C_0 = calculated average reaction-zone initial residual, mg/L

$HDT_{0\text{-}x}$ = hydraulic detention between the entrance of the reaction zone and the outlet of chamber x, min

$N_{0\text{-}x}$ = number of CSTRs (chambers) between the entrance of the reaction zone and the outlet of chamber x

The extended CSTR calculation approach has some advantages. The method does not use the T_{10}/T ratio and, as such, does not require a tracer test. The method can be easily programmed into an electronic spreadsheet or a treatment plant's computer-control software. Although the method might be conservative in some cases, it gives accurate estimates of log inactivation.

The method, as discussed, also has a disadvantage because of restrictions on k* variance. In the current USEPA draft *LT2ESWTR Toolbox Guidance Manual*, the method can be applied as long as k* variance is <20%. If k* variance is >20%, USEPA suggests that another set of samples be collected (USEPA, 2003). This could become time-consuming or may be impractical. An alternative to resampling is presented on page 41. (NOTE: This alternative was presented to

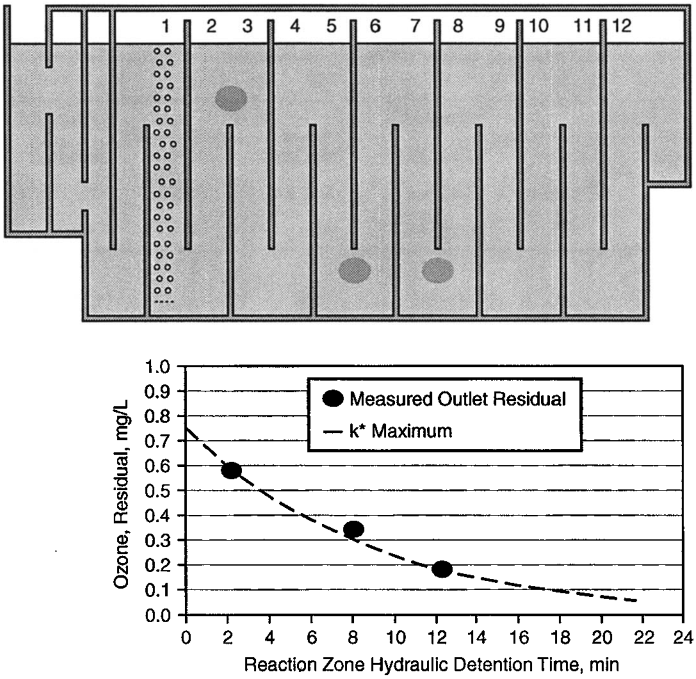


Figure 2-9 Example conservative ozone residual profile using k* maximum instead of k* average (see Table 2-10)

USEPA for their consideration for inclusion in the final *LT2ESWTR Toolbox Guidance Manual*, which was being prepared at the time this book was written.)

The alternative is to implement the calculations such that the most conservative residual profile is always used to estimate residual values in each individual chamber, as shown in Figure 2-9 and developed in Table 2-10. Equations 2-11 and 2-12 are used to determine $k^*_{1\text{-}2}$ and $k^*_{1\text{-}3}$, as previously discussed. However, the most rapid decay rate, k^*_{max}, is selected for subsequent calculations, instead of k^*_{avg}. The initial residual, C_0, is determined with the first sampling point residual $C_{0,1}$. Residual values from individual chambers are calculated with Eq. 2-16, and k^*_{max} and $C_{0,1}$ are used instead of k^*_{avg} and $C_{0,avg}$. Finally, as discussed, the individual chamber log-inactivation value is calculated using Eq. 2-10. The total contactor log inactivation is the sum of individual chamber values and is 0.96 log. The total log-inactivation credit is slightly lower than that shown in Table 2-9, but using k^*_{max} is a practical alternative to avoid re-sampling when k* variance is >20%.

As mentioned, the extended CSTR calculation is applicable for compartmentalized contactors but not for noncompartmentalized contactors. Alternatively, the

Table 2-10 Extended CSTR *Cryptosporidium* Log-Inactivation Data and Calculation Results Using k^*_{max}

	A	B	C	D	E	F	G
1	Chamber		Measured	HDT		Calculated	CSTR
2	Volume	Meter	Outlet	Chamber	Chamber	Residual	*Crypto*
3	Gallons	Number	Residual	Outlet	Number	Profile	Credit
4	#	#	mg/L	min	#	mg/L	Log
5	96,576				1	0.74	
6	96,486	1	0.58	2.2	2	0.58	0.20
7	96,576			4.4	3	0.45	0.17
8	96,486			6.5	4	0.36	0.14
9	96,576	2	0.34	8.7	5	0.28	0.11
10	96,486			10.9	6	0.22	0.09
11	96,576	3	0.17	13.1	7	0.17	0.07
12	96,486			15.3	8	0.13	0.06
13	96,576			17.5	9	0.10	0.04
14	96,486			19.6	10	0.08	0.04
15	96,576			21.8	11	0.06	0.03
16	96,486			24.0	12	0.05	0.02
17	Total Contactor *Crypto* Credit is Subtotal of Individual Chambers						0.96
18	N_{1-2}	3	N_{1-3}	5	HDT_{0-1}		
19	HDT_{1-2}	6.5	HDT_{1-3}	10.9	2.2		
20	C_1	0.58	C_1	0.58	N_{0-1}		
21	C_2	0.34	C_3	0.17	1		
22	k^*_{1-2}	0.0893	k^*_{1-3}	0.1275	$C_{0,1}$		
23	$k^*_{maximum}$ =	0.1275	min^{-1}	0.74			
24					C_o =	0.74	mg/L
25	Water Temperature, °C =		18		k_c =	0.2057	Log/CT

extended integrated CT_{10} method is applicable for both compartmentalized and noncompartmentalized ozone contactors. The following discussion uses an example of a compartmentalized contactor to illustrate similarities and differences between the extended integrated CT_{10} method and extended CSTR method.

The extended integrated CT_{10} calculations identify k^*_{max} and C_0, but the equations are plug-flow-based and not CSTR-based, as discussed previously. Ultimately, the CT_{10} value is determined using the T_{10}/T ratio. The most conservative residual profile is always used with this approach to estimate CT_{10} value, as shown in Figure 2-10 and developed in Table 2-11.

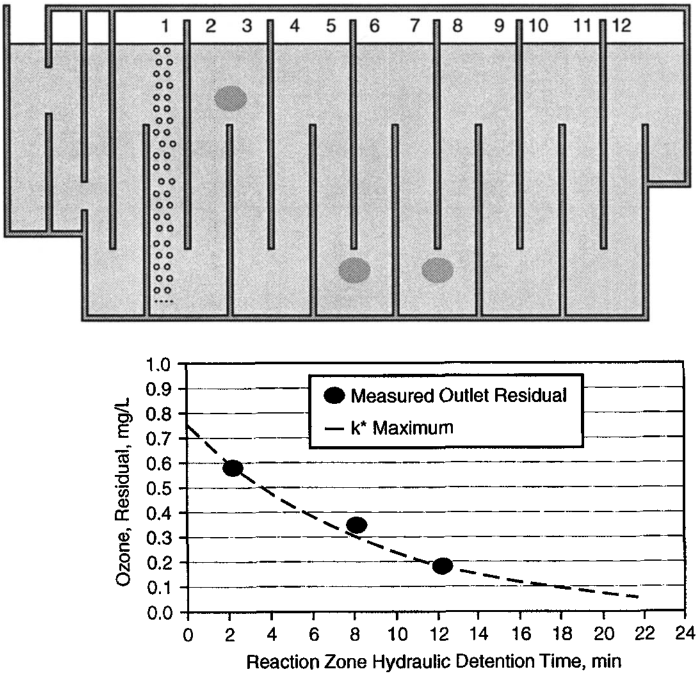


Figure 2-10 Example ozone residual profile for extended integrated CT_{10} method (see Table 2-11)

Equations 2-17 and 2-18 are used to determine k^*_{1-2} and k^*_{1-3}, which are 0.0816 and 0.1125 min^{-1}, respectively, in Table 2-11. The most rapid decay rate, k^*_{max} at 0.1125 min^{-1}, is selected for subsequent calculations. Equation 2-19 is used to determine the initial residual, $C_{0,1}$, which is 0.74 mg/L in Table 2-11. If desired, individual chamber residual values can be calculated with Eq. 2-20 using k^*_{max} and $C_{0,1}$. The extended integrated CT_{10} value is calculated using Eq. 2-21, which gives 4.30 mg-min/L. In this example the T_{10}/T ratio was 0.70. The total contactor log-inactivation credit is 0.89 log, which was determined using Eq. 2-4. The 18°C water temperature inactivation rate constant, k_c, is 0.2057 Log/CT.

$$k^*_{1-2} = \frac{\mathrm{Ln}\left(\frac{C_1}{C_2}\right)}{HDT_{1-2}} \qquad \text{(Eq. 2-17)}$$

$$k^*_{1-3} = \frac{\mathrm{Ln}\left(\frac{C_1}{C_3}\right)}{HDT_{1-3}} \qquad \text{(Eq. 2-18)}$$

$$C_{0,1} = C_1 \times e^{HDT_{0-1} \times k^*_{max}} \qquad \text{(Eq. 2-19)}$$

Table 2-11 Extended Integrated CT_{10} *Cryptosporidium* Log-Inactivation Data and Calculation Results Using k^*_{max}

Chamber		Measured	HDT		Calculated Residual	
Volume Gallons #	Meter Number #	Outlet Residual mg/L	Chamber Outlet min	Chamber Number #	Profile mg/L	CT Value mg-min/L
96,576				1	0.74	
96,486	1	**0.58**	2.2	2	0.58	
96,576			4.4	3	0.45	
96,486			6.5	4	0.36	
96,576	2	**0.34**	8.7	5	0.28	
96,486			10.9	6	0.22	
96,576	3	**0.17**	13.1	7	0.17	
96,486			15.3	8	0.13	
96,576			17.5	9	0.10	
96,486			19.6	10	0.08	
96,576			21.8	11	0.06	
96,486			24.0	12	0.05	
				Total Contactor CT Value =		4.30
				HDT_{0-1}		
HDT_{1-2}	6.5	HDT_{1-3}	10.9	2.2		
C_1	0.58	C_1	0.58			
C_2	0.34	C_3	0.17			
k^*_{1-2}	0.0816	k^*_{1-3}	0.1125	$C_{0,1}$		
$k^*_{maximum}$ =	**0.1125**	min^{-1}		0.74		
				C_o =	**0.74**	mg/L
Water Temperature, °C =		18		k_c =	0.2057	Log/CT
	T_{10}/T Ratio =	0.70	Total Log Inactivation =		0.89	Log

$$C_x = \frac{C_0}{e^{HDT_{0-x} \times k^*_{max}}} \tag{Eq. 2-20}$$

$$CT_{10} = \left(\frac{T_{10}}{T}\right) \times \left(\frac{C_0}{k^*_{max}}\right) \times (e^{k^*_{max} \times HDT_{reaction\ zone}} - 1) \tag{Eq. 2-21}$$

The k^*_{max}-developed extended CSTR log-inactivation credit was 0.96 log and the comparable extended integrated CT_{10} credit was 0.89 log. The extended integrated CT_{10} credit would be greater if the T_{10}/T ratio were higher than 0.70. The extended CSTR or extended integrated CT_{10} method can be used for compartmentalized reaction zones. The extended integrated CT_{10} method must be used for noncompartmentalized contactors, such as pipelines or long-channel vessels.

Synergistic *Cryptosporidium* Inactivation With Ozone, Chlorine, and Chloramines

Synergistic inactivation is the improvement in the secondary disinfectant's disinfection efficiency by pre-exposing the microorganisms to a primary disinfectant. Synergism between ozone and chlorine and ozone and chloramines has been studied for *Cryptosporidium*. Consistent synergistic improvement was noted for ozone and chloramines (Najm et al., 2004a), based on review of several research studies (Biswas et al., 2002; Driedger et al., 2001; Rennecker et al., 2000). Improvement was inconsistent when chlorine followed ozone (Biswas et al., 2002).

The proposed mechanism for synergism begins with damage to the *Cryptosporidium* shell by upstream ozonation. The damaged shell becomes vulnerable to downstream chloramine residual disinfection action, which might involve residual penetration into the shell and disinfection of the oocysts contained inside. Chloramine residual alone is ineffective in the presence of an undamaged oocyst shell. Chloramine residual is effective in the presence of *Cryptosporidium* oocysts that have been previously subjected to ozone oxidation action. The result of this proposed mechanism is that the required CT value for *Cryptosporidium* inactivation credit from chloramines depends on the degree of ozone exposure preceding chloramine treatment, plus water temperature (Najm et al., 2004a).

The effect on chloramine CT value as the result of ozone exposure is summarized below. For each water temperature condition, the chloramine CT value decreased as ozone exposure increased. The chloramine CT values shown below achieve 0.25-log *Cryptosporidium* inactivation (Najm et al., 2004a). Chloramine CT values are proportional to log inactivation; therefore, CT values would double for 0.5-log inactivation, quadruple for 1-log inactivation, etc. The chloramine CT values for 0.25-log (and also, perhaps, 0.5-log) *Cryptosporidium* inactivation are well within the range of values that might be achieved in the clearwell of existing water treatment plants. As such, *Cryptosporidium* inactivation credit from chloramine CT might become a viable treatment option.

Water Temperature = 1°C		Water Temperature = 10°C		Water Temperature = 25°C	
Ozone Exposure CT Value mg-min/L	Chloramine Exposure CT Value mg-min/L	Ozone Exposure CT Value mg-min/L	Chloramine Exposure CT Value mg-min/L	Ozone Exposure CT Value mg-min/L	Chloramine Exposure CT Value mg-min/L
5.6	836	2.5	468	1	246
11	475	5	266	2	140
23	270	10	151	4.1	80

OZONE OXIDATION TREATMENT

Ozone oxidation is used for a variety of water treatment purposes. Ozone systems that are designed to meet disinfection requirements provide considerable simultaneous oxidation reaction benefits. Ozone is usually installed at the beginning of the treatment plant (pre-ozonation), after sedimentation and before filtration (intermediate ozonation), or at both locations. Ozone is also used in water treatment plants that do not have filtration processes, primarily for disinfection but also for oxidation as a secondary benefit. Achieving disinfection with ozone (or other disinfectant) requires that the oxidizing demand for ozone (or other disinfectant) be satisfied first. This is necessary to develop an ozone (or other disinfectant) residual concentration that can be used to calculate the CT value. The CT value is then used to confirm that the required amount of disinfection has been achieved. Thus, all rapidly reacting organic and inorganic constituents will be oxidized *before* disinfection can be confirmed.

More information about ozone application points is presented in chapter 3. Ozone disinfection facilities usually achieve other oxidation benefits such as:

- Improved particulate removal from filtration, as evidenced by lower turbidity and lower particle count of the filtered water.
- Reduced coagulant dosage (e.g., alum or ferric). This applies for pre-ozone applications.
- Improved aesthetic quality through elimination of undesirable tastes, odors, and color.
- Oxidized synthetic compounds including pesticides and solvents.

Ozone can be installed for oxidation-only treatment applications for one or more of the following reasons. Additional information about each application is discussed below.

- Oxidation of unwanted inorganic compounds, such as iron, manganese, nitrite, cyanide, and hydrogen sulfide. In these applications the ozone reactions are very rapid and contact time is short (seconds or a few minutes).
- Oxidation of undesirable organic compounds that cause color. Ozone reaction time is moderately fast, with contact times of several minutes, but this varies depending on the types of color-causing organics present.
- Advanced oxidation of complex organic molecules that produce undesirable tastes and odors (MIB and geosmin by-products of algae growth in lakes and reservoirs) or synthetic organic compounds such as solvents and pesticides. Ozone reaction times are moderately fast, with contact times of several minutes. Advanced oxidation with ozone is discussed in a separate section in this chapter.

Organic molecules react with ozone and are often converted into structurally simpler organic molecules that can be more readily biodegradable. For this reason, ozone treatment generally is followed by biofiltration. Types of filter media include conventional sand, anthracite, granular activated carbon (GAC), or combinations of these. Conventional media allows biological oxidation that is considered adequate in many water treatment plants. The GAC media provides excellent biological oxidation and is installed in several US, European, Canadian, and Japanese water treatment plants. GAC media that is used for robust biological oxidation purposes does not require regeneration or replacement for extended periods (years).

GAC media also supplies organic-molecule adsorption capability that is sometimes used to remove nonbiologically degradable organics until the media adsorption sites are saturated. At these facilities the GAC media is removed periodically and is either regenerated or replaced.

Iron and Manganese

Iron and manganese are oxidized easily by ozone. Soluble ferrous iron Fe(II) is oxidized to ferric iron (FeIII), which slowly hydrolyzes to form particulate $Fe(OH)_3$. The reaction consumes 0.43 mg of ozone per mg of Fe(II) (Langlais et al., 1991). Manganese oxidation by ozone and subsequent manganese removal is quite complex. Ozone oxidizes soluble manganese [Mn(II)] to form particulate (removable) manganese dioxide [MnO_2 – Mn(IV)]. The reaction consumes 0.88 mg of ozone per mg of Mn(II) (Langlais et al., 1991). However, over-ozonation (over-oxidation by ozone) will form soluble (nonremovable) permanganate [MnO_4^- – Mn(VII)]. In the presence of readily oxidizable organics, most, if not all, ozone-produced permanganate can return to the insoluble manganese dioxide, given sufficient time, e.g., 20 to 30 min (Miller et al., 1978). Ozone treatment for manganese removal must be implemented carefully to ensure that manganese is captured in the treatment process and that soluble manganese (permanganate) is not formed and subsequently discharged from the filters. Reducing permanganate to MnO_2 must occur within the filters.

Following are highlights of this application:

- Soluble iron (Fe(II)) and manganese (Mn(II)) in drinking water are not related to specific health problems but are associated with aesthetic water quality issues, such as discoloration of water, bathroom fixtures, and clothing in clothes washers. Removal of innocuous levels is a recognized objective by regulatory authorities.
- Oxidation by aeration (oxygen is the oxidant) is effective for simple conversion of soluble iron (Fe(II)) to iron (Fe(III)), which hydrolyzes in water to produce $Fe(OH)_3$ and can be removed by settling and filtration.

Complexed iron compounds are difficult to oxidize by aeration alone but can be oxidized by ozone. Also, it is difficult to oxidize Fe(II) with oxygen at lower pH values (e.g., <7.0).

- Oxidation by aeration (oxygen oxidation) is insufficient for simple soluble and complexed manganese (Mn(II)) oxidation.
- Ozone will rapidly oxidize soluble iron and manganese and will destroy many organic complexes of these cations, thus liberating free iron and manganese. Ozone can also oxidize Fe(II) and Mn(II) complexes.
  - Oxidation of soluble iron (Fe(II)) is rapid and precedes oxidation of soluble manganese (Mn(II)) when both are present in the water supply.
  - Oxidation of soluble manganese (Mn(II)) initially forms particulate (settleable or filterable) manganese (MnO_2) (Mn(IV)).
  - Continued ozone oxidation (over-oxidation) forms soluble permanganate (MnO_4^-) (MnVII), which imparts pink coloration to the water. The potential for permanganate formation is a major consideration in the removal of manganese by ozone alone, because permanganate in the distribution system can slowly oxidize other organics present, thereby converting the permanganate to insoluble manganese dioxide. The problem is that insoluble manganese dioxide can precipitate in the distribution system and discolor the water. The treatment plant staff for the city of Arlington, Texas, has observed excellent manganese (permanganate) removal in well-operating biological filters that are backwashed with nonchloraminated water instead of water containing chloramine residual (telephone conversation with Chuck Vokes, Interim Assistant Director of Utilities, Arlington, Texas, April 2004).
  - The presence of organic matter inhibits the oxidation of iron and manganese by ozone, requiring higher ozone doses and/or longer contact times for effective treatment.
- Plants that have been, prior to ozone, treating water containing manganese and adding chlorine prior to filtration might have been removing soluble manganese (Mn(II) and permanganate) with the "greensand" effect, whereby the sand grains (or other filter media) become coated with manganese dioxide.
  - At such treatment plants, manganese removal by ozone and other means (e.g., permanganate addition) should be evaluated carefully, especially if the chlorine application point is moved to after the filters.
  - If the chlorine application point is moved to postfiltration, the greensand effect is stopped and manganese will likely slough off the sand (or

other filter media). This could cause significant manganese discharge from the filters and numerous customer complaints. The manganese coating on the filter media should be considered a potential problem and be removed by filter-to-waste, backwashing, or other means (see also chapter 5).

Hydrogen Sulfide

Hydrogen sulfide is oxidized easily by ozone to form (ultimately) sulfate. Oxidation proceeds in stages, first forming insoluble elemental sulfur, which is evidenced by a light-colored colloidal suspension. Further oxidation dissolves the elemental sulfur, forming soluble sulfite, and continued oxidation produces sulfate. More ozone is required to completely oxidize sulfide to sulfate than is required to produce the insoluble, colloidal elemental sulfur.

The Orlando Utilities Commission (OUC) installed ozone for hydrogen sulfide (H_2S) removal at eight water treatment plants that are supplied by sulfide-containing wells (Johnson et al., 1997). The H_2S concentration range is 0.9 to 3.5 mg/L, depending on the well source. The design hydraulic detention time of the ozone contactor is 10 min. The temperature of the deep well water is nearly constant at 78°F. The pH is about 7.5 units, hardness about 130 mg/L, and alkalinity about 110 mg/L. The typical H_2S concentration is about 2 mg/L and ozone dose is about 8 mg/L. The following operational strategies and experiences (telephone conversation with David Friess, Water Operations Department, Orlando Utilities Commission, Orlando, Florida, July 2002) are noted:

1. Ozone is added to the first chamber only of the bubble-diffuser contactor to minimize the presence of H_2S in the contactor off-gas. H_2S in the off-gas will "poison" the catalyst that is used to destroy excess ozone in the contactor off-gases (see additional information about ozone off-gas destruct in chapter 4). By adding all the ozone to chamber 1 only, as opposed to splitting the dose between chamber 1 and chamber 2, the life of the catalyst increases from a few weeks to about 2 years.
2. The heat-catalyst off-gas destruct system is operated at a delta temperature of 50°F, which is greater than the design delta temperature of 30°F. The higher delta temperature helps increase the life of the ozone-destruct catalyst.
3. The theoretical O_3 to H_2S ratio is 3:1 mg/L. The operating O_3 to H_2S ratio is 4:1 mg/L.
   a. The selected operating ratio is higher so that a moderate ozone residual (0.2 mg/L to 0.3 mg/L in chamber 2) can be maintained.
   b. The ozone residual in the downstream chamber is used for process control. The ozone dose is adjusted to meet the selected residual

control point. By maintaining ozone residual, full removal of H_2S is ensured during periods of variable H_2S concentration.

4. Liquid oxygen is used as the feed-gas at seven of the eight treatment plants. Air is the feed-gas at the first plant, which was placed on line in 1997. The oxygen-fed plants were put into service in 1998 and 1999.
   a. At the oxygen-fed plants, the last half of the ozone contactor is used for air stripping to reduce the dissolved oxygen (DO) concentrations.
   b. The DO is about 18 to 19 mg/L before stripping and about 10 to 11 mg/L at the contactor effluent. The saturation DO value is about 8 to 9 mg/L.
   c. There have been no water quality complaints (odor or color) and no evidence of corrosion in the distribution system since the ozone systems were installed.
5. The water treatment plants have been on line for about 5 years, and H_2S removal performance is excellent. The OUC is happy with their ozone H_2S oxidation process.

Color

A thorough description of color oxidation considerations is presented in *Ozone in Water Treatment: Application and Engineering* (Langlais et al., 1991). Following are highlights of this application:

- Color in water is removed for at least two reasons:
  - Color is unattractive and is responsible for customer complaints.
  - Color is linked to the presence of fulvic or humic acids, which consume large amounts of chlorine and form halogenated organics.
- Color can be removed sufficiently with coagulation in conventional and direct filtration water treatment plants, but color is removed very effectively by ozone oxidation.
- Ozone is an efficient oxidizer of many color-causing contaminants. The Mesa Consolidated Water District (Costa Mesa, California) uses ozone to remove color from two deep (>600 ft) wells (telephone conversation with Bill Johnson, Water Operations Department, Mesa Consolidated Water District, Costa Mesa, California, August 2002). The following operational strategies and experiences are noted:
  - Water well 4 (2,500 gpm) contains organic constituents that produce significant amounts of color (i.e., 60 to 80 color units [cu]) and trace but detectable amounts of hydrogen sulfide.

    - An air-fed bubble diffuser ozone system was installed in 1984. In 1996 the feed-gas was switched to oxygen and the bubble-diffuser dissolution system was augmented by a venturi injection system.
    - The ozone dosage range is 7 to 10 mg/L, and contactor hydraulic detention time is about 10 min.
    - Treated water consistently meets target color values between 5 and 8 cu, which were established to minimize customer complaints.
    - Treated water is chlorinated and transferred directly into the distribution system.
  - Water well 6 (4,000 gpm) contains organic constituents that produce even higher levels of color (i.e., 135 to 140 cu) and detectable amounts of hydrogen sulfide.
    - An oxygen-fed venturi injection ozone system was installed in 2001, along with biological filters (empty bed contact time of ~10 min) to remove biodegradable organic carbon. The medium is granular activated carbon, which is considered "spent" with respect to adsorption of organics and is now used only as support medium for biological activity, without regeneration.
    - The ozone dosage is ~18 mg/L, and contactor hydraulic detention time is about 10 min.
    - Treated water consistently meets target color values between 5 and 8 cu.
    - Ozonated and biologically treated water is then chlorinated and transferred into the distribution system.

Coagulating Effects and Enhanced Turbidity Removal

Ozonation prior to sedimentation and/or filtration has lowered coagulant dose and improved particle removal at numerous drinking water treatment plants (Langlais et al., 1991; Reckhow et al., 1993). In no known case has there been deterioration in particle removal. Also, particle removal enhancement was independent of media type. Early interest in the significant and beneficial effect of enhanced coagulation by ozonation was generated based on both pilot- and full-scale (600 mgd) results from direct filtration of surface water at the Los Angeles Aqueduct Filtration Plant in California (Reckhow et al., 1993). The following benefits were documented: increased filtration rate by 33%, lowered coagulant dose by 50%, and reduced filtered water turbidity by 50% (Reckhow et al., 1993). Another example is Worcester, Massachusetts, where filter run length was increased by nearly 100% (Reckhow et al., 1993). The author of this book also has observed that lower filtered water turbidity values have resulted from the application of ozone.

Laboratory-scale experiments on the coagulating effects of ozone often fail to show the same beneficial effects that are observed in full-scale water treatment plants (Langlais et al., 1991). This might be due to significant differences in the operation and design of these laboratory-scale systems as compared to full-scale systems. Ozone has been shown to enhance coagulation in several ways (Langlais et al., 1991):

1. *Increased association of aluminum with ozonated organic matter.* Oxygenated functional groups, such as carboxylic, aldehydic, and phenolic functional groups, increased in concentration with oxidized organic molecules following ozonation. It is reasonable to assume that these oxygenated functional groups effectively form complexes with aluminum oxide and clay surfaces and that these groups are, therefore, responsible for surface associations between organic matter and aluminum.
2. *Improvement in calcium complexation with ozonated organic matter.* An increase in the number of carboxylic acid groups also may lead to an increase in the degree of calcium complexation. An increase in calcium complexation may lead to improved adsorption of organics to both alum floc and other precipitating metal oxide surfaces, e.g., $Fe(OH)_3$, hydrated MnO_2.
3. *Loss of organic matter from the surface of clay particles.* One might expect that a decrease in molecular weight or increase in hydrophilicity of organic matter following ozonation would lead to desorption from clay particle surfaces. After alternation of the organic coatings, particle destabilization occurs by minimization of the negative surface charges or by shrinking of the adsorbed organic layers, which cause improved particle–particle contacts.
4. *Polymerization of organic matter.* It is believed that ozonation of natural organic material leads to the formation of metastable organics, such as ozonides, organic peroxides, and organic-free radicals, which continue to react long after the ozone has disappeared. Given enough time, these compounds might encounter other stable or metastable organics and undergo condensation or polymerization reactions. Such reactions may lead to the formation of polymers that can (a) precipitate spontaneously; (b) become more easily enmeshed by aluminum hydroxide; (c) associate more strongly with solid surfaces; (d) act as "bridging" polyelectrolytes; or (e) consume less aluminum coagulant by virtue of their large molecular sizes.

5. *Breakup of metal-humic complexes.* Ozone can break up metal-humic complexes. The subsequent release of oxidized metals, such as Fe(III) or Mn(IV), can be considered an in situ production of metal coagulant.
6. *Reactions with algae.* Ozone readily kills or lyses many types of algae. The subsequent liberation of biopolymers may be equivalent to the release of natural organic coagulants. Alternatively, some naturally released algal biopolymers can actually hinder coagulation, and the use of ozone may minimize this adverse effect.

Iron, organic matter, algae, and calcium concentration are important parameters in influencing ozone's effectiveness on subsequent coagulation (Reckhow et al., 1993). However, efforts to develop a predictive model of benefits have been unsuccessful (Reckhow et al., 1993). The author of this book has observed that potential beneficial effects at most water treatment plants are likely to be unknown prior to ozone startup, because pilot studies were not conducted or pilot studies did not demonstrate significant coagulation effectiveness. However, after startup, the plant staff is likely to notice significant improvement in filtered water turbidity and, in turn, might reduce coagulant dose and decrease backwash frequency to meet process needs. Although there may be little to no change in coagulant dose or backwash frequency, filtered water turbidity and/or particle count might be reduced significantly (e.g., turbidity or particle count might be one half or one quarter of the previous values). In no known case has ozonated, filtered water turbidity or particle count deteriorated.

In summary, ozone prior to the sedimentation basin has been shown to effectively lower coagulant dose and improve settled and filtered water turbidity. A significant reduction in filtered water turbidity (from 0.06 ntu to 0.03 ntu) occurred at the A.H. Weeks Water Treatment Plant, Windsor, Ontario (Figure 2-11)

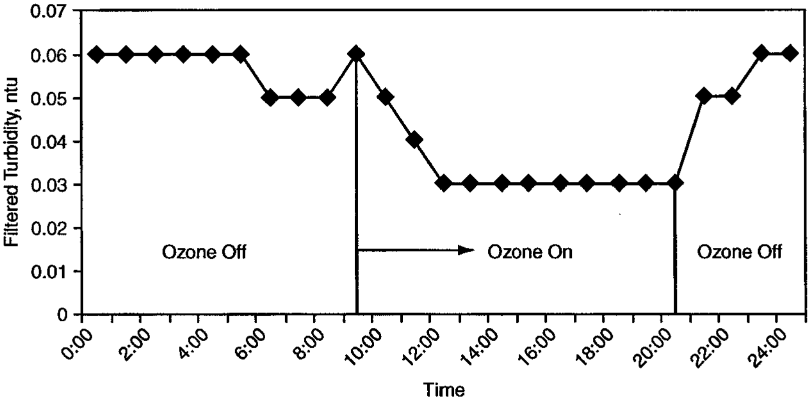


Figure 2-11 Precoagulation ozonation effect on turbidity during startup (Mazloum, 2004)

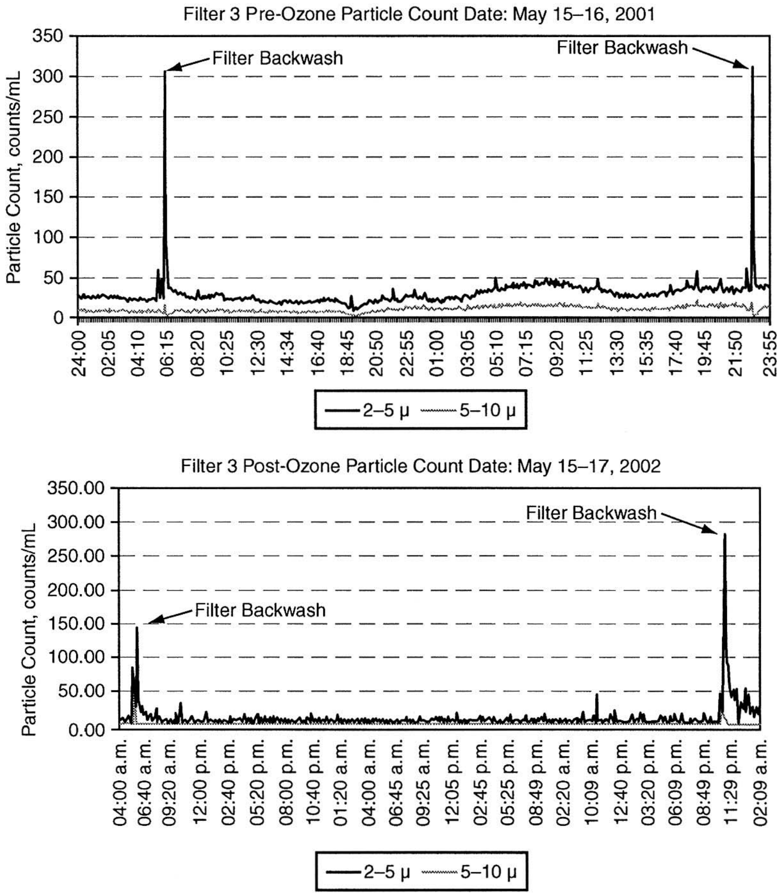


Figure 2-12 Particle count before and after ozone implementation (Mazloum, 2004)

(Mazloum et al., 2004). Particle count decreased (Figure 2-12), especially for size ranges of 2 to 5 µm and 5 to 10 µm, which are the size ranges of some pathogens. *Cryptosporidium parvum* oocysts are spheres of 3 to 5 µm, and *Giardia* cysts are elliptical with a size of 8 to 14 µm long and 7 to 10 µm wide (Mazloum et al., 2004). In addition to improved particle removal and enhanced disinfection protection (i.e., 1-log to 2-log *Cryptosporidium* inactivation credit), taste and odor complaints were eliminated and significant savings in chemical cost occurred, as shown in Table 2-12 (Mazloum et al., 2004). As a side benefit, operators found that overall plant O&M was easier, especially when the use of powdered activated carbon was eliminated (another benefit of ozone).

Not all ozone water treatment plants will achieve the cost savings experienced at Windsor, Ontario. However, most treatment plants will experience enhanced

Table 2-12 Chemical Cost for the Year Before Ozone and After Ozone Implementation at the A.H. Weeks Water Treatment Plant in Windsor, Ontario

Chemical	Prior to Ozone Cost June 2000–May 2001 $	After Ozone Cost June 2001–May 2002 $	Difference in Cost $
Alum	573,445	693,503	+120,058
Polyaluminum chloride	126,806	0	–126,806
Total coagulant cost	700,251	693,503	–6,748
Magnafloc LT-22	30,454	24,150	–6,304
Chlorine	102,153	109,347	+ 7,194
Powdered activated carbon	493,500	0	–493,500
Ozone	0	251,394	+251,394
Total	1,326,358	1,078,394	–247,964
Water flow (ML/year)	59,814	61,188	+1,374
Unit-volume cost ($/ML)	22.17	17.62	–4.55

Source: Mazloum et al., 2004.

particle removal, whether or not ozone is added before the sedimentation basin or after sedimentation and before filtration. When ozone is added before sedimentation, the coagulant dosage might be reduced. It will probably be unnecessary and even fruitless to conduct bench-scale or pilot-scale studies prior to design to determine if coagulation benefits will occur for the subject installation. However, some pre-installation pilot studies have proven beneficial and might be required, especially if changes in filter loading rate (e.g., increased loading rate) are contemplated as part of the plant design.

OZONE-BASED ADVANCED OXIDATION TREATMENT

Ozone in drinking water treatment is used primarily for disinfection and also for color removal, taste and odor control, manganese and iron oxidation, and other reasons. Disinfection occurs via reactions with ozone, and the degree of disinfection is assessed by ozone exposure (i.e., $\int[O_3]dt \sim$ ozone residual × contact time with organisms, or CT value). Ozone is a selective oxidant; some organic and inorganic compounds are oxidized quickly and others are not oxidized at all (Hoigné, 1998; von Gunten, 2003a, 2003b).

Oxidation during ozonation also occurs via hydroxyl radicals ($HO^\bullet$), which are secondary oxidants that are formed by ozone decomposition via a complex mechanism (Hoigné, 1998; von Gunten, 2003a, 2003b). $HO^\bullet$ are not selective and can oxidize organic and inorganic compounds. Ozone-based advanced oxidation processes (i.e., processes in which O_3 is purposefully decomposed into $HO^\bullet$) are important in drinking water treatment because of reactions with organic molecules such as some solvents (perchloroethylene [PCE] and trichloroethylene [TCE]), pesticides (atrazine), and compounds causing off-tastes and odors (MIB and geosmin) that are not readily oxidized by ozone. A discussion of ozone reactions with natural organic matter (NOM) is found in *Ozone in Water Treatment: Application and Engineering* (Langlais et al., 1991).

$HO^\bullet$ are always formed during ozonation. The $HO^\bullet$ concentration cannot be measured directly, but $HO^\bullet$ exposure can be calculated by measuring the depletion of an in situ $HO^\bullet$ probe (p-chlorobenzoic acid, pCBA), which is a compound that is oxidized by $HO^\bullet$ but not by ozone (Elovitz and von Gunten, 1999). The relationship between O_3 exposure ($\int[O_3]dt$) and $HO^\bullet$ exposure ($\int[HO^\bullet]dt$) can be established using the R_{CT} concept (i.e., $R_{CT} = \int[HO^\bullet]dt \div \int[O_3]dt$) (Elovitz and von Gunten, 1999). The R_{CT} value is determined by measuring O_3 exposure and $HO^\bullet$ exposure (i.e., depletion of in situ $HO^\bullet$ probe over time). The R_{CT} value is directly proportional to $HO^\bullet$ exposure, which means that for a given condition, $HO^\bullet$ exposure increases as the R_{CT} value increases.

R_{CT} is a function of operating temperature, pH, alkalinity, and NOM concentration and composition, as outlined here (Elovitz et al., 2000):

- R_{CT} increases with increasing temperature.
- R_{CT} increases with increasing pH.
- R_{CT} increases with decreasing carbonate concentration (alkalinity). Conversely, $HO^\bullet$ exposure decreases with increasing alkalinity due to the high $HO^\bullet$ scavenging rate with carbonate.
- R_{CT} increases with increasing NOM concentration (measured as dissolved organic carbon). This means $HO^\bullet$ exposure is greater at elevated NOM concentrations.

The important point from the previous discussion is that some level of advanced oxidation (i.e., $HO^\bullet$ exposure) occurs naturally during ozonation. The level of $HO^\bullet$ exposure depends on water quality parameters such as temperature, pH, alkalinity, and NOM composition and concentration. A typical R_{CT} value is $\sim 10^{-8}$ in conventional ozone applications at drinking water treatment plants (i.e., without hydrogen peroxide addition). In an advanced oxidation process (i.e., with hydrogen peroxide addition), the R_{CT} value can reach 10^{-6}, where $HO^\bullet$ exposure is 100 times greater than during conventional ozonation.

In many ozone applications, $HO^\bullet$ exposure is sufficient to oxidize background levels of organic micropollutants. Enhanced $HO^\bullet$ exposure, which is necessary to satisfactorily oxidize elevated concentrations of these compounds, is achieved when hydrogen peroxide is added or UV irradiation is applied to ozonated water to increase the R_{CT} (HO$^\bullet$ exposure). The degree of enhancement depends on pH (pK of H_2O_2 is 11.6 and enhancement in HO$^\bullet$ exposure is slowed at low pH [e.g., pH <7]). The combined ozone/hydrogen peroxide system is an advanced oxidation process, often called the PEROXONE process. Several drinking water treatment plants are designed with the flexibility to add hydrogen peroxide to increase HO$^\bullet$-based reactions, if needed (Rice, 1999).

Ozone/Hydrogen Peroxide (PEROXONE) Advanced Oxidation Process

Hydrogen peroxide (H_2O_2) in the presence of ozone (O_3) initiates and propagates decomposition of ozone that in turn generates hydroxyl radicals through a series of complex reactions, outlined below (Langlais et al., 1991):

$$H_2O_2 \leftrightarrow HO_2^- + H^+$$

$$O_3 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet -} + O_2$$

$$O_2^{\bullet -} + H^+ \leftrightarrow HO_2^\bullet$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$$

$$O_3^{\bullet -} + H^+ \leftrightarrow HO_3^\bullet$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2$$

Application Considerations

On occasion, H_2O_2 is added for ozone residual quenching, but sodium bisulfite and calcium thiosulfate are more common residual quenching chemicals (see chapter 5). Drawbacks of using H_2O_2 as a quenching agent include the noninstantaneous nature of ozone decomposition (i.e., several minutes might be required for complete ozone decomposition to occur) and difficulty in feeding hydrogen peroxide. Hydrogen peroxide chemical feed is discussed later in this chapter.

The PEROXONE process has been used for these applications:

- Oxidation of MIB and geosmin, which are by-products of algal blooms that cause undesirable tastes and odors (see separate discussion that follows concerning successful control of off-tastes and odors with ozone).
- Oxidation of synthetic organic chemical micropollutants including biocides, pesticides, hydrocarbons, and solvents. In some instances, the process is followed by GAC adsorption, because complete mineralization (transformation into CO_2) by oxidation is rare in water treatment applications (Langlais et al., 1991).

The ratio of H_2O_2 to O_3 is variable to achieve desired HO$^\bullet$ exposure, because water quality parameters (temperature, pH, alkalinity, DOC) also affect the production rate of HO$^\bullet$. However, reported dose-based ratios are generally 0.2 to 0.5 mg H_2O_2/mg O_3 (Coffey, 2000; Kachur, 2000). For example, the hydrogen peroxide dose might be 1 mg/L when the ozone dose is 3 mg/L, which gives an operating H_2O_2:O_3 dose ratio of 0.33.

Hydrogen Peroxide Feed Considerations

The molecular weight of 1 mole of hydrogen peroxide is 34 grams [(2 × 1) + (2 × 16)]. Hydrogen peroxide is available in 35 %wt and 50 %wt solutions, but a 35 %wt solution is commonly used (Coffey, 2000). The density of a 35 %wt hydrogen peroxide solution is 1.13 kg/L, or 9.43 lb/gal. The hydrogen peroxide feed rate is calculated in the following way: Assume that the water flow rate is 1 mgd, ozone dose is 2 mg/L, and desired H_2O_2:O_3 dose ratio is 0.3. This means the H_2O_2 dose is 0.6 mg/L. In this example, the mass of hydrogen peroxide to be delivered is 5.0 lb/d (i.e., 5 lb/d = 1 mgd × 0.6 mg/L × 8.34 lb/gal). From above, the weight of 35 %wt hydrogen peroxide solution is 9.45 lb/gal, thus the solution feed rate is 1.52 gpd (i.e., 1.52 gpd = 5.0 lb/d ÷ 35% × 9.45 lb/gal).

Hydrogen peroxide is a clear, colorless, odorless solution that is slightly viscous. Its boiling point is 108°C and freezing point is –33°C. Hydrogen peroxide can be purchased as a certified NSF Standard 60–compliant product. The decomposition rate is slow for 35 %wt solution at ambient temperature (<1%/yr at 20°C and <2.2%/yr at 30°C). However, the decomposition rate is accelerated by catalysts such as silver, lead, copper, chromium, mercury, and iron oxide rust (FMC MSDS Reference No. 7722-84-1-3 – 02/02/2004, FMC Corporation, Philadelphia, Pa.; Solvay Chemicals Technical Data Sheet TDS HH-092 – 01/25/2004, Solvay Chemicals, Inc., Houston, Texas).

The catalytic decomposition reaction and resulting gas-binding problems in the H_2O_2 feed system are often reported at facilities that feed H_2O_2. H_2O_2 decomposes into water and oxygen, with no toxic residues. The generation of oxygen gas results in gas binding inside the feed pipes, with a reduction or even stoppage of the H_2O_2 feed delivery. Gas binding can occur even when the storage tanks and piping are properly conditioned (by special passivation techniques). To reduce the potential for gas-binding problems, the length of the feed piping between the storage tank and the carrier water should be minimized. And, arrangements should be made to collect and remove gas from the piping. H_2O_2 concentration in the carrier water is typically between 1% and 5%, where the decomposition reaction does not cause problems.

Taste and Odor Reduction

A thorough description of the reduction of off-tastes and odors using ozone is presented in *Ozone in Water Treatment: Application and Engineering* (Langlais et al., 1991). Demonstration-scale study results from the Metropolitan Water District in Los Angeles, California, are presented in *Demonstration-Scale Evaluation of Ozone and Peroxone* (Coffey, 2000). Full-scale study results from the

Central Lake County Water District, Lake Bluff, Illinois, are presented in "Ozone/ Biofiltration for Removing MIB and Geosmin" (Nerenberg et al., 2000).

Following are highlights from these and other studies regarding the use of ozone to eliminate offensive tastes and odors:

1. Off-tastes and odors are most often attributable to organic compounds present in very low concentrations (nanograms per liter). These compounds may result from decaying plant matter but normally are produced by the activities of actinomycetes and blue-green algae (Langlais et al., 1991).
2. The compounds most frequently associated with off-tastes and odors are MIB, geosmin, and alicyclic alcohols (Langlais et al., 1991). The first two are most common, with taste and odor threshold values in the order 6 to 10 ng/L.
3. Ozonation alone, operated at disinfection dosages, has eliminated taste and odor complaints at several surface water treatment plants that this author has worked at, including plants located in California, Texas, Illinois, Ontario (Canada), Pennsylvania, Wisconsin, and New Jersey. The raw water concentrations of MIB and geosmin at these plants were generally <50 ng/L.
4. Studies indicate that MIB and geosmin are oxidized by chemical oxidation via hydroxyl radicals, followed by biological oxidation in filters:
   a. Geosmin is oxidized more rapidly than MIB. About 50% to 60% removal of MIB is expected at normal disinfection dosages (+10% for geosmin) (Coffey, 2000; Nerenberg et al., 2000). This observation can be explained by the rate constants given by von Gunten (2003a).
   b. After ozone disinfection CT credit is attained in the front end of the ozone contactor, additional ozone can be added, along with hydrogen peroxide, to create advanced oxidation conditions. The resulting advanced oxidation process generates $HO^{\bullet}$ and achieves additional oxidation of MIB (+70% to +85%) and geosmin (+80% to +90%) (Coffey, 2000).
   c. MIB and geosmin are also removed using biological filters (Nerenberg et al., 2000). Indeed, biological removal at plants that use ozonation might partially account for the author's observations noted in item 3 above. When the raw water MIB concentration was ~40 ng/L, the reported MIB removal was 55% to 65% after ozonation (Nerenberg et al., 2000). More important, the reported MIB removal totaled 93% to 100% after ozonation plus biological filtration (Nerenberg et al., 2000).

Ozonation is very effective in reducing or eliminating taste and odor complaints, and operators at plants using ozone are very appreciative of this fact. Ozone-only followed by biological filtration is usually sufficient for treating moderate MIB and geosmin concentrations (e.g., <50 ng/L). If MIB and geosmin concentrations are higher, use of the PEROXONE process might be necessary. For example, the East Bay Municipal Utilities District (California) used ozone and hydrogen peroxide when geosmin concentrations approached 1,000 ng/L (Kachur, 2000).

Oxidizing Endocrine Disruptors, Pesticides, Solvents, and Other Compounds

Ozone alone and advanced oxidation treatment (i.e., treatment by $HO^\bullet$) have been studied and used to remove micropollutants such as pesticides, solvents, pharmaceutically active compounds, plus others from water. Usually, removal of these organic compounds is a secondary treatment result that is unmonitored. However, in the future their removal is likely to become a more pro-active application for the ozonation process.

The occurrence and fate of pharmaceutically active and personal care products (PPCPs) in surface waters originating from urban sources is an emerging issue in environmental chemistry (Jasim et al., 2004). In addition, scientists have reported that certain synthetic and natural compounds could mimic natural hormones in the endocrine systems of animals; these are collectively known as endocrine-disrupting compounds (EDCs) (Snyder et al., 2003). Reports of PPCPs and EDCs in water have caused concern among public and regulatory agencies. Studies have shown that little removal occurs during conventional flocculation, sedimentation, and filtration treatment. Reaction with chlorine and ozone can oxidize some compounds, and advanced treatment such as activated carbon and reverse osmosis appear viable for removing many trace EDCs and PPCPs (Snyder et al., 2003).

Research on the effectiveness of ozone, chlorine, and UV in removing EDCs and PPCPs (phone discussion with Dr. Shane Snyder, principal investigator for the AwwaRF project titled "Evaluation of Conventional and Advanced Treatment Processes to Remove Endocrine Disruptors and Pharmaceutically Active Chemicals," which is currently in progress) at conventional disinfection doses is in progress. Results to date indicate that ozone is effective in achieving >70% removal of most compounds. UV with peroxide (i.e., advanced oxidation) is also effective. Chlorine is effective for some compounds.

Ozone oxidation of pesticides, solvents, aromatic and aliphatic hydrocarbons, phenols, substituted or nonsubstituted polyphenols, plasticizers, and surfactants is discussed in *Ozone in Water Treatment: Application and Engineering* (Langlais et al., 1991). And, numerous articles have been published in the *Journal AWWA*, *Ozone Science and Engineering* (International Ozone Association), and other scientific publications. A brief summary of micropollutants in water is presented here:

- Micropollutants might be oxidized by ozone alone or by $HO^\bullet$ (advanced oxidation), depending on their chemical structure.
  - Molecular reaction sites (i.e., oxidized by molecular ozone) are either multiple bonds (e.g., C=C) or atoms carrying a negative charge. Strong reactivity is predicted for ortho-activated aromatics by substituents such as OH, CH_3, or OCH_3. Weaker molecular reactivity is predicted for molecules with NO_2, CO_2H, or CHO groups.
  - Reactions by $HO^\bullet$ are nonselective (e.g., OH).
- Aliphatic hydrocarbons and halogenated derivatives include industrial products such as solvents. The electron densities attached to C or H atoms of alkanes cause this organic to be nonreactive with molecular ozone. $HO^\bullet$ can destroy species such as $CHCl_3$, $BrCHCl_2$, tetrachloroethylene, and trichloroethylene.
- Aromatic compounds are released either from the natural environment or via organic synthesis. Aromatic products with electron-donating groups (OH, NH_2) react readily with molecular ozone. Aromatic products with electron-withdrawing groups (NO_2, Cl) react much more slowly with molecular ozone but are oxidized by $HO^\bullet$.
- Phenolic products are characterized by the presence of the OH donor group on the aromatic nucleus. These compounds are strongly reactive to molecular ozone.
- Amines are highly reactive to molecular ozone because the electrophilic attack is promoted by the presence of a negatively charged nitrogen atom. Urea, ethylene diamine, hydrazine, and dimethyl nitrosoamine are oxidized very slowly by molecular ozone but are oxidized much faster with $HO^\bullet$.
- Chlorinated organic pesticides, which are slowly reactive and incompletely destroyed by molecular ozone, have been oxidized by $HO^\bullet$. Organophosphorous pesticides are much more susceptible to direct ozonation (i.e., molecular ozone oxidation). Herbicides of the phenoxyacetic class are readily degraded by molecular ozone.
- Surfactants can be divided into four families: anionic, cationic, non-ionic, and ampholyte. Surfactants are not readily oxidized by ozone. They are eliminated from water by adsorption onto floc, activated carbon, biomass, and similar solid surfaces.
- Dyes that cause color are primarily related to the presence of fulvic materials, although certain industrial micropollutants might occur in trace quantities. These organic substances are partially ionized, always present as conjugated aromatic structures, and strongly reactive to molecular ozone.

OXIDATION BY-PRODUCTS AND MITIGATION

The main by-products of ozonation are bromate (BrO_3^-), which is formed in bromide-containing water; simple-chained organic molecules, which are formed when NOM is oxidized; and brominated organic compounds, which are formed when HOBr reacts with NOM (von Gunten, 2003b). Bromate has been identified as potentially carcinogenic and is currently regulated at a running annual average maximum contaminant level value of 10 mg/L (USEPA, 1998). Concentrations of the simple-chained organic molecules are unregulated, but they are typically removed in biological filters to minimize potential for regrowth within the distribution system. Brominated organic compounds are regulated via total trihalomethane (TTHM) limitations. (NOTE: Brominated organic compounds are also formed in the absence of ozone via reaction with chlorine.) Other unregulated oxygenated by-products are formed by ozonation, similar to unregulated chlorinated by-products. This book emphasizes formation and mitigation of BrO_3^-, because BrO_3^- is currently the only regulated DBP of ozonation.

Biodegradable Organic Ozonation By-products

Many organic compounds are oxidized by O_3 and $HO^•$. The by-products of oxidation include short-chained organics such as aldehydes (formaldehyde, acetaldehyde, glyoxal, methylglyoxal); ketoacids (ketomalonic acid, pyruvic acid, and glyoxylic acids); and carboxylic acids (acetic, formic, and oxalic) (Huck et al., 2000). These organics are more easily biodegraded than their parent, long-chained organic compounds. Unless they are removed in the treatment plant by biochemical oxidation (i.e., biological filters), the potential exists for biological regrowth in the distribution system or development of TTHMs when chlorinated (Langlais et al., 1991).

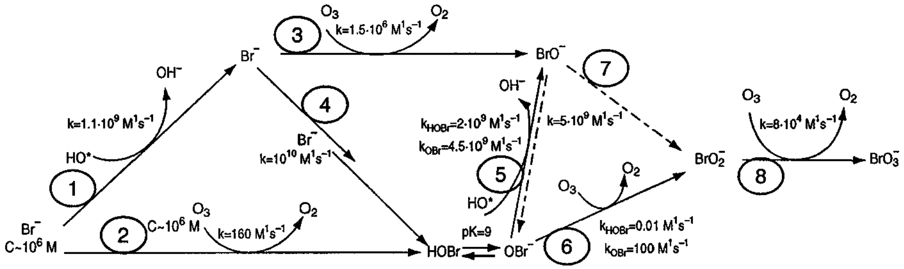
Biodegradable organic matter that is not removed during water treatment can, but might not, lead to biological regrowth problems. The Pine Hills Water Treatment Plant, operated by the Orlando (Florida) Utilities Commission, was sampled for 2 years—1 year prior to ozone addition and 1 year following ozone startup (Escobar and Randall, 2001). Biological filters were not used to treat this deep Floridian aquifer water. After ozone, the water's aesthetic quality (i.e., taste and odor) was improved, which was a primary objective of ozone introduction. The level of DOC was about 1 mg/L both before and after ozonation. Before ozonation, the assimilable organic carbon level of the raw and treated water was approximately 70 µg/L acetate-C; in the distribution system the level was between 60 and 80 µg/L acetate-C. After ozonation the AOC concentrations in the plant effluent and distribution system were significantly higher at 220 mg/L acetate-C, which was an increase of about 200%. The chlorine dose was 2 mg/L during both years. However, the average chlorine residual after ozonation was 0.2 mg/L higher at 1.1 mg/L, versus 0.9 mg/L before ozonation. Even though AOC increased significantly after the introduction of ozone, distribution system regrowth remained low because the chlorine addition (and residual) was high (Escobar and Randall, 2001).

Given that potential exists for bioregrowth problems, most plants that implement ozone treatment delay chlorine addition until after filtration, thus allowing the partially oxidized organics to mineralize (i.e., biochemical conversion to carbon dioxide and water) via biofiltration. More information concerning biological filter operation is presented in chapter 5.

Bromate Formation

Bromate formation and control has been the focus of intensive research efforts since the early 1990s when bromate (BrO_3^-) was implicated as a potential carcinogen (Buffle et al., 2004). Full-scale plant mitigation has been implemented since 1999 when the USEPA Stage I Disinfectant/Disinfection By-products Rule established the BrO_3^- MCL value at 10 µg/L (USEPA, 1998). Although the USEPA estimated the 10^{-4} lifetime excess cancer risk for BrO_3^- to be at 5 µg/L (USEPA, 1994), the Stage 1 MCL was set at the practical quantification limit of 10 µg/L (Williams et al., 2003). Research is ongoing to verify if bromate indeed is a carcinogen and to verify if the MCL value should remain at 10 µg/L. Ozone plants can be subdivided into the following three categories, which relate to their relationship to bromate issues and considerations:

1. Bromide is absent in the source water or is present at low concentration. Bromate formation is proportional to bromide concentration for given water quality and ozone dose operating conditions. Low bromide concentration means low bromate formation potential.
2. Bromide is present in the source water at moderate concentration (e.g., 50 to 100 µg/L), but ozone dose requirements are such that bromate formation is below the MCL value of 10 µg/L. Bromate formation is minimized when:
    a. Ozone dose is low as a result of plant operation at low CT value that is still sufficient to meet the disinfection treatment objective, such as 2-log virus or 0.5-log *Giardia* inactivation credit.
    b. Ozone dose is low even to meet elevated disinfection requirements (e.g., 0.5-log *Cryptosporidium* inactivation credit), because water quality characteristics are such that the ozone demand is low and ozone decay is slow (i.e., long ozone half-life).
3. Bromide is present in the source water at a relatively high concentration such that bromate formation would exceed the 10-µg/L MCL value unless bromate mitigation measures are implemented. Bromate mitigation



NOTE: Numbers are for reference purposes only.

Figure 2-13 Bromate formation with conventional ozonation (Buffle et al., 2004)

options are described here and include lowering pH, adding ammonia, adding chlorine and ammonia, or using chlorine dioxide.

a. Bromide concentration might be low (e.g., 50 to 100 µg/L), but bromate formation is elevated because the disinfection treatment objective necessitates high CT value, such as 2-log *Cryptosporidium* inactivation credit.

b. Bromide concentration might be elevated (e.g., 100 to 500 µg/L) such that bromate formation is above 10 µg/L even at a disinfection treatment objective that is achieved at a relatively low CT value, such as 2-log virus or 0.5-log *Giardia* inactivation credit.

In 1994 von Gunten and Hoigné presented a model that describes the complex pathway of bromate formation by ozone and hydroxyl radicals (von Gunten and Hoigné, 1994). By understanding the mechanism for bromate formation, mitigation measures can be formulated or described (Buffle et al., 2004). Figure 2-13 displays the pathway for bromate formation (von Gunten and Hoigné, 1994; Buffle et al., 2004). Reference numbers are shown in Figure 2-13 for the many and varied reactions. The numbers are not intended to indicate or suggest order or sequence of reactions. Indeed, all reactions occur simultaneously, some faster than others. Selected reactions are described below to provide insight into how bromate mitigation measures might be implemented, if needed.

Bromate formation is initiated by reactions 1 and 2 in Figure 2-13. Reaction 1 is by hydroxyl radical ($HO^{\bullet}$) oxidation and reaction 2 by ozone (O_3) oxidation. Refer to the advanced oxidation section earlier in this chapter for additional discussion concerning water quality parameters affecting $HO^{\bullet}$ and O_3 concentrations in natural waters (e.g., $HO^{\bullet}$ exposure is elevated at higher temperature, higher pH, high DOC concentration, and low alkalinity).

The ozone reaction occurs in two phases. The initial phase is recognized by elevated $HO^{\bullet}$ exposure and rapid ozone reaction and decomposition, which have been termed "ozone demand." The initial phase persists for <60 seconds. The second phase is recognized by lower $HO^{\bullet}$ concentration and slower O_3 decomposition, which is characterized by measurable ozone half-life (i.e., first-order decay). An ozone half-life of seconds to a few minutes is likely to occur in warm water (30°C) with high pH value (>8.0), high DOC (>3 mg/L), and low alkalinity (<60 mg/L). This same water quality might also exhibit an elevated ozone demand value. Conversely, ozone half-life might be 30 min, or longer, at low temperature, low pH, low DOC, and high alkalinity. Important considerations concerning reaction 1 and reaction 2 are as follows (Buffle et al., 2004):

1. The quantity of Br^--oxidation by-product is proportional to the Br^- concentration. A bromate mitigation measure might be to reduce available Br^- concentration.
2. The $HO^{\bullet}$ reaction pathway (i.e., reactions 1, 3, 5, and 7) is important during the initial phase (e.g., first minute of reaction). Bromate mitigation methods might include limiting $HO^{\bullet}$ exposure during the initial phase.
3. Bromate formation is dominated by O_3 reaction 2 during the second phase. However, O_3 exposure (i.e., CT value) itself must be maintained to meet disinfection requirements, thus ozone exposure cannot be changed. Bromate mitigation, then, includes methods to minimize subsequent reactions (e.g., reactions 6 and 8).

Bromate Mitigation With pH Depression

Implementation of pH depression alone minimizes bromate formation for reasons listed below (Buffle et al., 2004):

1. A lower pH reduces OBr^- concentration (i.e., $HOBr/OBr^-$ equilibrium shifts toward HOBr). Lower OBr^- concentration, in turn, slows the rate of BrO_2^- by-product formation via reaction 6. Details of reaction 6 in Figure 2-13 indicate that the reaction to produce BrO_2^- is significantly faster for the OBr^- species than for HOBr.
2. Reduced pH value lowers $HO^{\bullet}$ exposure and, therefore, minimizes BrO_3^- from reactions 1 and 5. Reduced pH lowers $HO^{\bullet}$ exposure primarily by lowering the required ozone dose, yet still meets the disinfection CT value, because the rate of ozone decay is slower (i.e., increased ozone half-life).

In summary, to mitigate bromate it works to reduce pH because there is lower $HO^{\bullet}$ exposure for the same ozone exposure (von Gunten, 2003b). In other words, for the same level of disinfection you have a lower overall oxidant exposure.

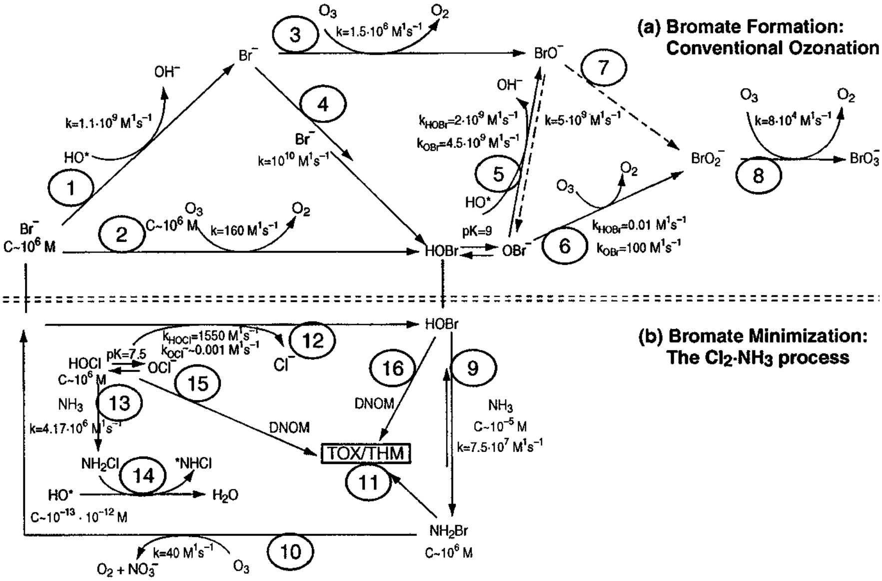
Water utilities that have implemented pH depression as a bromate mitigation strategy include the Metropolitan Water District of Southern California (MWD) in Los Angeles and Alameda County Water District (ACWD) in Fremont, California. As needed, MWD uses sulfuric acid to lower the pH value from ambient levels, which are between pH 8.0 and 8.3, to controlled values, such as 7.5, 7.0, or 6.5, depending on bromide concentration in the raw water supply (Coffey, 2000). Caustic soda (NaOH) is added to return pH to ambient levels or to raise pH even further to prevent corrosion in the distribution system. In some instances, the operating costs for adding acid and caustic are greater than the costs for producing ozone, primarily because of greater expense for caustic soda.

The ACWD adds carbon dioxide (CO_2) to reduce the pH value from ~8.1 to as low as 6.8. The selected operating pH depends on raw water bromide concentration. The pH value must be lowered when the bromide concentration is elevated to maintain an effluent bromate concentration <10 µg/L (Najm et al., 2004b). CO_2 addition facilities were installed in late 2001 and were operated at an average CO_2 dose of 15 µg/L during 2002. Similar disinfection credits (~2.2-log *Giardia*) were achieved in both years. Ozone dose averaged 2.3 mg/L without pH suppression (2001) and was much lower, at 1.5 mg/L, with pH suppression (2002). The reduction in ozone dose led to an overall chemical cost saving (i.e., the savings from the lower ozone dose was more than the cost of adding CO_2). Significantly, the average bromate concentration was only 3.5 µg/L with pH suppression (2002), as opposed to 10 µg/L without pH suppression (2001). Bromide concentration was about the same, at 234 µg/L in 2001 and 195 µg/L in 2002.

As an alternative to adding caustic soda to raise pH, air stripping was studied at the ACWD to remove excess CO_2 after ozonation (Najm et al., 2004b). Air stripping raised pH by 0.2 to 0.3 pH units at the installation tested. This effectively reduced the caustic soda dose, but the main challenge was the additional head loss (i.e., 1 ft in this project) that was created in the air-stripping chamber. The plant's hydraulic profile must be able to accommodate this additional head loss if air stripping is to be implemented.

Bromate Mitigation With Ammonia Alone

Addition of ammonia alone is another bromate-mitigation strategy. MWD tested ammonia alone for bromate mitigation at their oxidation demonstration plant located in LaVerne, California (Williams et al., 2003). Ammonia alone was not selected at MWD for two likely reasons: (1) Krasner and colleagues (1993) found that NH_3 addition alone was inconsistent in achieving bromate mitigation results; (2) aqueous or anhydrous ammonia addition increased operating pH value, which increased the rate of ozone decay that led to higher ozone dose requirement for meeting target disinfection CT value (Williams et al., 2003). Figure 2-14 illustrates how Buffle and associates (2004) added to their bromate-formation model (Figure 2-13) to illustrate the bromate-mitigation effect of NH_3 addition only and to illustrate the effect of Cl_2 followed by NH_3 addition. Following is a



NOTE: Numbers are for reference purposes only.

Figure 2-14 Bromate formation with conventional ozonation plus bromate mitigation with the Cl_2 + NH_3 process (Buffle et al., 2004)

summary of the rationale for bromate mitigation with ammonia alone, as well as potential reasons for the inconsistent results obtained at MWD (Buffle et al., 2004):

1. Reaction 9 in Figure 2-14 explains how BrO_3^- formation is mitigated by ammonia addition. Reaction 9 indicates that HOBr reacts with NH_3 to form monobromamine (NH_2Br). Through this reaction the HOBr concentration is reduced, which minimizes the concentration of BrO^- that is produced from reaction 5. This slows reaction 7 and subsequently reaction 8. Also, reaction 6 is slowed and ultimately reaction 8 is minimized.
2. Possible explanation for inconsistency in bromate mitigation with ammonia alone includes the following considerations:
    a. Reaction 10 partially explains any potential inconsistency. Ozone via reaction 10 oxidizes NH_2Br, which releases the Br^- (albeit sluggishly) that reacts with $HO^\bullet$ or ozone via reactions 1 and 2, respectively. This means that potential for BrO_3^- formation reemerges, because Br^- is only temporarily tied up in NH_2Br. Inconsistency in results might arise from variability in reemergence of Br^-.

   b. Another explanation is that bromide is available at the beginning of ozonation and, consequently, is available for oxidation by $HO^\bullet$. Variation in pH might lead to variation in $HO^\bullet$ exposure and variation in amount of bromate formed via reactions 1, 3, 7, and 8.

3. Reactions 11 and 16 indicate that some Br is tied up in TOX or, more specifically, a TOBr sink (TOX = total organic halogens of which trihalomethanes is a subgroup), depending on DOC concentration. More information is presented later regarding THM formation. Reaction 11 indicates that NH_2Br reacts with NOM, generating brominated organics, including THMs. Reaction 16 indicates that HOBr reacts with NOM, also generating brominated organics, including THMs. TOBr (total organic bromine) is a Br^- sink, which means that some Br^- is unavailable for release via reaction 10 because it is incorporated into the organic water matrix. The concentration and type of NOM greatly influences the quantity of Br^- that is contained in the TOBr sink.

Bromate Mitigation With the Chlorine-Ammonia Process

Chlorine followed by ammonia addition (called the "Cl_2-NH_3" bromate mitigation process) is a recently developed and quite promising bromate mitigation strategy. The Southern Nevada Water Authority (SNWA), in Las Vegas, has pilot-tested and is currently installing a Cl_2-NH_3 bromate mitigation process to achieve bromate concentrations <10 µg/L, while operating an ozone disinfection system that achieves 2-log *Cryptosporidium* inactivation credit (Neemann et al., 2004). Ammonia alone and chlorine alone were tested but were abandoned in favor of the combined Cl_2-NH_3 process. Chlorine alone was ineffective in reducing bromate concentration to below 10 µg/L (Neemann et al., 2004). Ammonia alone was effective but would have required a high chlorine dose at the filter effluent (prior to the clearwell) to "breakpoint" the residual ammonia (Neemann et al., 2004), because the SNWA operates with free chlorine residual in their distribution system. Also, ammonia alone would have increased the ozone dose. Fortunately, ozone dose did not change in the Cl_2-NH_3 process (i.e., unchanged compared to operation with no chemical addition).

When researchers involved with the SNWA pilot-plant project realized that they had developed an innovative bromate mitigation approach via the Cl_2-NH_3 process, they applied for and were granted a patent, titled "Water Treatment using Ozone Having a Reduced Likelihood of Bromate Formation From Bromides Formed in Water" (US 6,602,426 B2; issued August 5, 2003) (Neemann et al., 2004). The motivation for seeking a patent was to protect SNWA and other water utilities against those who might patent the process and charge for its use. The patent was placed in the public domain, where it is essentially available for use free of charge.

The Cl_2-NH_3 process is being installed at the two SNWA full-scale plants to achieve chlorine dosages in the range of 0.25 to 0.50 mg/L and ammonia dosages in the range of 0.1 to 0.5 mg/L. Chlorine contact time is 7 min at design flow. Ammonia contact time is short, with ammonia being added just upstream of the contactor inlet. Later in this section, rationale for these dosages and contact times is presented.

The SNWA operates with free chlorine residual in the distribution system. However, even if distribution system chloramine residual is used, it is still a good idea to develop *free chlorine residual* following biological filtration for a detention time of at least 2 to 5 min (see biological filter discussion in chapter 5). Therefore, with the requirement for free chlorine residual and consideration that ammonia addition is part of the Cl_2-NH_3 process, an elevated chlorine dose might be required following biological filtration to reach "breakpoint" for residual ammonia. However, the breakpoint chlorine dose might be reduced significantly via biological nitrification in the biologically active filters.

Pilot testing of ammonia removal via biological filtration and Cl_2-NH_3 bromate-mitigation studies (Zegers et al., 2001) were conducted by SNWA. Results indicated that the filters must be backwashed with dechlorinated water, because the nitrifying bacteria are sensitive to process upset. *Nitrosomonas* organisms that biologically oxidized ammonia to nitrite were first to develop. Their oxidation reaction reduced breakpoint chlorine demand by 50%. *Nitrobacter* organisms that biologically oxidize nitrite to nitrate developed more slowly, but their full development completely negated the need for breakpoint chlorination. The expectation is that the filter effluent ammonia concentration will be negligible most of the time, thus minimizing the need for an elevated plant-effluent chlorine dose for breakpoint ammonia removal.

Figure 2-14 depicts the relationship among bromate formation reactions and bromate mitigation reactions via the Cl_2-NH_3 process (Buffle et al., 2004). Following is a summary of the rationale for bromate mitigation using the Cl_2-NH_3 process, plus reasons for excellent performance and consistency in results (Buffle et al., 2004). The explanation describes the process in which chlorine is added first (pre-chlorine), followed by ammonia addition to water that has negligible natural ammonia concentration. Following Cl_2 and NH_3 addition, the water is directed to the ozone contactor. The pre-chlorine dose ranged between 0.35 mg/L and 1.05 mg/L; chlorine reaction time was 5 min; and ammonia dose ranged between 0.1 and 0.4 mg/L. Ammonia reaction time was a few seconds (Buffle et al., 2004).

1. Pre-chlorine addition and reaction 12 masks the Br^- concentration that would normally be available for reactions 1 and 2. The concentration of HOBr is a function of chlorine dose, chlorine contact time, and Br^- concentration. Ideally, chlorine dose and contact time are sufficient to

completely oxidize Br^- via reaction 12. However, THM is an undesirable by-product that might be formed by reactions 15 and 16. Therefore, it is desirable to minimize free chlorine exposure as much as possible so that BrO_3^- limits are achieved without increasing TTHM too much. Fortunately, the total sum of THM (TTHM) that is formed by all THM-forming reactions (subgroups of reactions 11, 15, and 16) is reasonably low (e.g., between 1 and 10 µg/L for the specific cases described by Buffle et al. [2004]).

2. Ammonia addition rapidly transforms HOBr via reaction 9 (i.e., product of reaction 12) into NH_2Br. This means that Br^- concentration is minimized (Br^- is masked as NH_2Br) before ozone addition and, subsequently, BrO_3^- formation is minimized. In second-phase reactions, ozone exposure and reaction 10 release Br^-, albeit fairly slowly. Ultimately, a small quantity of BrO_3^- might be formed by this release of Br^-. However, some NH_2Br in reaction 11 forms TOBr, which is a sink for Br^- (see point 1 above for THM discussion).
3. Ammonia should be added in excess, as opposed to an excess chlorine dose. Chlorine dose and reaction 12 produce HOBr, which might be available for oxidation by ozone to BrO_3^- via reactions 6 and 8 if ammonia dose is too low. Insufficient ammonia will leave nonreacted HOBr available for BrO_3^- formation via reactions 5, 6, 7, and 8. This also explains why chlorine dose alone is an ineffective bromate mitigation technique. Both chlorine and ammonia are equally important parts of the Cl_2-NH_3 process. The formation of HOBr with chlorine in reaction 12 (i.e., in the absence of ozone) is followed by rapid transformation of HOBr into NH_2Br by reaction 9, and both reactions tie up Br^- prior to ozonation.

This explanation assumes water with negligible ambient ammonia concentration. The following explanation assumes that the water to be ozonated contains ammonia. Chlorine addition tests were conducted with water that had a simulated, naturally occurring ammonia concentration of 0.17 mg/L (Buffle et al., 2004). The naturally occurring ammonia would help sequester HOBr via reaction 9, which is similar to bromate mitigation using ammonia alone. The chlorine reaction, on the other hand, is different. Chlorine is unable to form HOBr prior to ozonation via reaction 12, because of other, more rapid, chlorine reactions that take place, including chlorine to monochloramine (reaction 13). This means that Br^- remains available for $HO^\bullet$ oxidation via reactions 1, 3, 7, and 8. As such, it would be expected that the bromate mitigation results would be similar to results for tests that used ammonia alone. However, test results indicated that bromate mitigation was enhanced, even when Cl_2 dose was only one-fourth the NH_3 dose. This means that the Cl_2-NH_3 process is applicable even when the raw water contains ammonia. The addition of chlorine helped minimize the $HO^\bullet$ reactions, which was explained by Buffle et al. (2004) as follows:

1. A significant fraction of the HOCl can react with nitrogenous compounds of the dissolved NOM, which decreases their oxidation by ozone. Initial ozone decomposition is slower, which reduces the quantity of $HO^\bullet$ that is generated and reduces $HO^\bullet$ exposure. This mechanism was dominant in reducing $HO^\bullet$ exposure.
2. Reaction 14 is less effective (~5% effect) but nevertheless was a reason for lowering overall $HO^\bullet$ exposure. In reaction 14, $HO^\bullet$ are scavenged by NH_2Cl.

In summary, addition of ammonia alone is a possible but infrequently implemented bromate mitigation strategy. Fortunately, the Cl_2-NH_3 process is very effective. Lowering pH alone is also effective and has a synergistic impact on the Cl_2-NH_3 process. Site-specific conditions (pH, temperature, DOC, Br^-, CT requirements, etc.) will determine optimum dose and contact time requirements for the Cl_2-NH_3 process. However, generalized criteria are chlorine contact time of 5 to 10 min, chlorine dose <1 mg/L, and ammonia dose <0.5 mg/L.

Bromate Mitigation With Chlorine Dioxide

Zhou and Neemann (2004) achieved successful results from ClO_2 addition to raw water as a bromate mitigation strategy. Full-scale tests were conducted; mechanistic studies were not completed in this project. The full-scale tests were conducted at the Randall-Bold Water Treatment Plant, Oakley, California, which is operated by the Contra Costa Water District, Concord, California. The Randall-Bold plant has pre-ozone and post-ozone contactors for pre-oxidation and primary disinfection, respectively. The direct filtration plant uses granular activated carbon plus sand (GAC/sand) filters. Three pre-oxidation conditions were tested, including: (1) 1.5 mg/L of ClO_2 alone, (2) the combination of 1.0 mg/L of ClO_2 and 0.5 mg/L O_3, and (3) 1.0 mg/L of O_3 alone. Post-ozone contactor dose was controlled to achieve a disinfection CT value between 4 and 5 mg-min/L during long-term tests (i.e., several weeks). Short-term special studies were conducted in the pre-ozone contactor to evaluate bromate mitigation with chlorine dioxide, pH adjustment, and ammonia addition.

Water temperature was about 25°C during the special studies and gradually decreased to 15°C during the course of the long-term tests. Alkalinity was about 90 mg/L, and raw water pH ranged between 7.7 and 8.0. The total organic carbon value was about 2.6 mg/L during the special studies and for most of the long-term testing but suddenly increased to near 6 mg/L during the last 3 weeks of the 18-week long-term study. Bromide concentration was between 160 and

210 µg/L during the special studies and ranged between 250 and 350 µg/L during the long-term study.

Study conclusions are as follows:

- Although pre-oxidation with ClO_2 forms chlorite and chlorite creates ozone demand for the post-ozone contactor, the total ozone dose (pre-ozone and post-ozone) was reduced.
- The data from this study showed that pre-oxidation with ClO_2 substantially reduced bromate formation. In addition to reducing bromate formation by reducing the ozone dose through substitution with ClO_2, an unexpected result was that ClO_2 pre-oxidation also reduced the bromate formation at a constant ozone dose. Special testing showed that chlorite, which is formed after ClO_2 addition, plays an important role in reducing bromate formation.
- Results were as follows concerning special studies of three bromate mitigation techniques:
  - Pre-oxidation with ClO_2 was effective in reducing bromate formation in the pre-ozone contactor.
  - Adjusting pH to 6.0 was also effective in reducing bromate formation in the pre-ozone contactor.
  - Ammonia addition before the pre-ozone contactor was effective but to a lesser extent than ClO_2 or pH adjustment.
- The data from this study showed that ozone oxidized chlorite to chlorate to the extent that the plant effluent chlorite concentration was below the detection limit. Testing also showed that GAC filters removed some of the chlorite, while chlorate neither increased nor decreased through the GAC filters.
- Pre-oxidation with ClO_2 alone, or ClO_2 in combination with ozone, required similar coagulant dosages and produced similar filter effluent turbidity when compared to using ozone alone.
- The data showed similarity in results for TTHM and the total of five haloacetic acids formation potential following post-filter chlorination, among the three pre-oxidation conditions tested during the long-term study.
- Implementing ClO_2 in the treatment process at the Randall-Bold plant added time and complexity to the operation staff's workload, which included additional sampling, time-consuming amperometric analysis, and the need to closely monitor the post-ozone dose because of the ozone demand created by chlorite.

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3

Ozone Process Layout, Sizing, and Cost

Peak performance and cost optimization are primary goals when designing an ozone system. Treatment goals, plant layout, and water quality are also key considerations. Insufficient capacity is not an option.

This chapter discusses bench-scale and pilot-scale testing; interpretation of testing results; risk-tolerance and equipment standby considerations; and other capital- and operating-cost optimization considerations that are applied during predesign. These issues affect decisions such as:

- Location of application point for ozone addition, including pre-ozone, intermediate-ozone, or both.
- Type of feed-gas, including air-fed, liquid oxygen (LOX)-fed, or on-site oxygen-fed systems.
- Generator number and size, including standby considerations.
- Contactor number, size, and shape, including type of ozone dissolution system—ozone bubble-diffuser or ozone injection systems.

ESTABLISHING SITE-SPECIFIC PERFORMANCE GOALS

Performance goals at operating water utilities cover general treatment objectives, operations-related objectives, and disinfection-related objectives (Rakness et al., 1997; Rakness and DeMers, 1998; Rakness and Hunter, 2000). Performance goals must be clearly defined. Plants that are designed and operated using vague performance objectives cannot be optimized easily. Selecting specific disinfection-related objectives provides a good foundation for developing and communicating detailed design criteria, as well as implementing optimized process operation.

General treatment objectives are usually defined vaguely, e.g., "eliminate off-taste and odor compounds," "reduce total trihalomethanes (TTHMs)," "increase disinfection protection," or "improve filtration performance." These objectives are obtained when disinfection performance is achieved; alone, they provide imprecise design and operating criteria for determining required ozone production, gas flow rate, generator power demand, etc. In summary, general treatment objectives alone provide insufficient design criteria.

One operations-related objective is to maintain a specific ozone dose that is independent of the water (i.e., the quality of the water) being treated. Operations-related objectives provide design and operating targets but discourage optimization that might be achieved by varying ozone dose in response to changes in water quality, such as temperature, pH, and total organic carbon. Operations-related objectives should be supplemented by specific treatment performance objectives, such as disinfection-related criterion.

Development of disinfection performance goals begins by reviewing regulatory requirements (baseline), followed by establishing utility-specific goals that address local public health and aesthetic (e.g., color, taste, and odor) concerns. Historical water quality data might be reviewed to assist in setting these goals. All goals should be reviewed after bench-scale or pilot-scale results are compiled to confirm that implementation is feasible. For example, ozone might be impractical to achieve *Cryptosporidium* log inactivation if the water supply has moderate to high ozone decay rates (Schulz et al., 2005).

Ozone systems that are designed and operated to meet disinfection-related objectives can be optimized using the inactivation ratio (IR) concept (sometimes called performance ratio [PR] or concentration times time [CT] ratio [i.e., residual concentration multiplied by detention time]). The IR value is obtained by dividing measured ozone disinfection inactivation by the required inactivation. Required inactivation might include specific disinfection targets such as 1-log *Giardia*, 3-log virus, or 2-log *Cryptosporidium*. Methods for calculating IR values for these pathogens are discussed in chapter 2.

The operating goal is to maintain an IR value that is slightly above 1.0. The operating factor of safety can be determined on a case-by-case basis, such as "maintain the IR value between 1.1 and 1.3, or 1.5 and 2.5, or 2 and 3." The disinfection performance target and operating factor of safety should be established during predesign and carried forward into design and operation. However, the operating IR range might be higher at startup and decrease during the first year of operation as the system is being optimized.

CONTACTOR SIZE AND SHAPE AND DESIGN OZONE DOSE

Unused ozone generation capacity is costly. However, it has been observed in several plants (Rakness et al., 1997; Rakness and DeMers, 1998; Rakness and

Hunter, 2000). Reasons for excess capacity include elevated ozone dose due to improperly conducted bench-scale or pilot-scale studies and conservative risk-tolerance level. Operating ozone dose has been observed to be greater than necessary at some plants due to nonoptimized design criteria for ozone contactor size and shape (Rakness et al., 1997; Rakness and DeMers, 1998; Rakness and Hunter, 2000).

The most important design decisions include ozone generator size and number and ozone contactor location, size, and shape. Table 3-1 provides a checklist of items to consider when optimizing generator and contactor size and shape. Establishing ozone dose is the logical first step.

Table 3-1 Checklist for Ozone Generator and Contactor Sizing Optimization

Consideration	Comment
1. What is the performance target and operating factor of safety?	A. Select a specific, measurable performance target. *Giardia,* virus, or *Cryptosporidium* log inactivation is an example performance target. B. Select operating factor of safety such as 1.2, 1.5, or 2.0.
2. What is the expected ozone dose and residual profile when performance target is met?	A. Bench-scale or pilot-scale studies might be used to develop demand/decay data for the range of expected water quality and flow conditions. B. Results should be evaluated using a contactor-operation model, because contactor operating characteristics will affect required ozone dose and residual profile that are needed to achieve a given CT value that meets the disinfection performance target.
3. What is the acceptable design risk tolerance for ozone generator back-up/ standby capacity?	A. Ozone generators create and deliver ozone on site. B. Ozone standby equipment might be more expensive proportionally, because ozone is generated on site whereas other treatment chemicals are trucked in from off-site production facilities. C. The owner and engineer should determine generator standby capacity jointly, with due consideration of regulatory agency requirements and site-specific considerations.
4. What is the acceptable design risk tolerance for ozone contactor back-up/ standby capacity?	A. Most ozone contactor designs have few mechanical components. B. Ozone contactors might function satisfactorily without standby or back-up capability. C. Chlorine may be an acceptable standby primary disinfectant.

Standby or backup ozone contactors are rarely installed, because most ozone contactors have few mechanical equipment components. Contactors that do have ozone diffusers require only periodic maintenance. Diffusers are inspected once or possibly twice per year, preferably when water demand is low.

When two or more ozone contactors are selected to meet design hydraulic detention time (HDT) at the design water flow rate, another decision must be made concerning the maximum flow rate through an individual contactor. Should the flow rate be 50% of the design flow, 67% of the design flow, or some other percentage? The selected maximum flow rate through an individual contactor might be restricted by physical components, such as contactor inlet or outlet constraints. If physical constraints are absent, process operation (optimization) will dictate the number of contactors in service. Studies have shown that operating costs were lowered when one of two ozone contactors was removed from service and detention time was reduced by 50% (Rakness and DeMers, 1998). This action was possible because the required CT value was so low that residual did not extend to the outlet of the contactor, even when detention time was reduced. Conversely, for waters with low ozone decay rates (i.e., long half-life values), it might be advisable to maximize contactor detention time. Given this possibility, hydraulic constraints should be as broad as practical so that process control considerations dictate optimized operation. Standby or backup ozone contactors are generally unnecessary.

Applied ozone dose and contactor transfer efficiency affect the ozone dose that is transferred to the water. A portion of the transferred dose will react immediately; this is called ozone demand. Ozone residual, which develops after ozone demand is satisfied, follows a first-order decay profile, as discussed in chapter 2. Water quality, contactor shape, and contactor size influence the residual profile that is required to achieve a specific disinfection target. Bench-scale or pilot-scale ozone demand and decay tests might be used in conjunction with a contactor-operating model to determine relationships among ozone dose, residual profile, and disinfection performance.

Bench-Scale Ozone Tests

Bench-scale ozone testing is the least expensive way to develop insight into site-specific water quality effects on ozone demand and ozone decay, both of which impact the ozone dose required to achieve disinfection objectives. However, bench- or pilot-scale tests must be conducted properly to obtain valid data for full-scale system design. In this section, an example bench-scale testing approach is described. This approach was confirmed by comparing scale-up projections for ozone dose and disinfection performance, which were developed from bench-scale tests, to actual ozone dose and disinfection performance at full-scale facilities (Rakness and Hunter, 2000).

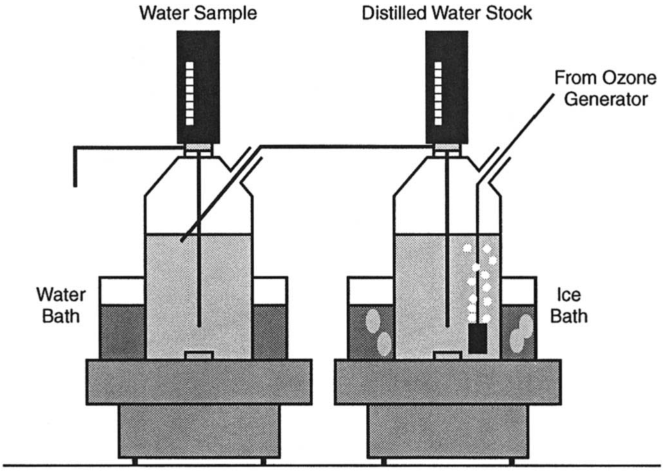

Figure 3-1 Bench-scale SOT for determining O_3 demand and decay

Types of Bench-Scale Tests

Elevated ozone demand and rapid decay will increase the design ozone dose. The ozone decay rate also impacts contactor size and shape. The solution ozone test (SOT) and the gas ozone test (GOT) are bench-scale methods used to conduct ozone demand and decay tests (Hoigné and Bader, 1994; Roustan et al., 1998; Richard, 1994; Carlson et al., 1997; Rakness and Hunter, 2000). The GOT requires a fairly elaborate laboratory setup that applies ozone gas directly to the water sample (Roustan et al., 1998; Richard, 1994). Required measurements include feed-gas flow, product-gas ozone concentration, reaction vessel off-gas ozone concentration, ozone-residual-in-water value, and ozone reaction time.

The SOT is less complicated, but its application is limited to a maximum ozone dose of approximately 4 mg/L due to dilution effects (Hoigné and Bader, 1994; Carlson et al., 1997; Rakness and Hunter, 2000). In the SOT, ozone stock solution is applied to the sample water. Required measurements include stock solution ozone residual, volume of sample water and volume of stock solution applied, ozone residual-in-water value, and ozone reaction time. Both the SOT and GOT methods have merit and, if interpreted properly, can be used successfully to develop design ozone dose.

Solution Ozone Test Example

Figure 3-1 shows the bench-scale test apparatus for the SOT. Ozone residuals of the stock solution and reacted samples are determined using Eq. 7-3 (see chapter 7). However, for this test the normal protocol, which is a 10-mL Indigo–reagent II solution, is modified to measure the elevated residual of the stock solution and also

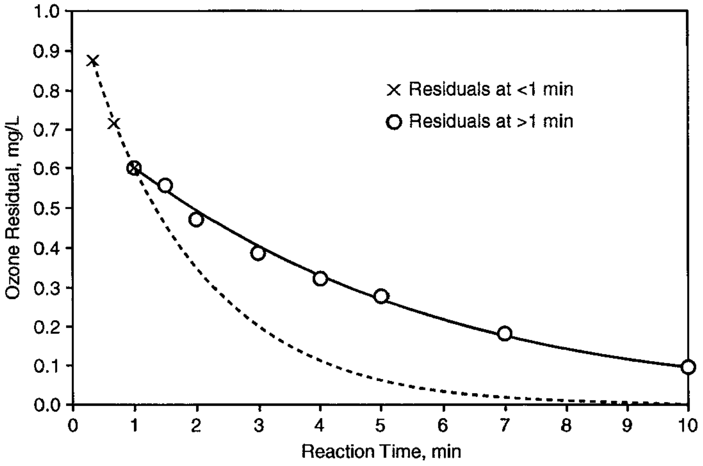

Figure 3-2 Measured residual for test 11 plant B, plus decay rate-based residual profile

to minimize volume that is used to compute reacted-sample residual value. For example, 50 mL of reagent II solution might be used to assess stock solution ozone residual value and 2 mL reagent II solution might be used for each reacted-sample residual test.

Ozone stock solution is prepared at 40 mg/L residual, or higher, by bubbling high-concentration ozone (about 8 to 10 %wt) into chilled distilled water for about 1 hour. Longer bubbling time is unnecessary and might create conditions of catalytic fast-decomposition of stock solution ozone residual. The residual decays slowly in properly prepared ozone stock solution, but stock-solution residual is determined at the outset of each test. New stock solution should be prepared when the stock solution residual is too low (e.g., < 35 mg/L).

A predefined volume of stock solution is added to a known volume of sample. The stir bar is shut off about 10 sec after stock-solution delivery. Sixty seconds (alternatively 20 sec, 40 sec, and 60 sec) after delivery, the first aliquot of ozonated water sample is directed into a flask that contains a preset volume of reagent II solution, such as 2 mL. Samples are collected at recorded times until the reacted-sample residual value is less than, say, 0.1 mg/L.

Figure 3-2 displays the ozone residual results from an example plant (plant B). Stock solution ozone residual was 41.1 mg/L and sample volume was 950 mL. A stock solution volume of 39 mL with an ozone mass of 1.603 mg (i.e., 1.603 mg = 41.1 mg/L × 39 mL ÷ 1,000 mL/L) was added to the sample, which resulted in an applied (also transferred) ozone dose of 1.62 mg/L (i.e., 1.62 mg/L = 1.603 mg ÷ 989 mL × 1,000 mL/L). Residuals were collected at 20 sec, 40 sec, and 60 sec and then at varying times for 9 min.

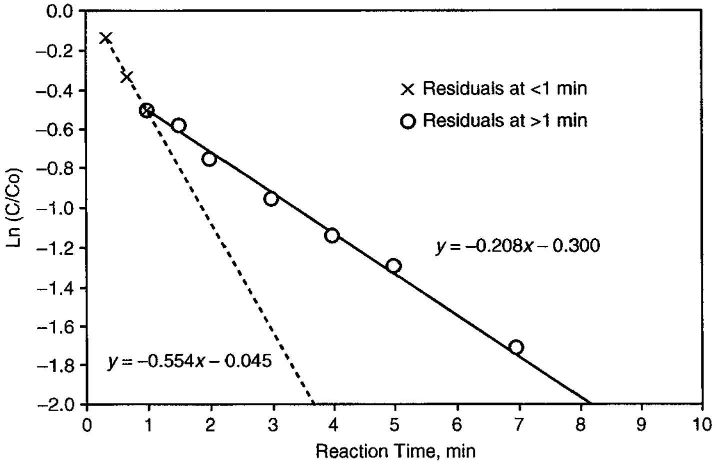

Figure 3-3 Ozone decay profile between 20 sec and 60 sec and beyond 60 sec

Data from test 11 plant B that are used in subsequent analyses include the ozone residual value at 60 sec and the ozone half-life value after 60 sec of reaction time. The ozone residual value at 60 sec (0.60 mg/L in Figure 3-2) represents the expected initial residual that will develop after 60 sec of ozone reaction time, which takes into account the initial ozone demand and first minute of fairly rapid ozone decay. After 1 min of ozone reaction time the rate of ozone decay is quite steady, as shown in Figures 3-2 and 3-3. The residual values that were collected between 20 sec and 60 sec have a fast decay rate of $-0.554\ \text{min}^{-1}$, which is an ozone half-life of 1.3 min (i.e., $1.3\ \text{min} = \ln[0.5] \div -0.554\ \text{min}^{-1}$). The ozone decay rate between 1 and 10 min of reaction time was $-0.208\ \text{min}^{-1}$, which is an ozone half-life of 3.3 min. The ozone half-life of 3.3 min portrays the expected ozone residual profile within the ozone contactor.

Six bench-scale tests were conducted on plant B water at a controlled sample temperature of 12°C and a pH of 6.5. The test data established the relationship between transferred ozone dose and 60-sec residual value, as shown in Figure 3-4. The 60-sec residual value increases with increasing dose at the linear rate indicated by the equation in Figure 3-4 but is always less than the transferred ozone dose due to the effect of ozone demand. Additional test data presented in Figure 3-5 are used to compare plant B results with results from three other plants. In all cases the 60-sec residual value increases in proportion to ozone dose. However, as seen in Figure 3-5, the 60-sec residual value is also affected by water temperature and pH, as well as other factors such as alkalinity and natural organic matter (NOM) type and concentration.

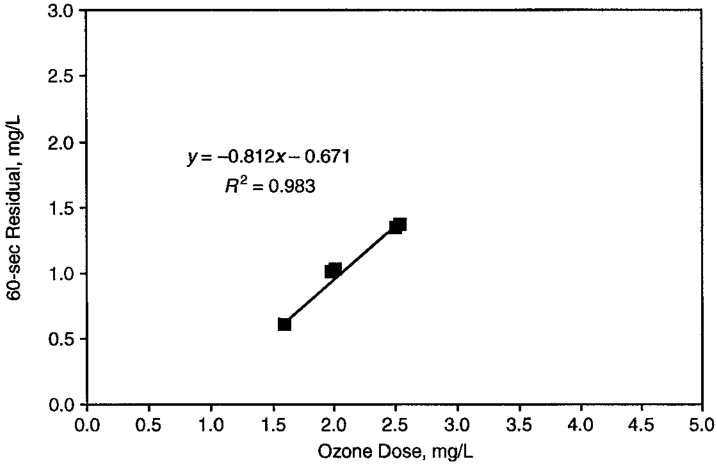

Figure 3-4 Transferred ozone dose versus 60-sec residual value for plant B (pH = 6.5 and temperature = 12°C) sample

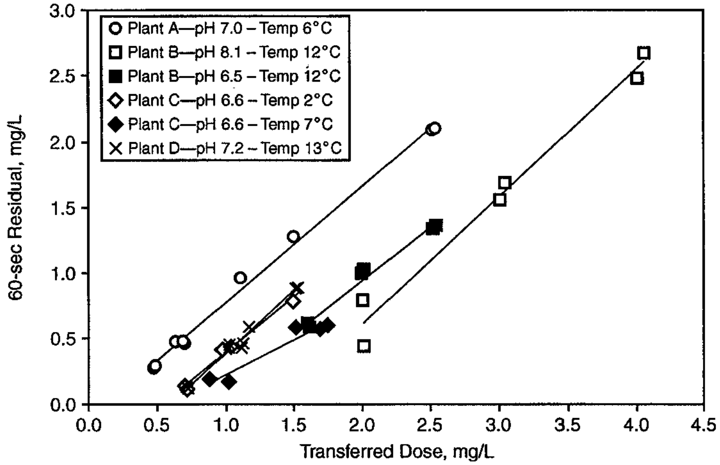

Figure 3-5 Transferred ozone dose versus 60-sec residual value for five water samples (Rakness and Hunter, 2000)

The value of the difference between transferred dose and 60-sec residual (i.e., "ozone demand" until 60-sec residual is established, or the initial ozone demand) also increases with ozone dose. This means that "initial ozone demand" is a variable number that changes with ozone dose. In the following paragraph, it is shown that ozone decay (i.e., half-life value) also changes in response to ozone dose. The important point is that neither ozone demand nor ozone decay is a fixed

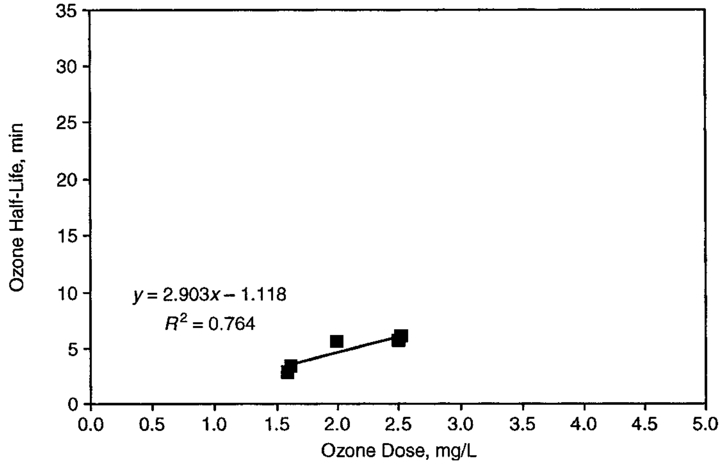

Figure 3-6 Transferred ozone dose versus ozone half-life for plant B (pH = 6.5 and temperature = 12°C) water sample

number and both depend on transferred ozone dose as well as water quality characteristics of pH, temperature, and NOM type and concentration.

The test relationship between ozone dose and ozone half-life value at plant B is shown in Figure 3-6. Here, too, the ozone half-life value increases as ozone dose increases. This might be due to increased oxidation of ozone-demanding substances as the ozone dose is increased. The ozone half-life value increased linearly for this test, which is indicated by the equation in Figure 3-6. For a given water quality (i.e., same pH, alkalinity, and NOM concentration), ozone half-life decreases as water temperature increases. Therefore, as a minimum, ozone half-life versus transferred dose data should be determined for the expected range of operating water temperatures (also water pH) at the full-scale plant.

Additional test data relating to half-life versus ozone-dose are shown in Figure 3-7 for three other plants that are compared to plant B. In all cases the ozone half-life value increased linearly as ozone dose increased. Similar to 60-sec residual, the ozone half-life value is affected by water temperature and pH as well as alkalinity and NOM type and concentration. An important observation from the half-life data is that the ozone decay rate is *not a single number* for a given water sample but is influenced by the transferred ozone dose (also applies to ozone demand, as discussed above). As a result of this occurrence, the bench-scale data must be incorporated into a model to properly assess the ozone dose for a full-scale disinfection system. The model should incorporate the type and size of the ozone contactor.

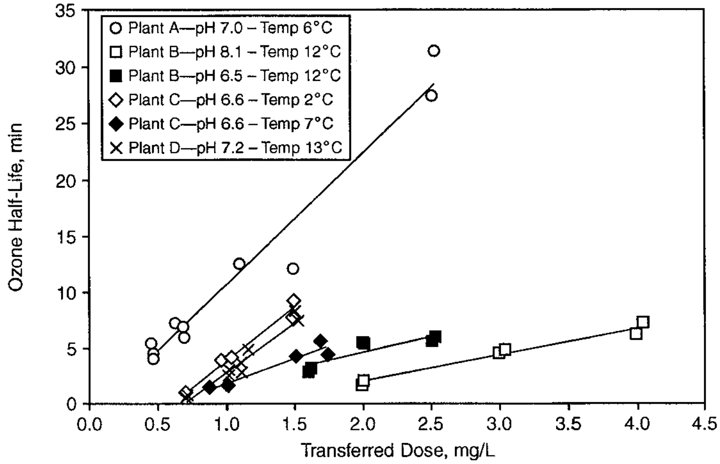

Figure 3-7 Transferred ozone dose versus ozone half-life for five water samples (Rakness and Hunter, 2000)

Full-Scale Contactor Modeling From Bench-Scale Ozone Test Results

The three steps for modeling contactor disinfection performance using bench-scale test data are:

1. Select a full-scale contactor size and type (e.g., number of chambers).
2. Using bench-scale data, forecast ozone residual profile as a function of detention time (volume ÷ flow) for a given ozone dose.
3. Calculate resulting CT value and inactivation credit.

Results from an example model are shown in Table 3-2 and Figure 3-8. The contactor is a six-chamber bubble-diffuser contactor with ozone added to chamber 1 only. (NOTE: This contactor was in operation at plant B, and model results are compared to full-scale results later in this section.) The ozone residual profile in Figure 3-8 was forecast from bench-scale test data for a selected ozone dose and individual-chamber HDT. HDT is used to develop residual profile projections, whereas T_{10} time is used in CT value calculations. Table 3-2 contains data that are used in the calculations as well as calculated results.

The assessed operating conditions shown in Table 3-2 are:

- Water temperature of 12°C and pH of 6.5 units;
- Applied ozone dose of 1.79 mg/L and transferred ozone dose of 1.70 mg/L (i.e., 95% transfer efficiency);
- Applied ozone dose to chamber 1 only;

Table 3-2 Estimated Residual Profile Using Bench-Scale Demand and Decay Data

Assessment Condition		
Water temperature	°C	12
Water pH	Units	6.5
Hydraulic detention time	min	12
Applied ozone dose	mg/L	1.79
Ozone transfer efficiency	%	95
Transferred dose	mg/L	1.70
Bench-Scale Demand/Decay Information		
Bench 60-dose slope	—	0.812
Bench 60-dose intercept	mg/L	–0.671
Bench half-life dose slope	min per mg/L	2.904
Bench half-life dose intercept	min	–1.118
Estimated Values From Bench-Scale Information		
60-sec residual	mg/L	0.71
Ozone half-life	min	3.82
Ozone decay rate	per min	–0.181
Estimated Residual Profile		
Location—Contactor Inlet	HDT min	Estimated Residual mg/L
Chamber 1	2.0	0.60
Chamber 2	2.0	0.42
Chamber 3	2.0	0.29
Chamber 4	2.0	0.20
Chamber 5	2.0	0.14
Chamber 6	2.0	0.10

- Bench-scale 60-sec residual and half-life slope and intercept values were taken from Figures 3-4 and 3-6, respectively; and
- Contactor HDT of 12 min, or 2 min per chamber.

The estimated residual value of 0.60 mg/L at the outlet of chamber 1 is developed using mixed-reactor Eq. 3-1 and Eq. 3-2. Required operating information is transferred ozone dose and individual chamber HDT. Required information from bench-scale tests are 60-sec residual and ozone half-life values. The 60-sec residual value is 0.71 mg/L at a transferred dose of 1.70 mg/L, as shown in Figure 3-4 (i.e., 0.71 = 1.70 × 0.812 – 0.671). The ozone half-life value is 3.82 min at a transferred dose of 1.70 mg/L, as shown in Figure 3-6 (i.e., 3.82 = 1.70 × 2.905 – 1.118). The

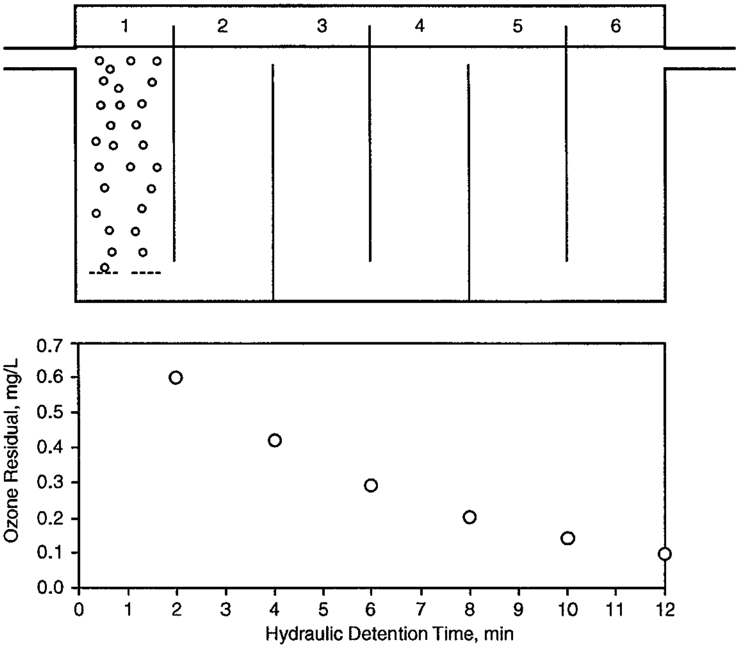

Figure 3-8 Estimated residual values from plant B demand and decay data

HDT in chamber 1 is 2 min; therefore, an additional 1 min of reaction time accounts for the predicted condition of C_1 = 0.60 mg/L (chamber 1 outlet residual), which is less than $C_{60\text{-sec}}$ at 0.71 mg/L.

$$C_1 = \left[\frac{C_{60-\text{sec}}}{1 - k^* \times (\text{HDT}_{\text{chamber 1}} - 1.00)}\right] \qquad \text{(Eq. 3-1)}$$

$$k^* = \frac{\text{Ln}(0.5)}{T_{1/2}} \qquad \text{(Eq. 3-2)}$$

Where:

C_1 = estimated outlet residual of chamber 1, mg/L
$C_{60\text{-sec}}$ = 60-sec ozone residual value from bench-scale results, mg/L
k^* = first-order ozone decay coefficient based on ozone half-life, min^{-1}
$T_{1/2}$ = ozone half-life from bench-scale results, min
$\text{HDT}_{\text{chamber 1}}$ = hydraulic detention time of chamber 1, min
1.00 = accounts for the fact that the initial residual is the 60-sec (1-min) residual value and not the residual at time zero

$$\text{solution} = k^* = -0.181 = \frac{\mathrm{Ln}(0.5)}{3.82}$$

$$\text{solution} = C_1 = 0.60 = \left[\frac{0.71}{1 + 0.181 \times (2 - 1.00)}\right]$$

The residual values at the outlet of downstream reactive chambers are determined using plug-flow reactor Eq. 3-3. The example solution of 0.42 mg/L is the outlet residual from chamber 2. The inlet residual, $C_{x\text{-}1}$, is 0.60 mg/L. The HDT of chamber 2 is 2 min. The ozone half-life is 3.82 min, which gives an ozone decay rate of –0.181 min^{-1} (see above). Residuals in downstream chambers are calculated similarly.

$$C_x = C_{x-1} \times e^{\text{HDT}_x \times k^*} \qquad \text{(Eq. 3-3)}$$

Where:

C_x = estimated outlet residual of downstream reactive chamber x, mg/L

C_{x-1} = estimated residual value from preceding upstream, mg/L

k^* = first-order ozone decay coefficient based on ozone half-life, min^{-1}

HDT_x = hydraulic detention of downstream reactive chamber x, min

$$\text{solution} = C_2 = 0.42 = 0.60 \times e^{2 \times (-0.181)}$$

The estimated residual values shown in Table 3-2 are applied to disinfection CT-value and log-inactivation calculations in Table 3-3, as discussed in chapter 2. *Giardia*- and virus-inactivation values are calculated using the C_{effluent} method for the CT-value calculation. The design T_{10}/T ratio was 0.60. The calculated CT value was 1.38 mg-min/L. The *Giardia*- and virus-inactivation values were 3.87 log and 7.95 log, respectively. Associated IRs for *Giardia* and viruses were 3.87 and 2.65, respectively, when the target log credits were 1 log and 2 log, respectively. (NOTE: Minimum requirement was 0.5 log and 2 log, respectively, but the assessment in this example was for 1 log and 2 log, respectively.)

The assessment of bench-scale data (discussed earlier) included use of an ozone contactor model designed for a given size (HDT) and number of individual chambers. This modeling approach can be used with variable water quality (e.g., summer and winter conditions) and different contactor design criteria. The approach could be used to determine design criteria for either raw water (pre-ozone) or settled water (intermediate-ozone) applications. For new plants, evaluation of settled water might utilize bench-scale jar testing procedures to approximate settled water conditions. The end point in the analysis is the required ozone dose and contactor size and shape. The ultimate design ozone dose might be increased slightly to account for untested water quality conditions or scale-up inaccuracy.

Table 3-3 Estimated Disinfection From Bench-Scale Demand and Decay Data

T_{10}/T Ratio is	0.60	Typical range is 0.5 to 0.7				
Water temperature	12.0	°C				
	Gas Added	Predicted Residual	HDT	C for CT	T for CT	CT
	Y or N	mg/L	min	mg/L	min	mg/L × min
Chamber 1	Y	0.60				
Chamber 2		0.42	2.00	0.42	1.20	0.50
Chamber 3		0.29	2.00	0.29	1.20	0.35
Chamber 4		0.20	2.00	0.20	1.20	0.24
Chamber 5		0.14	2.00	0.14	1.20	0.17
Chamber 6		0.10	2.00	0.10	1.20	0.12
			Subtotal for Measured CT			1.38
			Virus Inactivation Credits			
	Virus Inact. Rate	From CT	Direct	Total	Required	Virus IR
	k_v	Log I	Log I	Log I	Log I	—
	5.04	6.95	1.00	7.95	3.0	2.65
			Giardia Inactivation Credits			
	Giardia Inact. Rate	From CT	Direct	Total	Required	*Giardia* IR
	k_g	Log I	Log I	Log I	Log I	—
	2.45	3.37	0.50	3.87	1.0	3.87

Contactor Modeling Comparisons and Cautions

Rakness and Hunter (2000) assessed potential scale-up inaccuracy of the contactor modeling approach just discussed. Bench-scale tests were conducted on water samples collected at full-scale ozone facilities. Measured disinfection results from full-scale operation were compared to projected disinfection results from bench-scale testing. Table 3-4 shows plant B's full-scale measured residual values and calculated disinfection results. In this case the full-scale disinfection results are nearly identical to bench-scale projections. Assessments were also completed for other plants (referenced in Figures 3-5 and 3-7) (Rakness and Hunter, 2000). The goal of the assessments was to determine the bench-scale ozone dose that was required such that the full-scale measured and bench-scale estimated disinfection results are identical. Figure 3-9 compares the required bench-scale dose with the measured full-scale dose. In several cases the estimated bench-scale dose was nearly equal to the measured full-scale dose. In all cases the estimated bench-scale dose was within ±20% of measured full-scale dose. In most cases when doses were

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Table 3-4 Achieved Disinfection Performance for Full-Scale Plant B Measured Data

T_{10}/T Ratio is	0.60	Typical range is 0.5 to 0.7				
Water Temperature	12.0	°C				
	Gas Added	Predicted Residual	HDT	C for CT	T for CT	CT
	Y or N	mg/L	min	mg/L	min	mg/L × min
Chamber 1	Y	0.60				
Chamber 2		0.40	2.00	0.40	1.20	0.48
Chamber 3		0.32	2.00	0.32	1.20	0.39
Chamber 4		0.21	2.00	0.21	1.20	0.25
Chamber 5		0.14	2.00	0.14	1.20	0.17
Chamber 6		0.10	2.00	0.10	1.20	0.12
			Subtotal for Measured CT			1.40
				Virus Inactivation Credits		
	Inact. Rate	From CT	Direct	Total	Required	Virus IR
	k_v	Log I	Log I	Log I	Log I	—
	5.04	7.08	1.00	8.08	3.0	2.69
				Giardia Inactivation Credits		
	Inact. Rate	From CT	Direct	Total	Required	*Giardia* IR
	k_g	Log I	Log I	Log I	Log I	—
	2.45	3.43	0.50	3.93	1.0	3.93

unequal, the bench-scale dose was less than the full-scale measured dose. Given this finding, a factor of safety of at least 20% might be applied to bench-scale dose assessments.

Incorporation of contactor design into the assessment of ozone dose is one of the most important factors affecting the accuracy of scale-up using bench-scale and pilot-scale data (Rakness and Hunter, 2000). Consider the often, but incorrectly, implemented pilot-plant setup of a single-column bubble-diffuser contactor that has 10-min hydraulic detention time. The ozone residual value that is measured at the outlet of this single tank will be discounted significantly because the residual is subjected to 10 min of ozone decay (and also 10 min of ozone reaction) before the water leaves the vessel. Full-scale ozone contactors are not single-chamber vessels but are compartmentalized into several chambers or are pipeline (long-channel) units. In either case, ozone residual is measured along the contactor and *not solely at the contactor outlet.* Similarly, bench-scale and pilot-scale

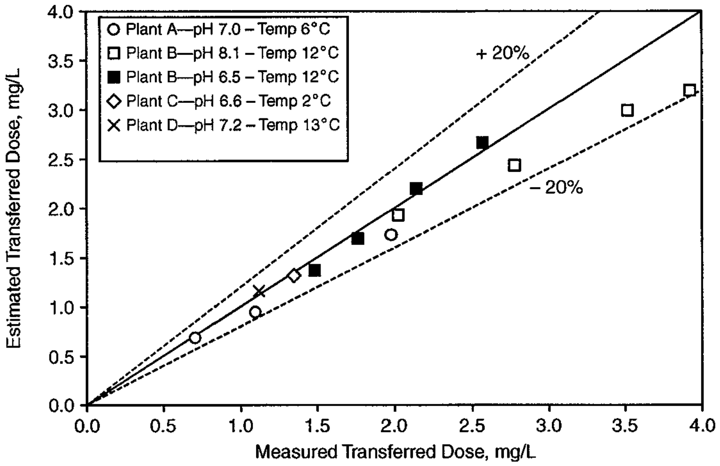


Figure 3-9 Comparison of bench-scale estimated ozone dose versus full-scale measured ozone dose to achieve equivalent disinfection performance

tests must take into account the fact that ozone residual is measured within the ozone contactor.

The preferred setup for a pilot plant is to have multiple columns that mimic full-scale contactor chambers, as shown in Figure 3-10. The 12 individual columns (chambers) shown in Figure 3-10 have 2 min HDT. If funding prevents a multiple-chamber installation, as a minimum, the HDT of pilot-plant ozone-dissolution chamber 1 should match the HDT of full-scale contactor chamber 1. The outlet from chamber 1 can then be used to measure ozone decay rate. A sample can be collected in a container (i.e., vessel with minimum head space to avoid off-gassing) and residual samples subsequently collected over time. Ultimately, the full-scale residual profile can be projected using the information from the chamber 1 outlet residual and ozone decay rate.

GENERATOR DESIGN SIZE AND STANDBY CAPACITY

The capital cost for ozone generators increases in proportion to size, which is frequently listed by production capacity only. However, operating ozone concentration and cooling water temperature also affect generator cost. Achieving a specified production capacity at high ozone concentration (e.g., 12 %wt) and elevated cooling water temperature (e.g., 90°F) requires higher power demand than achieving that same ozone production rate at lower ozone concentration (e.g., 8 %wt) and reduced cooling water temperature (e.g., 60°F). All of these parameters—production, concentration, and cooling water temperature—must be specified.

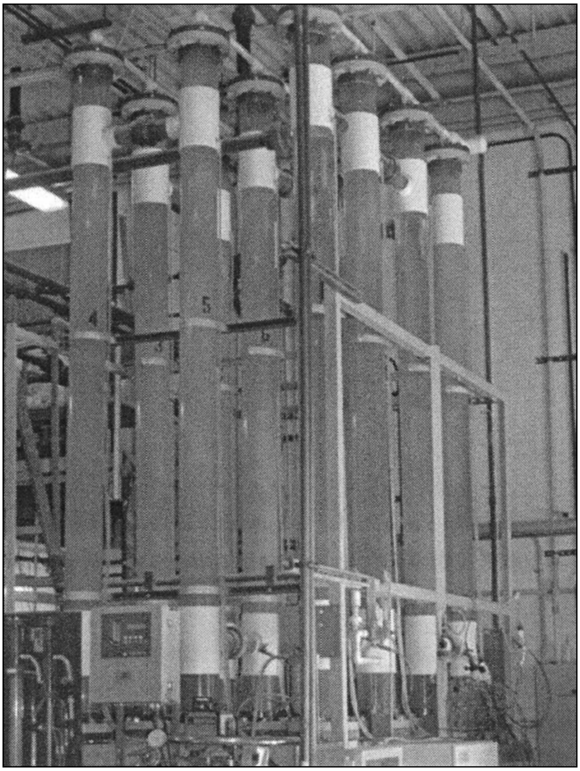


Figure 3-10 Multicolumn ozone pilot plant that mimics full-scale contactor chambers

Generator Capacity—Availability and Sizing

Individual ozone generators can produce lab-scale ozone quantities of less than 1 lb/d to large plant-scale amounts of 4,000 lb/d and possibly higher. Lab-scale generators are usually air-cooled units; plant-scale generators are water-cooled vessels.

Ozone system suppliers currently offer self-contained units (both the PSU and generator vessel) for capacities up to 200 lb/d. Larger-capacity units separate the power supply unit (PSU) and the ozone generator vessel. The ozone generator vessel, with inlet piping, outlet piping, and instrumentation, is generally remotely assembled and skid-mounted, as shown in Figure 3-11. The PSU cabinet can be located next to the vessel or placed in a separate room. The American Water Works Association and the International Ozone Association have listings of ozone system suppliers to contact concerning recent updates and improvements in ozone generation equipment.

Generator size is defined precisely by its required power demand. Ozone production capacity is the primary factor to consider when determining the

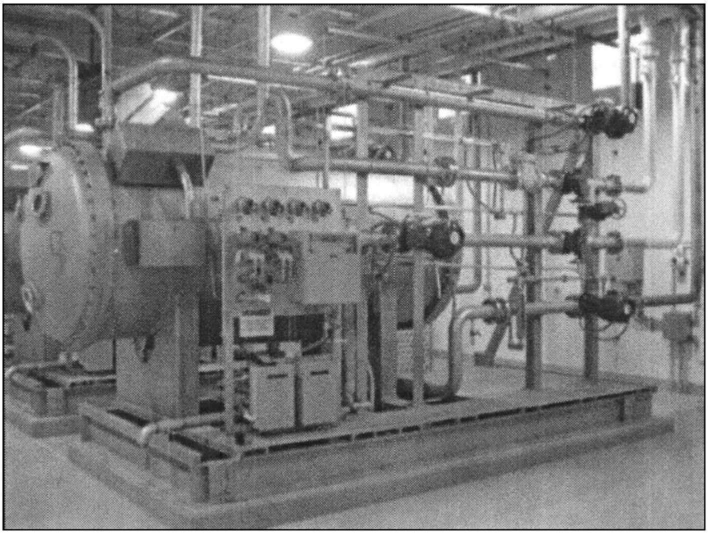


Figure 3-11 Skid-mounted 1,600-lb/day ozone generator vessel with instrumentation

amount of power required, but cooling water temperature and operating ozone concentration also influence power demand. Figure 3-12 depicts the effect of cooling water temperature on ozone production and power demand. In the figure, the ozone generator was sized to achieve 100% design production capacity when operating at 100% power. The cooling water entered the vessel at 25°C and exited at 28°C (i.e., 3°C ΔT). Figure 3-12 indicates that the ozone production rate was 15% higher at a cooling water temperature of 10°C, with the same 3°C ΔT, same gas flow, and same generator power. Given the effects of cooling water temperature on production capacity, the design specifications for the ozone generator must state the maximum cooling water temperature and operating ozone concentration, along with the required ozone production capacity.

Generator Cooling Water Considerations

Chillers are rarely used to reduce cooling water temperature. Several ozone installations are designed to operate at ambient cooling water temperatures between 85°F and 95°F. The ambient temperature cooling water is used to cool the generator vessel itself; however, air conditioners are often used to cool the PSUs. Ozone system suppliers size the generator vessels and PSU to meet production rates, with due consideration given to elevated cooling water temperature. Alternatively, some ozone system suppliers prefer to use chillers to cool both the generator vessel and PSU when the ambient cooling water temperature is elevated. Chillers do not necessarily reduce overall energy efficiency,

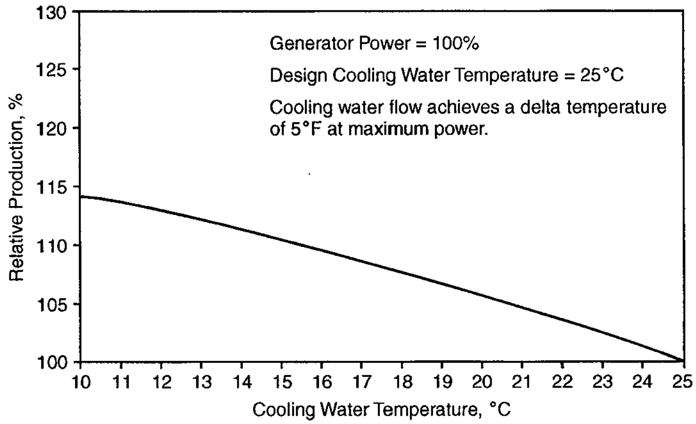


Figure 3-12 Effect of cooling water temperature on ozone production capability (somewhat variable among ozone system suppliers)

because energy is required to operate the chiller. Chillers generally do increase overall operation and maintenance (O&M) activities, because chillers and circulation pumps are additional equipment components.

The flow rate of the cooling water affects ozone production capacity to a limited extent. Typically, the specified ΔT across the ozone generator vessel is between 5°F and 10°F, with the lower ΔT value used when ambient cooling water temperature is elevated (e.g., above 75°F). The corresponding flow rate of cooling water through the generator vessel is between 1.2 and 0.6 gpm/kW of applied power, respectively. Additional cooling water flow is directed to the PSU, at about 0.1 gpm/kW of applied power. Ozone system suppliers generally require site-specific flow rates of cooling water, depending on individual equipment design considerations.

The cooling water must be noncorrosive, nonscaling, void of particles that would settle or collect inside the generator vessel, and low in chloride concentration (this component is variable, and the ozone system supplier should be consulted). Some plants use once-through cooling water systems in which nonchlorinated filtered water is directed through the generator vessel and returned to the head of the plant or to the ozone contactor inlet. Other plants use once-through chlorinated utility water (this component is variable, and the ozone system supplier should be consulted), which also is returned to the head of the plant or to the ozone contactor inlet. Ozone generators in standby often receive a small amount of cooling water flow to avoid development of stagnant water inside the generator vessel (this component is variable, and the ozone system supplier should be consulted).

Alternatively, many plants use open-loop–closed-loop cooling water systems with a plate-frame heat exchanger, like the one shown in Figure 3-13. The water

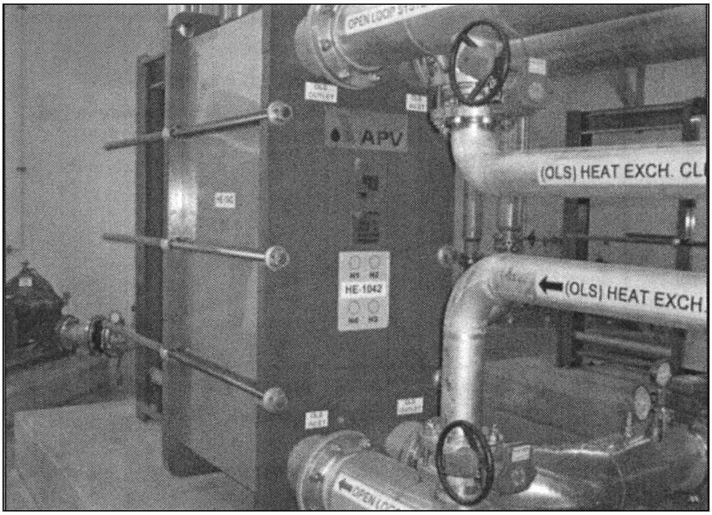


Figure 3-13 Open-loop–closed-loop cooling water system with plate-frame heat exchanger

quality in a closed-loop system is controlled to maintain nonscaling and noncorrosive characteristics. Water in an open-loop system is good quality raw water, settled water, or filtered water. More information concerning cooling water flow and O&M considerations is presented in chapters 4 and 5.

Operating Ozone Concentration Considerations

The rate of gas flow through the ozone generator and resultant ozone concentration also affect ozone production capacity at given generator power demand (Figure 3-14). In the figure the oxygen-fed ozone generator was sized to achieve 100% design production capacity for two design scenarios. One scenario was to size the generator power demand to achieve design ozone production while operating at 11 %wt. Then, when gas flow is increased such that the ozone concentration is 6 %wt, ozone production increases by more than 45%. The second scenario was to size the generator power demand to achieve design ozone production while operating at 10 %wt (i.e., smaller generator is required). Then, when gas flow is increased such that ozone concentration is 6 %wt, ozone production increases by more than 30%. In either case, ozone production increases as ozone concentration decreases (i.e., as gas flow increases, all other operating conditions—power, cooling water flow, etc.—are unchanged). The operating cost might increase when operating at 6 %wt instead of 10 %wt or 11 %wt (see chapter 5). However, operating less efficiently for a short period of time is likely to be more cost effective to meet peak production than installing larger and more

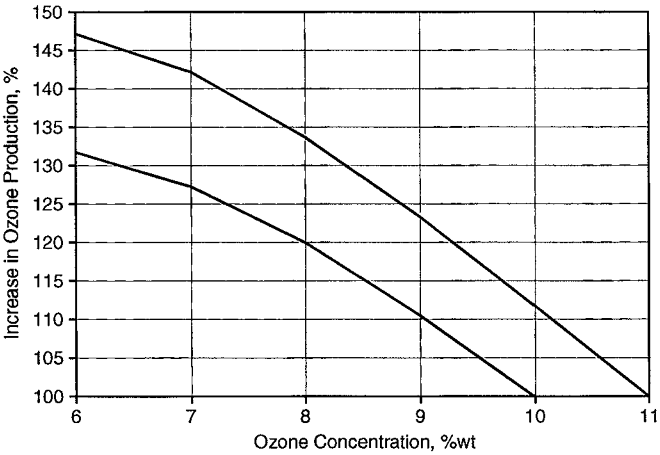


Figure 3-14 Effect of ozone concentration on ozone production capability (based on specific energy data from Figure 4-56)

expensive ozone generators that have greater power demand. (NOTE: Gas flow rate to the contacting system [sidestream and bubble diffuser] must be designed to accept the higher flow rate.)

The ozone production capacity should be assessed carefully to avoid overdesign. Design capacity should be based on expected water flow and ozone dose conditions, which will be other than maximum water flow and maximum ozone dose unless both maximums are expected simultaneously. For example, design production capacity should be assessed for each month of the year, considering the expected flow and dose operating conditions for the subject month. This can be completed using production frequency analysis (Huang and Edmonson, 2004). Bench-scale studies can be conducted to assess dose requirements for the month or season of the year in question, as discussed earlier. Water flow rate can be determined from historical water use records. An approach used in some designs is to size the ozone generator at 10 %wt, 11 %wt, or 12 %wt ozone concentration for the evaluated seasonal average production rate and consider that extra production capacity is available for the maximum production condition by operating at a lower ozone concentration of 6 %wt. (NOTE: The capacity of the LOX-to-gaseous oxygen [GOX] vaporizers should be sized based on the maximum design ozone production rate and lowest ozone concentration value.)

Generator Number and Standby Capacity

Because ozone is unlike other water treatment chemicals, standby capacity should be assessed carefully. Most water treatment chemicals (e.g., alum or chlorine) are produced off site, stored on site, and delivered to the process by chemical feed pumps. Standby capacity is achieved relatively inexpensively by simply installing redundant chemical feed pumps. In contrast, ozone equipment both produces and delivers ozone on site. Consequently, the capital cost for standby capacity is higher because installed standby capacity includes redundant on-site ozone production capability.

Standby "ozone" can be provided by:

- Switching to chlorine disinfection for short periods of time, even if TTHM concentration is elevated during this short time frame;
- Increasing production capability of operating generators by increasing gas flow rate and reducing operating ozone concentration; and
- Installing redundant ozone generators.

Depending on plant size, a treatment plant will have one generator plus one standby, two plus one standby, three plus one standby, etc. Equipment reliability is another consideration. Should another generator be installed in case one unit fails and a second unit is out for maintenance? Most plants find that their ozone generators are reliable, but owner conservatism and design risk tolerance ultimately influences the final design criterion for standby/backup capacity.

The number of ozone generators is also influenced by ozone generator power, gas flow, and production turndown capability. The capability for turndown in the production rate is influenced by the capability for turndown of both gas flow and applied power. Medium-frequency ozone generators on the market today typically are capable of 10:1 turndown in applied power, or better. Some are capable of similar turndown in gas flow, which gives an overall 10:1 turndown in ozone production rate while ozone concentration remains unchanged. Other suppliers have 6:1 turndown of gas flow (i.e., higher value is required for minimum gas flow rate), which means that overall ozone production turndown capability is 8:1 or 9:1 instead of 10:1. The minimum expected ozone production rate should be established to ensure that a single ozone generator can meet minimum ozone dose requirements at the minimum water flow rate. (NOTE: Contactor operation and turndown conditions also must be evaluated.)

LOCATION OF OZONE APPLICATION

Ozone is applied at different locations within a water treatment plant to achieve a variety of treatment objectives. Three common locations are:

- Pre-ozone: ozonation of the raw water prior to rapid-mix.
- Intermediate-ozone: ozonation of settled water prior to filtration.
- Pre-ozone and intermediate-ozone: both raw water and settled water ozonation.

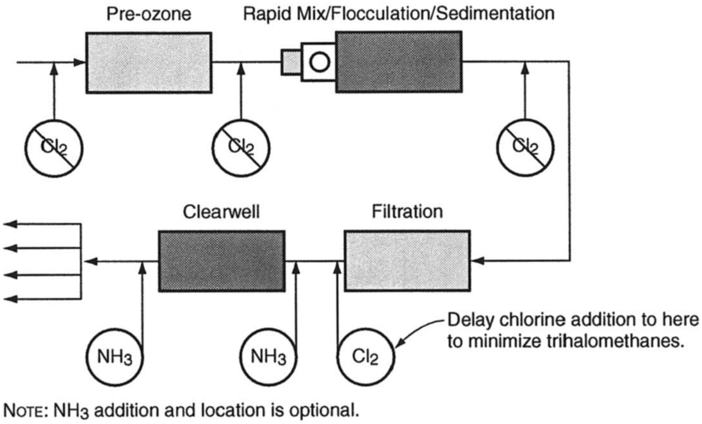


Figure 3-15 Pre-ozone location for the ozone contactor

Figure 3-15 shows a pre-ozone location. The ozone contactor is placed in front of rapid mix in a conventional or direct filtration plant. Some water utilities that have very high-quality raw water use ozone without filtration to meet disinfection regulations.

Pre-ozone applications provide a variety of water quality benefits such as disinfection; disinfection by-product reduction that is achieved by moving the chlorine application point downstream; elimination of undesirable tastes, odors, and color; enhanced particle removal; reduction in coagulant dose; and biological stability of filtered water that also is achieved by moving the chlorine application point downstream of the filters. Figure 3-15 illustrates that chlorine is added after the filters. Development of chlorine residual is necessary for secondary disinfection in the distribution system. Chloramine residual in the distribution system can be achieved by adding ammonia. However, when chloramination is implemented it is important to provide free-chlorine residual contact time after biological filters to reduce the heterotrophic plate count value in the filter effluent and achieve chloramine residual stability in the distribution system (Wilczak et al., 2003). The importance of a free chlorine contact time has been observed in other facilities as well (telephone conversation with Chuck Vokes, Interim Assistant Director of Utilities, Arlington, Texas, April 2004). Preliminary investigations indicate that 2- to 5-min free chlorine contact times are necessary in Arlington, Texas, to prevent excessive chloramine decay in the distribution system.

Intermediate ozone addition is a preferred location in some plants, especially when raw water quality is poor and disinfection ozone dose is too high. In these plants ozone is often added at an intermediate location, i.e., after sedimentation and before filtration, to achieve disinfection only. Figure 3-16 illustrates an

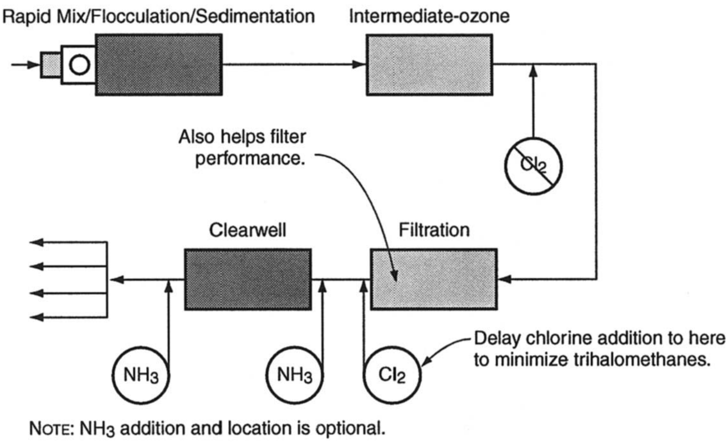


Figure 3-16 Intermediate-ozone location for the ozone contactor

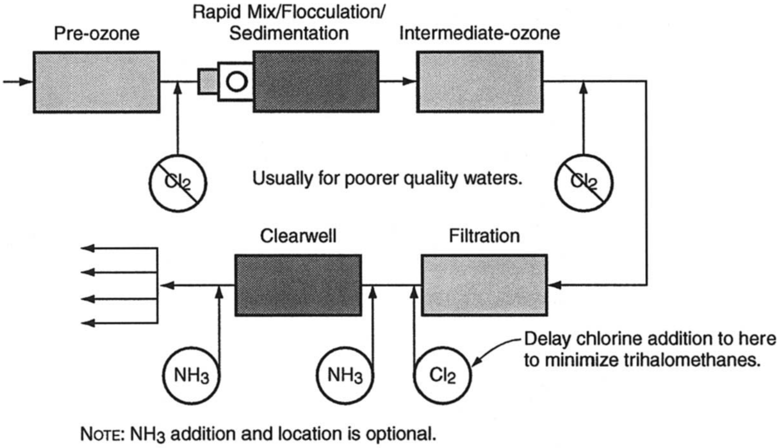


Figure 3-17 Pre-ozone and intermediate-ozone locations for ozone contactors

intermediate-ozone location. All benefits described for pre-ozonation are achieved, except for reduction in coagulant dosage. To obtain pre-oxidation benefits, plants add a small ozone dose at a pre-ozone location and a disinfection dose at an intermediate-ozone location, as shown in Figure 3-17. Pre-ozone and intermediate-ozone together is called two-stage ozonation.

Some water treatment plants have insufficient hydraulic head (e.g., 2 ft to 4 ft) to insert an ozone contactor between the sedimentation basins and the filters, even if water depth in the sedimentation basin is increased and/or filter operating water level is decreased. The Helix Water District, Lakeside, California, solved this

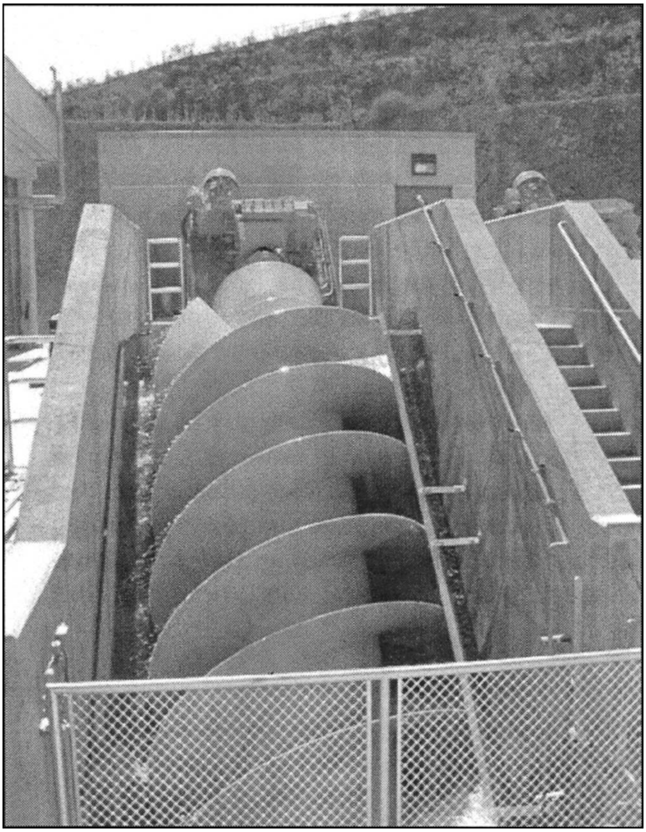


Figure 3-18 Screw pump installation between sedimentation basin and filters for intermediate-ozone contactor application

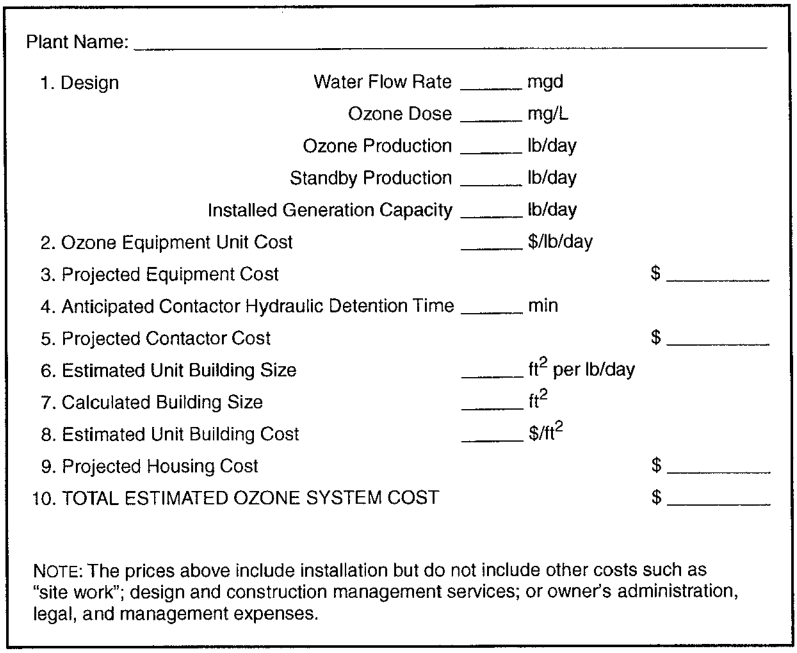
dilemma by installing screw pumps (Figure 3-18) to elevate and direct the sedimentation basin effluent through the intermediate ozone contactors before returning settled water flow to the filter influent. The East Bay Municipal Utility District, Oakland, California, converted a portion of their existing sedimentation basins to ozone contactors (Bellamy, 1995).

ESTIMATES OF OZONE SYSTEM COSTS

Developing estimates for ozone system capital and operating costs is a key component of ozone system design. Capital costs are the most difficult to estimate because there are so many factors that affect cost, such as level of instrumentation and automation, local construction costs, quantity of stainless steel piping (i.e., distance between equipment), and other factors. Charts that present capital cost estimates discussed here were obtained from *Ozone in Water Treatment: Application* *and Engineering* (Langlais et al., 1991). These charts are 13 years old and were developed based on capital cost information for air-fed ozone systems. However, even though inflation has occurred over the years, the capital costs of a LOX-fed ozone system are lower and the charts are considered to still be applicable.

Operating cost information is geared to a LOX-fed ozone system. Operating cost estimates are generally better than capital cost estimates, because energy price (\$/kWh) and LOX price (\$/lb O_2) can be obtained for a site-specific application. Also, generator efficiency is fairly well defined (see Figure 4-2, chapter 4) and overall ozone system energy usage can be estimated considering that energy consumption by equipment other than the ozone generator (e.g., off-gas destruct system, cooling water pumps, etc.) is a minor contribution to overall system power demand (e.g., +5% to +10%).

Capital cost estimates for an ozone system may be obtained by completing the form in Figure 3-19, which can be used in two ways. One way is to use the form to assist with an independently developed cost estimate that considers the factors outlined in the form, such as ozone generation plus supporting equipment, ozone contactors, building for equipment housing, design engineering, construction inspection, and other costs. The second way is to use the form, along with the



Plant Name: ______________________________

1. Design Water Flow Rate ______ mgd
Ozone Dose ______ mg/L
Ozone Production ______ lb/day
Standby Production ______ lb/day
Installed Generation Capacity ______ lb/day
2. Ozone Equipment Unit Cost ______ \$/lb/day
3. Projected Equipment Cost \$ __________
4. Anticipated Contactor Hydraulic Detention Time ______ min
5. Projected Contactor Cost \$ __________
6. Estimated Unit Building Size ______ ft^2 per lb/day
7. Calculated Building Size ______ ft^2
8. Estimated Unit Building Cost ______ \$/ft^2
9. Projected Housing Cost \$ __________
10. TOTAL ESTIMATED OZONE SYSTEM COST \$ __________

NOTE: The prices above include installation but do not include other costs such as "site work"; design and construction management services; or owner's administration, legal, and management expenses.

Figure 3-19 Blank order-of-magnitude capital cost form

Plant Name: ____________________

1. Design	Water Flow Rate	30	mgd	
	Ozone Dose	3	mg/L	
	Ozone Production	750	lb/day	
	Standby Production	250	lb/day	
	Installed Generation Capacity	1,000	lb/day	
2. Ozone Equipment Unit Cost		2,000	\$/lb/day	
3. Projected Equipment Cost				\$ 2,000,000
4. Anticipated Contactor Hydraulic Detention Time		10	min	
5. Projected Contactor Cost				\$ 1,000,000
6. Estimated Unit Building Size		3.6	ft^2 per lb/day	
7. Calculated Building Size		3,600	ft^2	
8. Estimated Unit Building Cost		150	\$/ft^2	
9. Projected Housing Cost				\$ 540,000
10. TOTAL ESTIMATED OZONE SYSTEM COST				\$ 3,540,000

NOTE: The prices above include installation but do not include other costs such as "site work"; design and construction management services; or owner's administration, legal, and management expenses.

Figure 3-20 Completed order-of-magnitude operating cost form

figures described in the following paragraphs, to obtain an order-of-magnitude cost estimate.

A completed capital cost estimate form is shown in Figure 3-20 for a 30-mgd water treatment plant that has a design ozone dose of 3 mg/L. The firm ozone capacity is 750 lb/d and the estimated total installed capacity is 1,000 lb/d (i.e., capital cost is developed using total installed ozone capacity). From Figure 3-21, the unit cost of ozone equipment, including installation, is \$2,000 per lb/d, which results in a total installed equipment cost of \$2,000,000.

The ozone contactor detention time is projected to be 10 min. Figure 3-22 is used to obtain an estimate for contactor capital costs in the following way. The cost chart was developed assuming that two contactors are installed, with each contactor sized for 50% of the design water flow rate. The design water flow rate is 30 mgd in the example; therefore, the contactor cost value of \$1,000,000 is obtained from the chart using 15-mgd flow for *each* contactor (i.e., 15 mgd is 50% of 30 mgd). The contactor detention time chosen was 10 min, but longer or shorter detention times can be selected for site-specific applications. Contactor costs increase as detention time increases, and vice versa. For example, costs might be 50% higher if the detention time is doubled to 20 min or decreased by 25% if detention time is cut in half to 5 min.

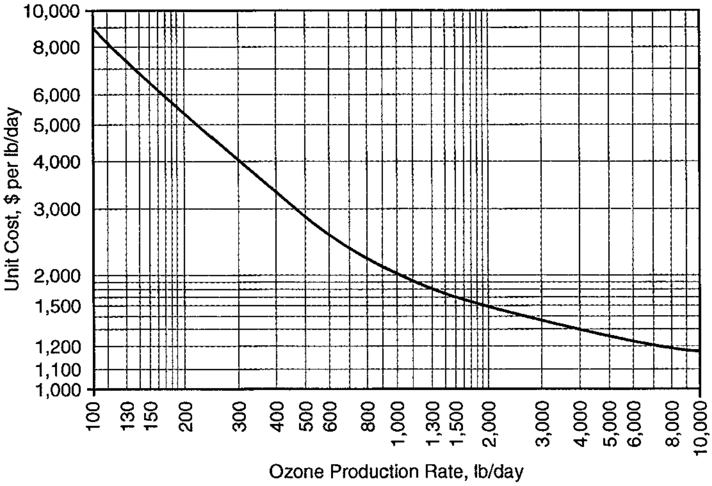


Figure 3-21 Order-of-magnitude cost for ozone system based on installed generation capacity (Langlais et al., 1991)

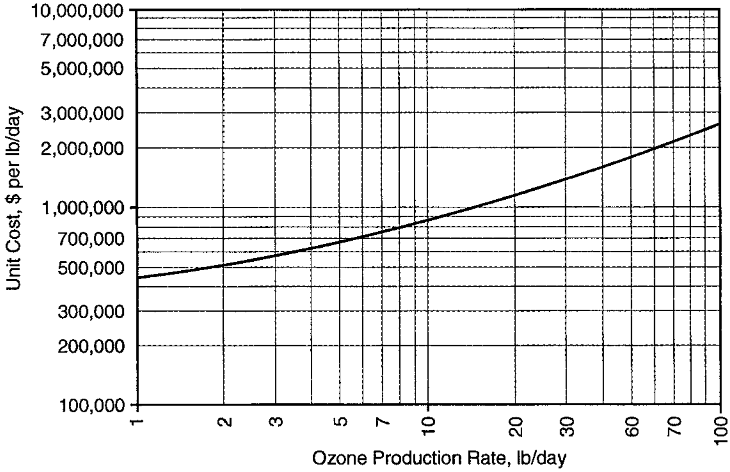


Figure 3-22 Order-of-magnitude cost for ozone contactors (assume 10-min detention time) (Langlais et al., 1991)

The approximate building floor space sizing criterion for equipment housing, at 3.6 ft^2 per lb O_3/d, is obtained from Figure 3-23. Estimated total building floor space is 3,600 ft^2 (i.e., 3,600 ft^2 = 3.6 ft^2 per lb/d × 1,000 lb/d). The assumed unit price is \$150/ft^2 for construction of the equipment housing structure that matches other buildings at the water treatment plant. These estimates result in a total building cost of \$540,000.

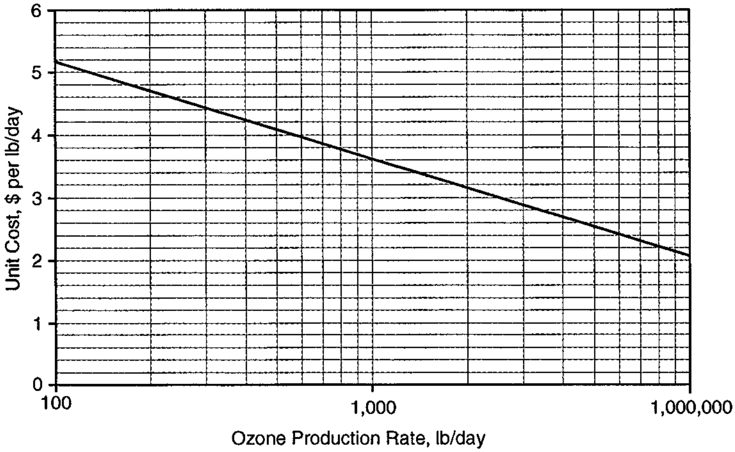


Figure 3-23 Estimated unit floor space for ozone equipment (Langlais et al., 1991)

The estimated total ozone system cost is $3,540,000 for this example with assumptions, which include costs for ozone equipment, ozone contactor, and ozone building. This estimate includes equipment installation but excludes other costs such as site work; design and construction management services; and owner's administration, legal, and management expenses.

The form in Figure 3-24 can be used to develop an estimated operating cost of a LOX-fed ozone system. A completed form is shown in Figure 3-25 for a plant with an average annual water flow rate of 20 mgd that is operating at an average annual ozone dosage of 2 mg/L, which is an average annual ozone production rate of 333 lb/d. The estimated total system specific energy value of 5.5 kWh/lb for the system was determined by assuming that the operating ozone concentration is 10 %wt, ozone generator specific energy is 5.0 kWh/lb (see Figure 4-2), and other equipment energy consumption is 10% of ozone generation consumption (i.e., 0.5 kWh/lb = 10% × 5.0 kWh/lb). The resulting total system energy cost is $53,480 per year at an assumed energy price of $0.08/kWh (i.e., $53,480 = 333 lb/d × 5.5 kWh/lb × $0.08/kWVh × 365 days/year). At an assumed LOX price of $0.04/lb O_2, the estimated annual LOX cost is $48,618 (i.e., $48,618 = 333 lb O_3/d ÷ 10 lb O_3 × 100 lb O_2 × $0.04/lb O_2 × 365 days/year). The total annual cost of energy and LOX is $102,098, which is a unit-mass cost for ozone generation of $0.84/lb O_3.

For an air-fed ozone system, O&M cost was estimated to be 20% to 35% of the total energy cost (Langlais et al., 1991). The maintenance of a LOX-fed ozone system is significantly reduced compared to maintenance of an air-fed ozone system and is assumed to be 20% of the energy + LOX cost in the example in Figure 3-25, or $20,420 (i.e., $20,420 = 20÷100 × $102,098). The total energy, Plant Name: ____________________

1. Operating Information
    Average Annual Water Flow Rate ______ mgd
    Average Annual Dose ______ mg/L
2. Average Annual Production ______ lb/day
3. Estimated System Specific Energy ______ kWh/lb (range 4 to 6.5 kWh/lb)
4. Estimated Price of Energy ______ $/kWh
5. Estimated Annual Cost of Energy (2 × 3 × 4 × 365) $ ______
6. Estimated Operating Ozone Concentration ______ %wt
7. Estimated Oxygen Price ______ $/lb (typical range $0.03 to $0.05/lb O_2)
8. Estimated Annual Cost of Oxygen (2 / 6 × 100 × 7 × 365) $ ______
9. Estimated Annual Cost of Energy and Oxygen (5 + 8) $ ______
10. Unit-Mass Cost of Ozone Generation (i.e., $/lb O_3) $ ______
11. Estimated Cost Factor of O&M ______ %
12. Estimated Annual Cost for O&M (9 × 10) $ ______
13. TOTAL ESTIMATED OZONE SYSTEM ANNUAL OPERATING COST $ ______
14. Unit-Volume Cost of Ozone (i.e., $/mil gal) $ ______

Figure 3-24 Blank order-of-magnitude operating cost form

Plant Name: ____________________

1. Operating Information
    Average Annual Water Flow Rate 20 mgd
    Average Annual Dose 2 mg/L
2. Average Annual Production 333 lb/day
3. Estimated System Specific Energy 5.5 kWh/lb (range 4 to 6.5 kWh/lb)
4. Estimated Price of Energy 0.08 $/kWh
5. Estimated Annual Cost of Energy (2 × 3 × 4 × 365) $ 53,480
6. Estimated Operating Ozone Concentration 10 %wt (e.g., 8 %wt)
7. Estimated Oxygen Price 0.04 $/lb (typical range $0.03 to $0.05/lb O_2)
8. Estimated Annual Cost of Oxygen (2 / 6 × 100 × 7 × 365) $ 46,618
9. Estimated Annual Cost of Energy and Oxygen (5 + 8) $ 102,098
10. Unit-Mass Cost of Ozone Generation (i.e., $/lb O_3) $ 0.84
11. Estimated Cost Factor of O&M 20 %
12. Estimated Annual Cost for O&M (9 × 10) $ 20,420
13. TOTAL ESTIMATED OZONE SYSTEM ANNUAL OPERATING COST $ 122,517
14. Unit-Volume Cost of Ozone (i.e., $/mil gal) $ 17

Figure 3-25 Completed order-of-magnitude operating cost form

LOX, and O&M costs are $122,517 per year, or $17/mil gal of ozonated water. O&M activities include daily equipment readings, spare parts replacement, preventive and emergency maintenance, and other activities, which are discussed in chapter 5.

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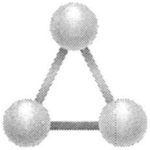


4

Ozone Process and Equipment Design and Operation

The ozonation process includes four primary components that work together when treating drinking water: the ozone generator, feed-gas supply, ozone contactor, and ozone destruct system. The ozone generator is the core component for ozone production. It consists of the power supply unit (PSU) and generation vessel that contains the dielectrics and cooling system. The ozone equipment manufacturer provides the PSU and the generation vessel that will meet the design criteria for the installation. These components are unique to each manufacturer. The other three ozone system components are more generic by nature. The ozone equipment manufacturer is also the ozone system supplier for most new facilities and provides equipment for the entire ozone system, including a stand-alone control panel that incorporates programmable controller logic. However, in some situations, such as retrofit applications, the ozone equipment manufacturer supplies only the PSU and generator vessel.

Considerations for selecting generator size and number are presented in chapter 3. Figure 4-1 outlines five options for feed-gas supply to the generator. The feed-gas must contain oxygen molecules, which exist in ambient air (21 %vol) and high-purity oxygen (90 to ~100 %vol) feed-gas supplies. Feed-gas options noted in Figure 4-1 include ambient air; cryogenic oxygen (cryo); liquid oxygen (LOX); pressure-swing adsorption oxygen (PSA); and vacuum-pressure–swing adsorption oxygen (VPSA, which is sometimes called vacuum swing adsorption, or VSA).

The ozone contactor is a bubble-diffuser or injection unit, as indicated in Figure 4-1, which also describes its ozone dissolution system (i.e., dissolving ozone gas into the water). Considerations for contactor placement within the treatment

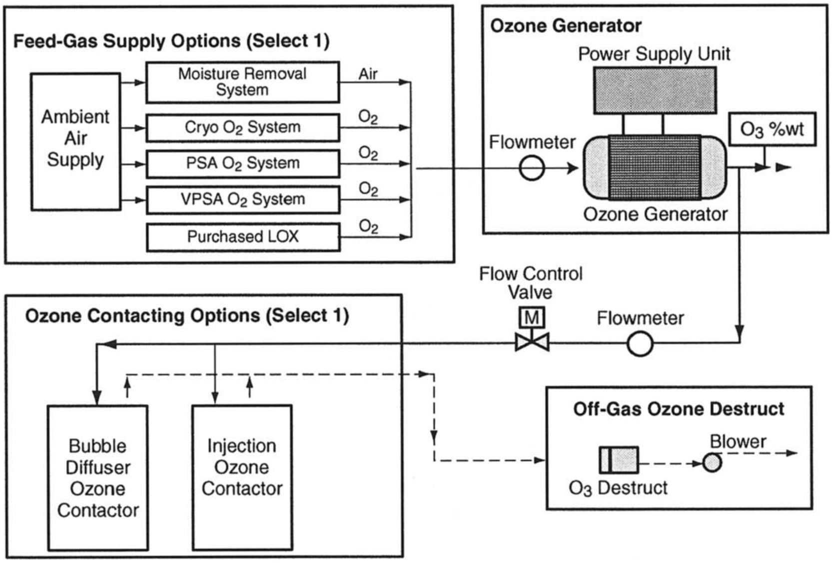


Figure 4-1 Primary components of an ozone process

plant and determination of contactor size and configuration are discussed in chapter 3. The ozone destruct unit converts unused ozone back to oxygen.

OZONE GENERATION DESIGN CONSIDERATIONS

Ozone molecules are created inside the generator vessel by electron flow across a narrow discharge gap in the presence of oxygen molecules. The discharge gap is only 0.3 mm to 3 mm wide (see Figure 1-3, chapter 1). The feed-gas must be very dry and particle free. Particles in the feed gas cause arcing and sparking that could damage the generator dielectrics. In addition, moisture in the feed-gas forms nitric acid. Consequently, excessive moisture in the feed-gas must be avoided to prevent reduced energy efficiency and failed dielectrics or blown fuses. Feed-gas supply equipment includes subcomponents that minimize moisture and particle content of the feed-gas.

Ozone Concentration and Energy Efficiency

The ozone generator can be designed to operate with either air or high-purity oxygen feed-gas. Figure 1-3 (chapter 1) illustrates that inlet feed-gas oxygen concentration ranges from 23 to 100 %wt (i.e., 21 to 100 %vol). The outlet ozone concentration ranges from 1 to 16 %wt (typically 1 to 4 %wt in air-fed systems and 8 to 12 %wt in oxygen-fed ozone systems). Figure 1-3 also shows that applied power to the dielectrics ranges from 3,500 to 20,000 V and operating frequency ranges from 60 to 6,000 Hz. In most plants, conventional three-phase power, such as 480 V and 60 Hz, is supplied to the PSU of the generator. However, the supply voltage is likely to be higher in large plants or lower in small plants.

Low-frequency ozone generators contain equipment within the PSU that converts the three-phase low-voltage (480 V) power supply to single-phase high-voltage (8,000 to 20,000 V) power that is directed to the dielectrics in the generator vessel. The voltage is limited to about 20,000 V to minimize glass dielectric breakage.

Medium-frequency ozone generators contain equipment (rectifiers/converters, inverters, and transformers) within the PSU that also changes electrical frequency. A major improvement of ozone systems over the past 15 to 20 years is the ability of medium-frequency ozone generators to increase the flow of electrons across the discharge gap without a rise in voltage levels that break dielectrics. Increased electron flow allows increased ozone concentration and decreased oxygen gas flow, making oxygen-fed ozone systems more efficient. Oxygen-fed ozone systems are lower in both capital and operating costs.

Prior to the late 1980s, most ozone generators operated at 60 Hz and were classified as “low-frequency” units. Voltage was adjusted between about 10,000 and 20,000 V to control electron flow across a 2- to 3-mm discharge gap, which adjusted electron flow and ozone production rate. The maximum allowable voltage was restricted to reduce breakage of glass dielectrics. Limitations in maximum applied voltage also restricted electron flow, because frequency was fixed at 60 Hz. With air as the feed-gas, the design ozone concentration generally ranged between 1.0 and 1.5 %wt. If oxygen instead of air was applied to low-frequency generators, the ozone concentration would double. Purchasing LOX was uneconomical when operating low-frequency ozone generators at 2 to 3 %wt ozone concentration, because oxygen gas flow and cost were too great. Consequently, ozone systems prior to the late 1980s and into the early 1990s were generally air-fed designs.

In the late 1980s and early 1990s, ozone generator suppliers developed PSUs that increased operating frequency, lowered applied voltage, and increased electron flow across the discharge gap. These ozone generators were classified as “medium-frequency” units. With medium-frequency generators the operating ozone concentration increased to 2.5 %wt using air and to 6 %wt using oxygen feed-gas supplies. Some ozone systems of the early 1990s were air-fed systems designed to operate at 2 to 2.5 %wt ozone concentration. During the same time frame, LOX-fed systems that were designed to operate at 5 to 6 %wt ozone concentration were installed.

Since the mid-1990s, ozone generator suppliers have decreased discharge gap width and optimized dielectric and PSU designs to further reduce energy consumption and increase ozone concentration. The operating ozone concentration

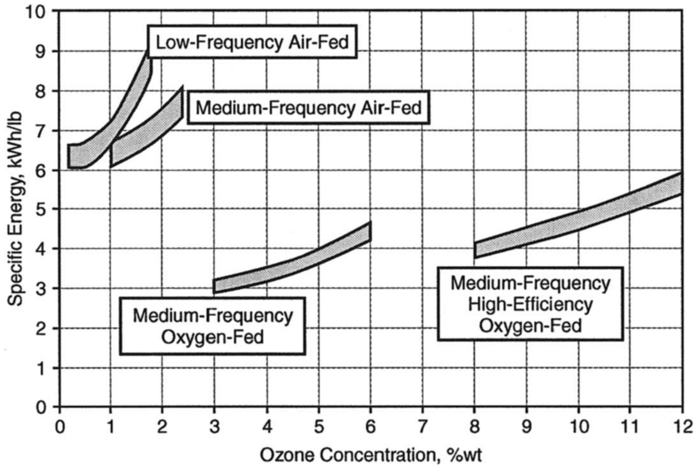


Figure 4-2 Specific energy profile for air-fed and oxygen-fed ozone generators

at municipal drinking water plants has remained fairly steady since that time at 8 to 12 %wt for oxygen-fed ozone systems (air-fed systems might reach 3 to 4 %wt). Some industrial applications for ozone operate at 16 %wt with oxygen feed-gas, but concentrations greater than 12 %wt have not been applied at drinking water treatment plants, where the ozone demand is reached and ozone residual is developed without having to operate at a high ozone concentration. In some industrial applications the ozone reaction kinetics are concentration dependent and operation at a higher ozone concentration is justified.

Figure 4-2 shows specific energy values at variable ozone concentrations for low-frequency air (LFA); medium-frequency air (MFA); medium-frequency oxygen (MFO); and medium-frequency, high-efficiency oxygen (MFHEO) ozone generators. LFA generators are designed for an ozone concentration between 1 and 1.5 %wt. MFA generators are designed for an ozone concentration between 1.5 and 2.5 %wt. MFO generators are designed for 5 to 6 %wt ozone concentration, and MFHEO generators are currently designed for 8 to 10 %wt ozone concentration. An MFHEO generator might be designed for 12 %wt ozone concentration when LOX price is high and/or for some sidestream ozone injection systems.

Cooling Water Flow

Ozone generators are inefficient by nature. The specific energy needed to split oxygen molecules and form ozone molecules is 0.372 kWh/lb_{O_3}. However, the operating specific energy value for LOX-fed medium-frequency ozone generators is about 10 times greater and is 20 times greater for air-fed low-frequency ozone

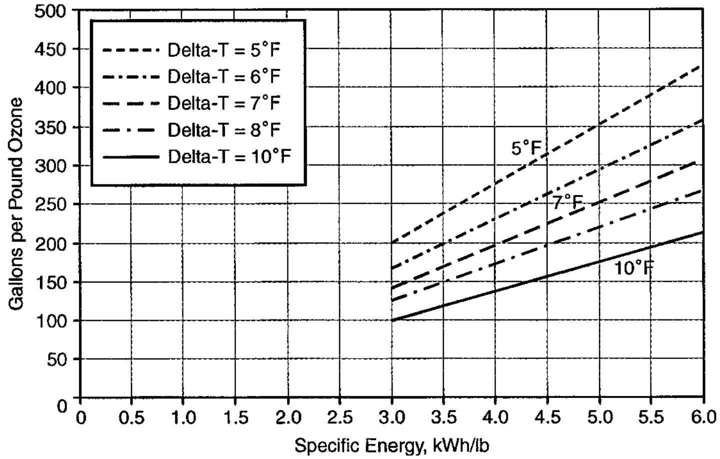


Figure 4-3 Generator vessel cooling water volume per unit (lb) ozone production for variable generator specific energy value, assuming PSU power loss is 6%

generators. Consequently, cooling water flow is needed to remove the heat that is produced by the excess energy supply. In medium-frequency ozone generators, heat is removed from the PSU cabinet and from the generator vessel.

The required cooling water flow rate is a function of maximum heat gain (i.e., temperature increase) by the cooling water flow and the amount of energy "lost" in heat. The relationship between cooling water volume through the generator vessel per unit ozone production (pounds) is summarized in Figure 4-3 for variable generator-specific energy values, assuming the PSU energy loss is 6%. For example, at an operating specific energy value of 4.0 kWh/lb$_{O_3}$, about 280 gpd per lb$_{O_3}$/d is required when the cooling water temperature increase is 5°F. However, if the allowable temperature increase is 10°F, the cooling water flow requirement is reduced to 140 gpd per lb$_{O_3}$/d. Cooling water flow rate through the PSU is typically 5% to 10% of the cooling water flow rate through the generator vessel.

The temperature rise of the cooling water is calculated in the following example for a MFHEO ozone generator. From Figure 4-2, the ozone generator's specific energy consumption value is 4.0 kWh/lb$_{O_3}$ at an ozone concentration of 8 %wt. This means that 9.3% of the applied power (0.372 kWh/lb$_{O_3}$ ÷ 4.0 kWh/lb$_{O_3}$) splits oxygen molecules to form ozone and 90.7% of the energy (3.628 kWh/lb$_{O_3}$) is lost as light, sound, and heat (mostly heat). The value of 3.628 kWh/lb$_{O_3}$ is a heat loss of 12,380 Btu/lb$_{O_3}$ (i.e., 12,380 Btu/lb$_{O_3}$ = 3.628 kWh/lb$_{O_3}$ × 3,412 Btu/kWh).

Heat gain (energy loss) is dispersed among feed-gas flow, generator vessel cooling water flow, and PSU cooling water flow. Assume that 6% energy loss occurs in the PSU, which is 820 Btu/lb$_{O_3}$ (i.e., 820 Btu/lb$_{O_3}$ = 4.0 kWh/lb$_{O_3}$ ×

0.06 × 3,412 Btu/kWh). Assume that the gas temperature increase is 40°F through the ozone generator. (NOTE: Gas temperature increase ranges from 20°F to 60°F, depending on discharge gap width, gas flow rate, and other operating conditions.) At an operating ozone concentration of 8 %wt, the feed-gas flow rate is 12.5 $\text{lb}_{O_2}/\text{lb}_{O_3}$. The specific heat value for oxygen is 0.219 $\text{Btu/lb}_{O_2}/°\text{F}$, which yields a heat gain value of 110 Btu/lb_{O_3} (i.e., 110 Btu/lb_{O_3} = 12.5 $\text{lb}_{O_2}/\text{lb}_{O_3}$ × 0.219 $\text{Btu/lb}_{O_2}/°\text{F}$ × 40°F). This heat gain value is only 0.9% of the total energy loss (i.e., 0.9% = 110 Btu/lb_{O_3} ÷ 12,380 Btu/lb_{O_3}).

The remaining energy loss will increase the temperature of the generator vessel cooling water, which is a heat gain value of 11,450 Btu/lb_{O_3} (11,450 = 12,380 – 820 – 110). The specific heat of water is 1.0 $\text{Btu/lb}_{H_2O}/°\text{F}$. Therefore, 275 gal of cooling water will have a temperature rise of 5°F for every 1.0 lb_{O_3} produced (i.e., 275 gal/lb_{O_3} = 11,450 Btu/lb_{O_3} ÷ 1.0 $\text{Btu/lb}_{H_2O}/°\text{F}$ ÷ 5°F ÷ 8.34 $\text{lb}_{H_2O}/\text{gal}$). A cooling water volume of half that amount (i.e., 138 gal/lb_{O_3}) would have a temperature rise of about 10°F.

The estimated flow rate of the generator vessel cooling water can be determined as described below using Figures 4-2 and 4-3. From Figure 4-2, find the approximate specific energy value for the ozone generator for an estimated ozone concentration. For example, the approximate specific energy at 10 %wt ozone concentration is 4.7 kWh/lb_{O_3}. Select a desired temperature rise across the ozone generator, such as 7°F. From Figure 4-3, find the gallons of cooling water flow per unit ozone production for 4.7 kWh/lb_{O_3} and 7°F temperature rise, which is ~240 gal/lb_{O_3}. Assume that the design ozone production rate is 1,000 lb/d. Therefore, the design cooling water flow rate is 240,000 gpd, or 0.24 mgd. The cooling water flow rate to the PSU is an additional 5 to 10% of the cooling water flow to the generator vessel.

LOW-PRESSURE AIR-FED OZONE SYSTEM

A process schematic for a low-pressure (<25 psig) air-fed ozone system is shown in Figure 4-4. Equipment required includes air compressors, heat exchangers to remove the heat of compression, refrigerant and desiccant dryers, and ozone generators. The schematic includes example data at selected points along the schematic. Ozone production is 1,500 lb/d, which is 60-mgd water flow at an ozone dose of 3 mg/L. In the example, the assumed ozone concentration is 2 %wt and cooling water temperature is 79°F.

Air-fed ozone systems were used widely prior to the mid 1990s and typically operated at ozone concentrations between 1 %wt and 2.5 %wt. Since then, oxygen-fed ozone systems have been used more frequently, but air-fed systems might be selected when oxygen feed is undesirable, such as in a confined space where an oxygen leak could be particularly hazardous. New air-fed systems use

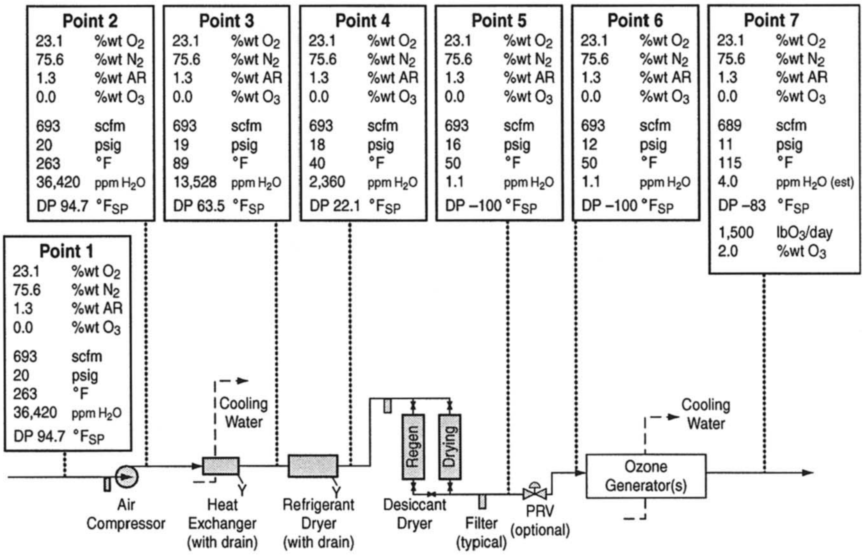


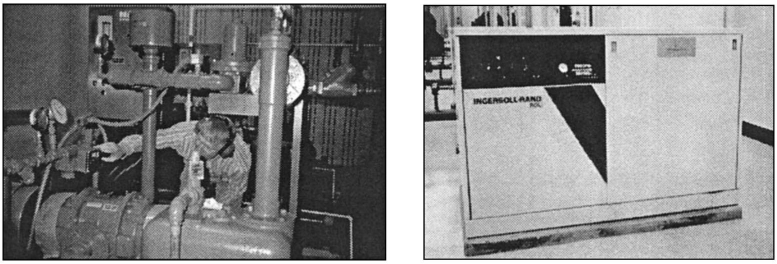
Figure 4-4 Feed-gas and ozone generation process schematic for low-pressure air-fed ozone system

improved ozone generators that operate at a higher ozone concentration (3 %wt to 4 %wt) and possibly at a higher operating pressure (~30 psig).

Air Compressor and After-Cooler

Point 1 in Figure 4-4 is located at the inlet of the air compressor(s). The oxygen, nitrogen, argon, and ozone concentrations of ambient air are 23.1, 75.6, 1.3, and 0.0 %wt, respectively. Gas concentrations are expressed in %wt units in this example to match ozone concentration, which usually is expressed as %wt. The feed-gas flow rate is 693 scfm_{68F}. This value is obtained considering that 1,500 lb/d of ozone is produced at 2 %wt ozone concentration, which requires 75,000 lb/d (1,500 ÷ 0.02) of dry feed-gas supply to the ozone generator. Additional compressed gas is required if the desiccant dryer consumes purge air, which is discussed in relation to point 5 in the following text. The density of dry air is 0.07516 $\text{lb/ft}^3{}_{\text{STP68F}}$ from Table A-5 (appendix A), therefore, 75,000 lb/d of air flow is 693 scfm_{68F}.

The parameters requiring calculation at point 1 are moisture content and dew point temperature at standard pressure. Known or measurable parameters are ambient air temperature (100°F), relative humidity (80%), gauge pressure (0 psig), and plant elevation (1,200 ft_{MSL}). From Eq. 8-6 (chapter 8) the average barometric pressure value is calculated as 728 mm Hg, which is 14.08 psi. Ambient air temperature, relative humidity, and barometric pressure influence moisture content



Liquid Ring

Rotary Screw

Figure 4-5 Oil-free air compressor options for low-pressure air-fed ozone systems

in the feed-gas, which is calculated in chapter 8 as 36,420 ppm_{wt}. The associated ambient air dew point temperature at standard pressure is 94.7°F, also calculated in chapter 8. The importance of defining pressure conditions for dew point temperature value is discussed in relation to point 5, which follows the desiccant dryer.

Point 2 is located between the air compressor and after-cooler. Figure 4-5 shows liquid-ring and rotary-screw oil-free air compressors in air-fed ozone installations. Other types of air compressors are vane, rotary lobe, and centrifugal units (Langlais et al., 1991). All compressors must deliver *oil-free* feed-gas to the ozone generator. The air compressor operating pressure is 20 psig in the example. Gas temperature is increased to 263°F in the example due to the heat of compression, which is estimated at 163°F. The dew point temperature at standard pressure and moisture content is unchanged from point 1 and is 94.7°F and 36,420 ppm_{wt}, respectively.

Point 3 is located between the after-cooler and refrigerant dryer. The after-cooler lowers process-gas temperature from 263°F to 89°F, which is estimated at 10°F above the cooling water temperature of 79°F. The moisture content is reduced to 13,528 ppm_{wt} by lowering gas temperature, as described by example calculations shown in chapter 8. The dew point temperature at standard pressure is 65.3°F, again as calculated in chapter 8. Moisture content was reduced to 13,528 ppm_{wt} from 36,420 ppm_{wt} through the after-cooler, which is a reduction of 22,892 ppm_{wt}. Since dry-gas flow is 75,000 lb/d, approximately 206 gpd of water will be extracted from the air passing through the after-cooler (i.e., $75{,}000 \text{ lb/d} \times 22{,}892 \div 1{,}000{,}000 \div 8.34\ \text{lb}_{\text{w}}/\text{gal}$). The after-cooler must include facilities to drain away the water that condenses inside the feed-gas supply line.

Refrigerant Dryer

Point 4 is located between the refrigerant dryer and the desiccant dryer. Figure 4-6 shows a refrigerant dryer at an existing ozone installation. The refrigerant dryer cools the process gas to about 40°F, which further reduces moisture content of the

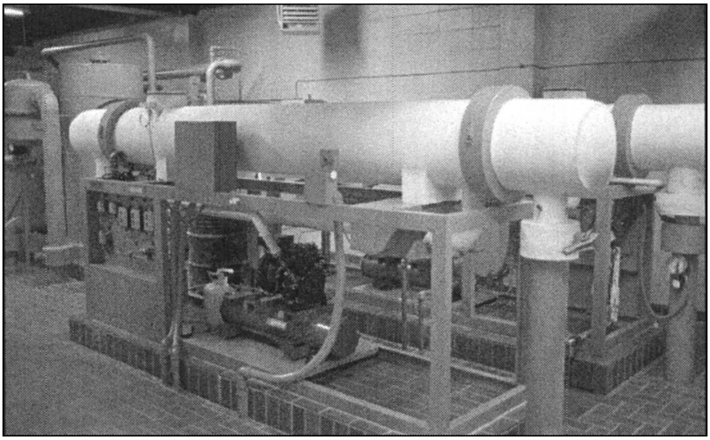


Figure 4-6 Refrigerant dryer for low-pressure air-fed ozone system

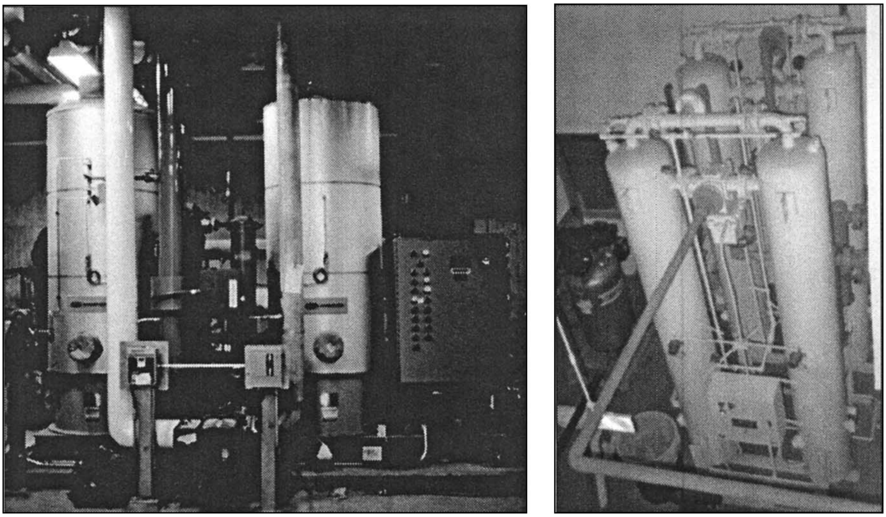
feed-gas. Robust design of the refrigerant dryer is essential for this important component of a low-pressure air-fed ozone system, otherwise, ineffective performance will overload the desiccant dryer.

The oxygen, nitrogen, argon, and ozone concentrations are unchanged at point 4. Flowing-gas pressure is 18 psig (assume 1-psig loss through the refrigerant dryer) and flowing-gas temperature is 40°F. The moisture content is reduced to 2,400 ppm_{wt} by lowering gas temperature through refrigeration, as described by calculations of the moisture content of process gas, which are described in chapter 8. The dew point temperature at standard pressure is 22.1°F at point 4.

By cooling the feed-gas flow via refrigeration, moisture content was reduced to 2,400 ppm_{wt} from 13,528 ppm_{wt}, which is a reduction of 11,128 ppm_{wt}. At a dry-gas flow rate of 75,000 lb/d, approximately 100 gpd of water is removed by cooling in the refrigerant dryer (i.e., 75,000 lb/d × 11,128 ÷ 1,000,000 ÷ 8.34 lb_{W}/gal). If the refrigerant dryer malfunctions and does not cool the air, an additional 100 gpd of water in the feed-gas must be removed by the desiccant dryer, which might overload the desiccant and discharge moisture into the ozone generator. Desiccant dryer loading rates are discussed in the following section.

Heat-Reactivated Desiccant Dryer

Point 5 is located between the desiccant dryer and the ozone generator. Robust and reliable service of desiccant dryers is critical for air-fed ozone systems. Figure 4-7 shows two types of heat-reactivated desiccant dryers installed in low-pressure air-feed ozone systems. Both types have two towers; each tower contains desiccant material, usually activated alumina at 75% of the total quantity of desiccant and molecular sieves at 25%. One tower dries the process gas and the second tower is



External Heat-Reactivated Internal Heat-Reactivated

Figure 4-7 Heat-reactivated desiccant dryers for low-pressure air-fed ozone systems

being regenerated. The full cycle of drying and regeneration typically lasts at least 16 hours—8 hours drying and 8 hours regeneration; 20 to 24 hours is preferred. Regeneration consists of heating the tower to vaporize and remove the adsorbed moisture from the media and purging to transport vaporized water into the ambient atmosphere.

Filters are located before and after the desiccant dryer, as shown in Figure 4-8. The predesiccant dryer filter is a coalescing filter that minimizes, as much as possible, moisture loading to the desiccant. The postdesiccant dryer filter is a particulate filter that is typically designed to remove 99% of particles 0.1 µm in size or larger. The particulate filter captures the "dust" that might be dislodged from the desiccant media.

The purge-gas source of the *internal* heat-reactivated desiccant dryer is dry process gas from the tower that is drying. Purge-gas flow rate is 5% to 15% of the process-gas flow rate. This means that the upstream air compressor and refrigerant dryer must be upsized accordingly. Internal heat-reactivated desiccant dryers must be operated through at least two full cycles before process gas is sufficiently dry for ozone generator operation. This lack of readiness is an inherent disadvantage for these less-expensive dryers, as is slightly higher operating cost due to consumption of process gas as purge-gas flow. Also, the heating elements are usually embedded within the media, which creates temperature gradients that shorten desiccant media life. The desiccant is typically heated for 3 to 4 hours of the 8-hour regeneration step and cooled by the purge gas for the remaining 4 to 5 hours.

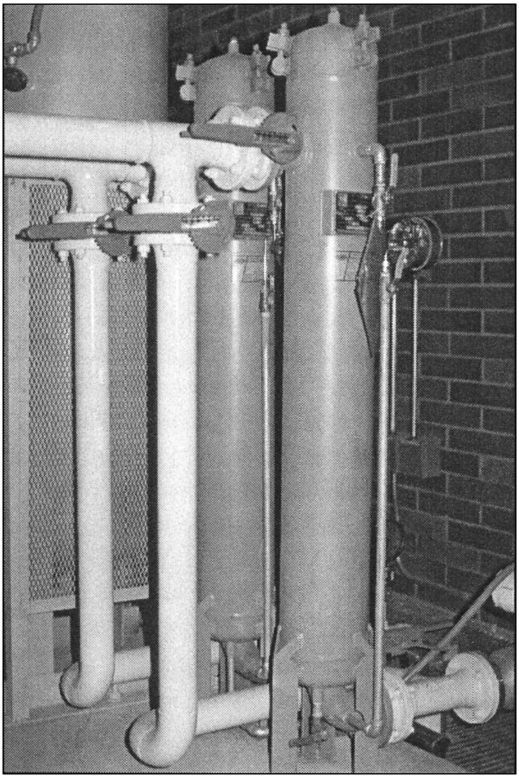


Figure 4-8 Coalescing filters before and particulate filters (0.1 μm) after the desiccant dryer

The *external* heat-reactivated desiccant dryers have self-contained drying systems. Initially, during regeneration, a blower directs ambient air through a heating element that increases the air temperature, which increases the temperature of the desiccant media to dislodge and vaporize adsorbed moisture. The hot purge air is vented to the ambient atmosphere. When the vented purge-air temperature reaches a preset value, the heating cycle is stopped and cooling is initiated. Cooling consists of cycling contained air from the blower through a heat exchanger (similar to an after-cooler) through the media and back to the blower. The cycling period continues until the gas temperature reaches a preset value or until the end of the regeneration step.

Initially, the external heat-reactivated desiccant dryer is more expensive but it does have operating advantages. The dryer is ready to process gas after one tower has been regenerated, and the desiccant has longer life expectancy because the media is heated more uniformly and internal-bed hot spots do not exist. Also, all dry process gas is used for ozone generation, and the air compressors and refrigerant dryers are sized for that purpose only (i.e., upsizing is unnecessary).

Conservative design of heat-reactivated desiccant dryers helps to maintain dry feed-gas conditions that lead to successful operation of many air-fed ozone facilities. Conversely, marginally designed heat-reactivated desiccant dryers cause operational problems such as moisture breakthrough and excessive nitric acid formation inside the ozone generator. The excessive nitric acid necessitates frequent cleaning of generator dielectrics (e.g., every 6 months). Trouble-shooting, desiccant replacement frequency, and general operation and maintenance activities for heat-reactivated desiccant dryers are presented in chapter 5.

An important design feature is quantity of desiccant installed. Desiccant quantity for heat-reactivated desiccant dryers has been established at a minimum of 18 lb desiccant/lb water applied (Stover et al., 1986). Moisture loading to the desiccant can be determined from moisture content information provided for point 4 (discussed earlier). The 40°F flowing gas from the refrigerant dryer has a moisture content of 2,400 ppm_{wt}. The resulting moisture loading rate is 180 lb_{w}/d for the gas flow rate of 75,000 lb/d (2,400 $\text{ppm}_{\text{wt}} \div 1{,}000{,}000 \times 75{,}000$ lb/d), which is 90 lb water in 12 hours of drying time (i.e., 24-hour cycle time). The minimum quantity of desiccant in one tower is 1,620 lb_{d}, using 18 $\text{lb}_{\text{d}}/\text{lb}_{\text{w}}$. At 75% and 25% quantity distribution, 1,215 lb of activated alumina and 405 lb of molecular sieves are required. A conservative approach would be to consider that the flowing-gas temperature from the refrigerant dryer is 45°F at times, which would increase moisture content by 22% to 2,940 ppm_{wt}. Desiccant quantity would be increased by 22% accordingly. Conservative design of heat-reactivated desiccant dryers generally leads to long-term excellent performance of air-fed ozone systems.

The required maximum standard pressure dew point temperature of the ozone generator feed-gas is generally –76°F (Stover et al., 1986). The corresponding moisture content is 6.7 ppm_{wt}. However, successful air-fed ozone systems generally operate at a much lower standard pressure dew point temperatures of –100°F or lower. Moisture content is reduced significantly to 1.1 ppm_{wt}.

Moisture-reacting probes are installed to continuously monitor dew point temperature and sound an alarm and shut down ozone generator power in case high dew point temperature is reached (e.g., above –76°F). In some ozone facilities the probe is installed at line pressure, such as 16 psig in the example in Figure 4-4. In other ozone installations the process gas is directed past the probe and vented to atmosphere, which means that the probe is operating at ambient pressure conditions. Displayed dew point temperature is affected by pressure. For example, as discussed in chapter 8, a dew point temperature reading of –108°F from a probe that is installed at an atmospheric pressure of 14.08 psia will display a reading of –100°F when installed at a line pressure of 16 psig. The displayed reading of –100°F is more conservative (i.e., more desirable) than –108°F for ozone system alarm and shut-down considerations. As such, dew point probes are usually installed to detect moisture content at operating pressure conditions.

Point 6 in Figure 4-4 is located between the pressure-regulating valve and the ozone generator. The pressure-regulating valve location is noted as optional. The illustrated location creates an ozone generator operating pressure of 12 psig, which is optimum for some ozone generation equipment. Other manufacturers optimize ozone generator performance at higher pressure, such as 20 psig. In this case, the pressure-regulating valve is usually located after the ozone generator. However, not all air-fed ozone systems have a pressure-regulating valve; some operate at natural operating pressure of the ozone installation.

Ozone Generator

Point 7 in Figure 4-4 is located after the ozone generator and before the ozone contactor. The significant change in process gas parameters is the result of ozone production from oxygen molecules. In the illustration, oxygen concentration is decreased to 21.1 %wt from 23.1 %wt and ozone concentration is increased to 2 %wt. Nitrogen and argon concentrations are unchanged at 75.6 %wt and 1.3 %wt, respectively. Another process-gas parameter that changed after ozonation is gas flow rate, which is slightly lower at 689 scfm instead of 693 scfm. The mass (lb/min) flow rate is unchanged, but volumetric flow (ft^3/min) is reduced slightly because fewer gas molecules exist when three oxygen molecules combine to form two ozone molecules. The overall reduction in gas molecules is insignificant and is generally ignored in design details.

The ozone process-gas temperature after the generator is shown as 115°F, which is a characteristic value when the generator is operating at 100% power. Generator outlet gas temperature is affected primarily by cooling water temperature and level of applied power. Inlet gas temperature has a minor effect because of the cooling water's large capacity for heat transfer. The inlet gas temperature is shown as 50°F, which is slightly higher than the refrigerant dryer outlet temperature (40°F) because heat is released when moisture is adsorbed onto the desiccant media. The generator outlet gas temperature would be lower at reduced operating power level, e.g., 97°F at 50% applied power.

The dew point temperature at standard pressure (DP_{sp}) is shown as –83°F for point 7 in Figure 4-4, which is higher than the inlet DP_{sp} of –100°F. In this example, hydrocarbons that might be converted to water vapor during ozonation were assumed to exist in the ambient air supply. It is emphasized that hydrocarbon conversion to water vapor is an assumption that cannot be quantified easily because moisture-sensing dew point probes are incompatible with ozone. The point is that some water vapor will enter the ozone generator naturally or will develop in the ozone generator naturally and form nitric acid. Eventually (months or years) the nitric acid reduces generator efficiency, i.e., increases specific energy and generator must be cleaned.

Design and operation of the ozone generator and feed-gas treatment system must be implemented with careful attention to minimizing moisture content within the ozone generator. Excess moisture loading will significantly increase nitric acid formation and shorten the time between generator cleanings (i.e., to a few months instead of a few years). Considerations for reducing moisture loading to the ozone generator include, but are not limited to, the following:

1. The dew point reading (i.e., moisture content reading) should be kept as low as possible (e.g., <–100°F) by robust refrigerant and desiccant dryer design and should incorporate operating practices that maintain peak performance from these units (see chapter 5 for additional operating considerations).
2. The ozone generator should be purged with dry air before power is applied to the dielectrics such that extremely dry conditions exist within the generator when ozone is being produced. Purge time is several hours after a generator is opened for maintenance or several minutes when an off-line unit is brought into service.
3. An off-line but operable ozone generator should be kept under positive pressure by an open inlet valve and closed outlet valve. This procedure will ensure that the off-line generator maintains pressure and thus minimizes moisture entrance into the vessel from the smallest of openings, considering that the moisture content of the ambient air is likely to be 30,000 ppm_{wt} (see above discussion of moisture content in ambient air) and the desired moisture content inside the ozone generator is about 1 ppm_{wt}.

Ozone Contactor

The ozone contactor shown in Figure 4-9 is a bubble-diffuser over-under baffled basin, which is typical for air-fed ozone systems. Ozone is delivered into the first chamber of the contactor, which is the most common application point. Chapters 2 and 3 describe cases and operating conditions when ozone might be added to chambers other than chamber 1.

The ozone production rate is 1,500 lb/d in the example; this is an ozone dose of 3.0 mg/L at water flow rate of 60 mgd. The example assumes that the dissolved oxygen and dissolved nitrogen levels at the contactor inlet are at a 100% saturation level, or 8.0 mg/L and 13.2 mg/L, respectively, for the water temperature of 79°F and plant elevation of 1,200 ft_{MSL}. The outlet dissolved oxygen (DO) and dissolved nitrogen (DN) levels are increased to 9.1 mg/L and 16.2 mg/L, respectively, as the gas is bubbled into the contactor. More information about ozone, oxygen, and nitrogen transfer efficiency is presented later in this chapter.

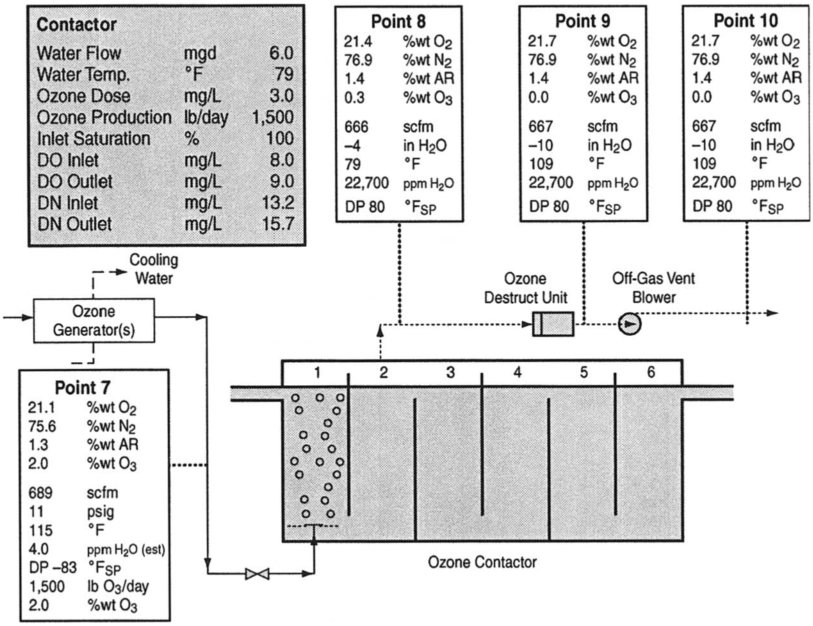


Figure 4-9 Contactor and off-gas process schematic for low-pressure air-fed ozone system

Ozone Off-Gas and Destruct

The ozone contactor off-gas parameters are displayed at point 8 in Figure 4-9. The most important operating and design value is the ozone concentration, which is 0.3 %wt. This implies that the ozone transfer efficiency is 85% (i.e., 85% = [2.0 %wt – 0.3 %wt] ÷ 2.0 %wt × 100), which is typical for an air-fed bubble-diffuser contactor that has a diffuser depth of about 20 ft. More information about ozone transfer efficiency is presented later in this chapter.

The oxygen, nitrogen, and argon concentrations are 21.4 %wt, 76.9 %wt, and 1.3 %wt, respectively. The off-gas flow rate (666 scfm$_{68F}$) is about 3.3% lower than the contactor inlet gas flow rate (689 scfm$_{68F}$) due to transfer or dissolution of ozone, oxygen, and nitrogen gas into the water flow (see inlet and outlet DO and DN information above). However, the actual off-gas flow rate might be different from the theoretical off-gas flow rate due to change in water level in the contactor. Indeed, water level change can create significantly higher off-gas flow rates that could overpressurize the contactor or significantly lower off-gas flow rates that could underpressurize the contactor. Given this situation, the contactor is designed with pressure-vacuum relief valves, as shown in Figure 4-10.

The normal operating pressure at point 8 is –4 in. water, which is a slight vacuum that is drawn by the off-gas vent blower. The typical operating range is –2 to

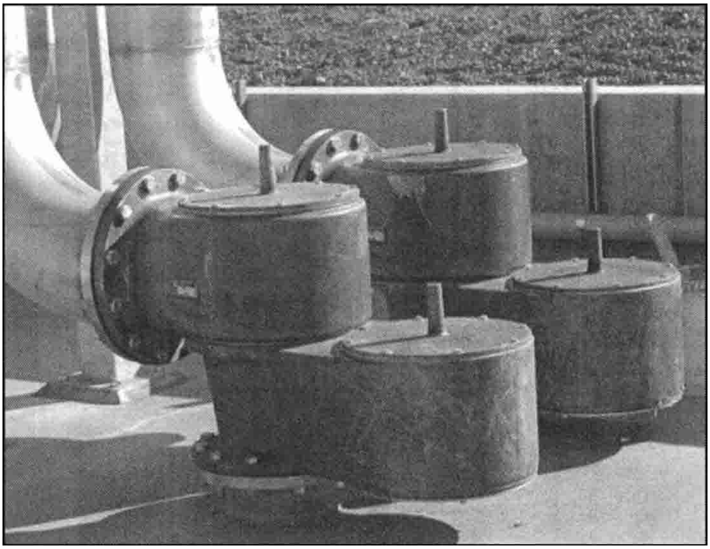


Figure 4-10 Two ozone contactor pressure-vacuum relief valves for structural protection

−4 in. water, and the vacuum relief valve is usually set at −6 in. water. The operating level of −2 to −4 in. water is controlled automatically by a pressure-control valve, variable-speed blowers, or other control options.

Many plants operate successfully with the vacuum relief valve open much of the time (i.e., at increased vacuum condition). The only drawback to this operating strategy is that the off-gas ozone concentration is inaccurate (i.e., it is diluted with ambient air) and the off-gas destruct system is operating at slightly higher operating cost (i.e., slightly higher gas flow rate). However, operating with the vacuum relief valve open is much better (i.e., safer) than operating in an overpressure condition where the ozone off-gas is vented into the ambient air.

The off-gas temperature at point 8 is the temperature of the water inside the contactor, or 79°F in this example. The moisture content is increased significantly to 22,700 ppm_{wt}, because the off-gas is 100% saturated at the operating pressure and temperature conditions of 14.08 psi and 79°F, as calculated in chapter 8. It is important to note that in this situation, moisture can condense within the off-gas piping if the ambient temperature cools down the off-gas piping. For example, if the ambient temperature is 55°F (e.g., in the fall when water temperature might be higher than ambient temperature) and the off-gas temperature drops to, e.g., 60°F, moisture will condense within the off-gas piping. The moisture content of the gas at 60°F is only 11,141 ppm_{wt}, as calculated in chapter 8. Therefore, at least 11,629 ppm_{wt} of moisture content will condense as the off-gas temperature decreases. At the off-gas flow rate of 666 $\text{scfm}_{68\text{F}}$ (about 3,000 lb_{gas}/hr), the

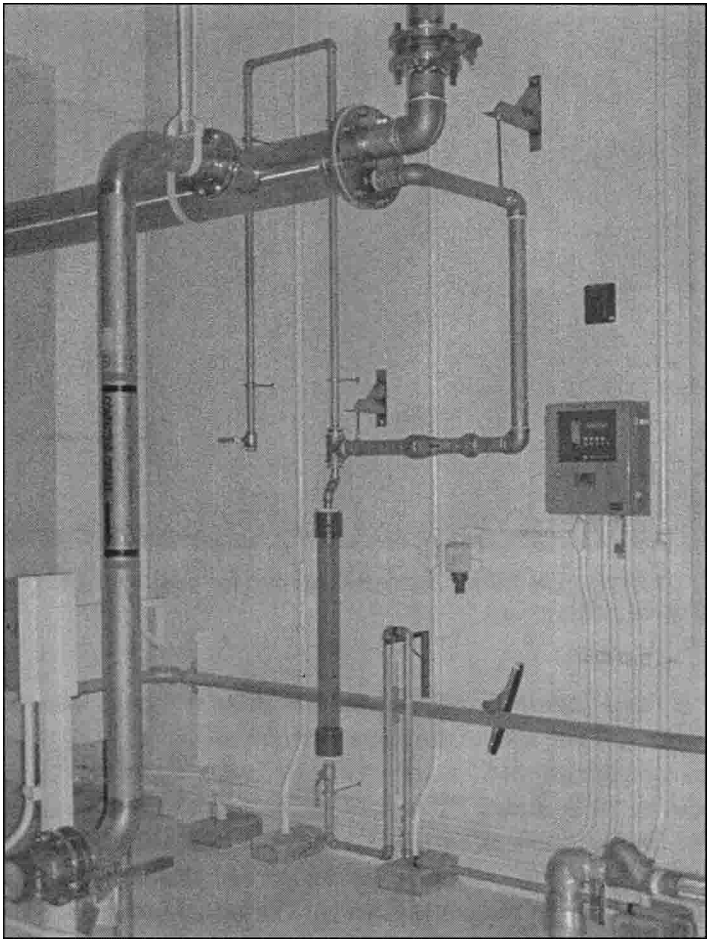


Figure 4-11 Ozone contactor moisture collection and drain at low point of off-gas piping

quantity of moisture that condenses is about 33.2 lb_w/hr (i.e., 34.9 lb_w/hr = 11,629 $ppm_{wt} \div 10^6 \times 3{,}000$ lb_{gas}/hr), or 4.2 gal/hr. This water *must be drained* from the off-gas piping or significant damage could occur to the off-gas destruct heater and catalyst. An example drain system at the low point of the off-gas piping is shown in Figure 4-11.

Following the ozone destruct unit in Figure 4-9, the significant change in data taken from point 9 is the ozone concentration, which has been reduced from 0.3 %wt to zero. The oxygen concentration is increased by 0.3 %wt and nitrogen and argon concentrations are unchanged. The ozone destruct unit consists of a heating element and catalyst, which is typically manganese dioxide (MnO_2).

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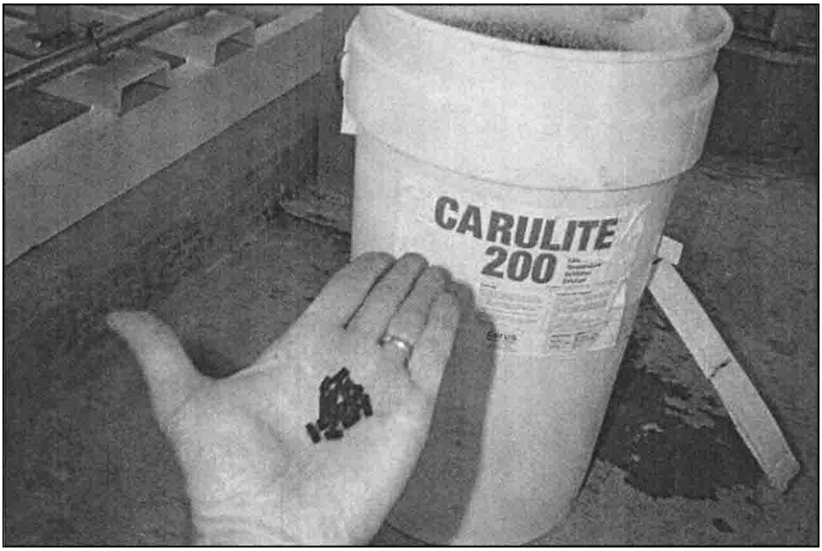

Figure 4-12 Catalyst media (Carus Chemical Company) for a heat-catalyst off-gas ozone destruct unit at an existing plant

Granular activated carbon (GAC) media will destroy ozone; however, because GAC can burn, it is not used in the ozone destruct unit.

Off-gas temperature also has changed. The heater has raised the temperature of the off-gas by 30°F, from 79°F to 109°F. Through this action, the moisture is certain to be in vapor form as it passes through the catalyst and does not exist as a liquid. Water in liquid form will coat the catalyst and prevent catalytic reaction of ozone molecules back to oxygen molecules. The saturation moisture content at 109°F is more than 49,000 ppm_{wt} (see Table 8-1, chapter 8), which means that the relative humidity of the heated off-gas is less than 50% since the actual moisture content is 22,700 ppm_{wt}. Figure 4-12 shows MnO_2 catalytic media.

The operating pressure at point 9 is at greater vacuum after the catalyst bed because of the pressure drop through the catalyst. Pressure for point 9 in Figure 4-9 is –10 in. water, which indicates a pressure drop of 6 in. water. The gas flow increases slightly (666 scfm_{68F} to 667 scfm_{68F}) due to conversion of two ozone molecules to three oxygen molecules. Parameters for moisture content and DP_{sp} are unchanged.

Point 10 in Figure 4-9 follows the off-gas vent blower, which is sometimes called an exhaust blower. Figure 4-13 shows an off-gas ozone destruct skid that contains the heater, catalyst bed, and exhaust blower. The only change in operating parameters at point 10 is the operating pressure, which is shown as 28 in. water.

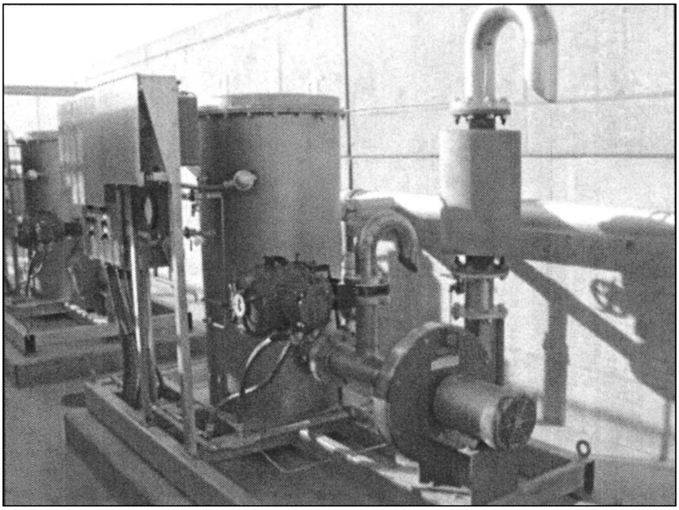

Figure 4-13 Off-gas ozone destruct skid showing heater, catalyst, and exhaust blower

HIGH-PRESSURE AIR-FED OZONE SYSTEM

A high-pressure (about 100 psig) air-fed ozone process schematic is shown in Figure 4-14. Required equipment includes air compressors, heat exchangers to remove the heat of compression, heatless desiccant dryers, and ozone generators. The schematic includes data that might be recorded at selected points along the process train. Ozone production for the high-pressure example is 150 lb/d (6 mgd and 3 mg/L ozone dose), which is one-tenth the value for the low-pressure example. High-pressure air-fed ozone systems are used at smaller plants (<10 mgd). Although they have higher operating costs (see discussion concerning total system energy consumption presented later in this chapter), capital costs are less due to smaller desiccant dryers and no refrigerant dryer. Also, maintenance activities are decreased because less ozone equipment is installed.

Air Compressor and After Cooler

Point 1 in Figure 4-14 is located at the inlet of the air compressor(s). Most parameters are similar to those presented in Figure 4-4 because the same ambient conditions are used for both examples. The feed-gas flow rate is 83.2 $\text{scfm}_{68\text{F}}$ to the desiccant dryer and 69.3 scfm_{68} to the ozone generator. The difference is due to the fact that the heatless desiccant dryer requires 20% purge flow in this example. The feed-gas flow to the ozone generator is 69.3 scfm, which is 7,500 lb/d (150 ÷ 0.02) of dry feed gas at a density of 0.07516 $\text{lb/ft}^3{}_{\text{STP68F}}$ (Table A-5, appendix A) and one-tenth the feed-gas flow shown in Figure 4-4. All other parameters at point 1 are similar to those in Figure 4-4.

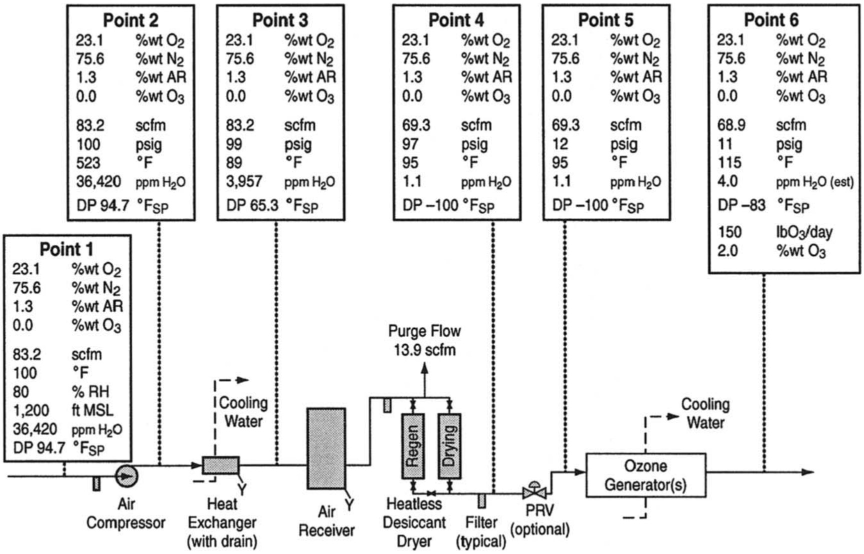

Figure 4-14 Feed-gas and ozone generation process schematic for high-pressure air-fed ozone system

Point 2 is located between the air compressor and after-cooler. Figure 4-15 shows a rotary-screw oil-free air compressor that is currently in use at a high-pressure air-fed ozone installation. Figure 4-16 shows an oil-lubricated air compressor installation for an ozone application that also includes extensive oil-separation filtration equipment. Both compressor and compressor-filter options deliver oil-free feed-gas to the ozone generator.

The operating pressure of the air compressor is 100 psig in the example. Gas temperature is increased to 523°F due to the heat of compression. The DP_{SP} and moisture content are unchanged from point 1, at 94.7°F and 36,420 ppm_{wt}, respectively.

Point 3 is located between the after-cooler and air receiver. The after-cooler lowers process-gas temperature from 523°F to 89°F, which is estimated at 10°F above the ambient cooling water temperature of 79°F. The moisture content is reduced to 3,957 ppm_{wt} due to the effects of high pressure and lower gas temperature, as discussed in chapter 8. The DP_{SP} is 32.9°F (see calculation approach in chapter 8). The moisture content is reduced to 3,957 ppm_{wt} from 36,420 ppm_{wt} through the after-cooler, which is a reduction of 32,462 ppm_{wt}. Because dry-gas flow is 7,500 lb/d, approximately 29 gpd of water will be extracted from the air within the after-cooler (i.e., 7,500 lb/d × 32,462 ÷ 1,000,000 ÷ 8.34 lb_W/gal). The after-cooler must include facilities to drain away the water that condenses inside the feed-gas supply line.

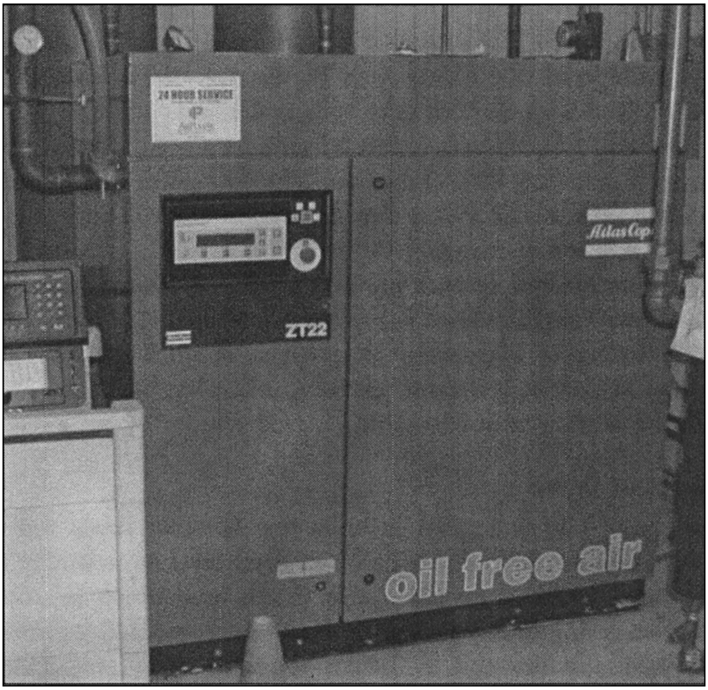

Figure 4-15 Rotary-screw oil-free air compressor for high-pressure air-fed ozone system

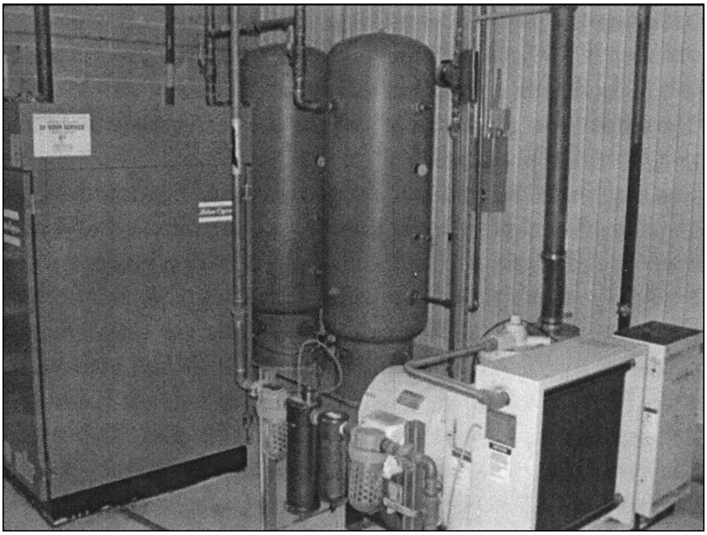

Figure 4-16 Oil-lubricated air compressor with oil-separation filters at an existing high-pressure air-fed ozone system (note air-receiver tanks in background)

Following the after-cooler is an air receiver that includes a drain for removing condensed water vapor. High-pressure air-fed ozone systems usually have air compressors that operate with a duty cycle. For example, the air compressor for this plant might be sized with an 80% duty cycle at design conditions. Therefore, the compressor size might be 104 $\text{scfm}_{68\text{F}}$ to deliver 83.2 $\text{scfm}_{68\text{F}}$ continuously, so that the compressor is operating 80% of the time. The duty-pressure set points might be 100 psig to 110 psig, which means that the compressor will engage at operating pressure of 100 psig and disengage at 110 psig.

High-pressure air-feed systems are also used in LOX-fed ozone systems to deliver a small percentage (between 0.3% and 3% normally) of nitrogen molecules into the flow stream of high-purity oxygen gas. A small quantity of nitrogen molecules improves ozone generator operating efficiency, which is discussed later for the LOX-fed ozone system schematic.

Heatless Desiccant Dryer

Point 4 in Figure 4-14 is located between the desiccant dryer and the ozone generator. Again, robust and reliable desiccant dryer service is critically important. Figure 4-17 shows a heatless desiccant dryer that is in service at an existing ozone installation. Two drying towers are shown. Each tower contains desiccant material, usually activated alumina and molecular sieves at 75% and 25% quantity distribution, respectively. One tower dries the process gas while the second tower is regenerating. The full cycle of drying and regeneration is typically 6 min (range 4 min to 6 min), which is 3 min of drying and 3 min of regeneration. Regeneration consists of reducing the pressure to ambient level and purging with dry process gas at a flow rate that is 15% to 20% of the flow rate of the process gas flow that is passing through the drying tower. Because the purge flow at ambient pressure has a lower vapor pressure than the adsorbate on the desiccant, moisture will desorb and be carried away with the purge gas.

The most important and helpful design feature of heatless desiccant dryers is their longer, rather than shorter, cycle time (e.g., 6 min instead of 4 min, or 3 min drying time instead of 2 min drying time). A dryer with a longer cycle time might result in a slightly more expensive unit. However, this might be warranted considering the fact that dry gas is critically important for long-term robust ozone operation. Heatless dryers are designed on the basis of bed volume throughputs (Langlais et al., 1991). One throughput is defined as follows: Assume that the gas flow rate is 1 $\text{scfm}_{68\text{F}}$ and operating pressure is 100 psig. This means that the actual gas flow rate (i.e., flow at operating pressure or "acfm") is 0.128 $\text{ft}^3\text{/min}$ (i.e., $0.128\ \text{ft}^3\text{/min} = 14.7 \div [14.6\ \text{psi} + 100\ \text{psig}]$, where 14.6 psi is the assumed barometric pressure). At this flow rate one throughput will occur in 1 min if the bed (desiccant media) volume is 0.128 ft^3.

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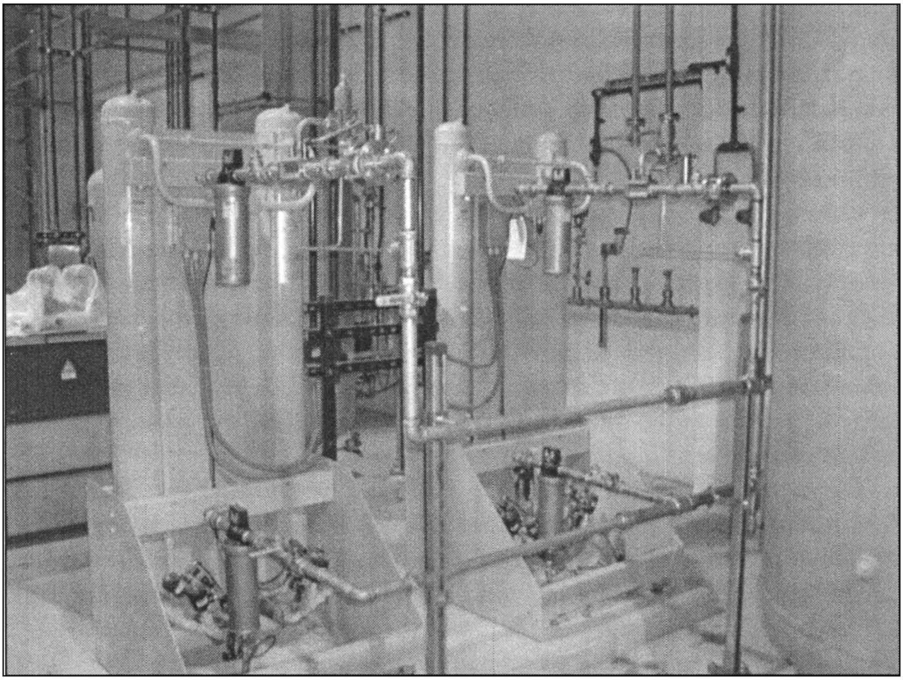
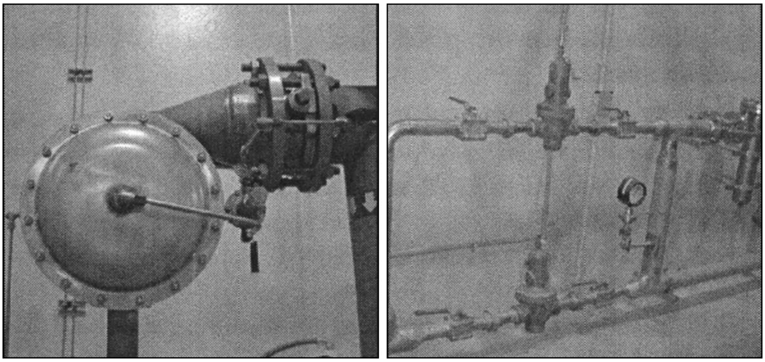


Figure 4-17 Heatless desiccant dryer and filters for high-pressure air-fed application

The actual volume of air that is passed through one desiccant tower should be <50 throughputs maximum, with higher purge flow rate percentage at higher throughput value (Langlais et al., 1991). For example, determine the maximum gas flow rate for a design cycle time of 6 min (3 min drying time) and bed media volume of 1 ft^3. First, find the actual (i.e., at pressure) volume allowed during 50 throughputs, which is 50 ft^3 (i.e., 50 ft^3 = 1 ft^3 × 50). Next, find the actual gas flow rate allowed during 3-min drying time, which is 16.7 ft^3/min (50 ft^3 ÷ 3 min), or 130 $scfm_{68F}$ (i.e., 130 $scfm_{68F}$ = 16.7 ft^3/min × [100 psig + 14.6 psi] ÷ 14.7 psi). In this example, the purge flow is 26 $scfm_{68F}$, which yields a process gas flow rate of 104 $scfm_{68F}$.

It is important to use high-quality switching valves and to perform routine valve maintenance (e.g., yearly) for successful heatless dryer performance. Valve failure results in moisture breakthrough, which is highly probable considering the inlet moisture content to the heatless dryer is about 4,000 ppm_{wt} and the target dry-air quality is about 1 ppm_{wt}. Heatless desiccant dryers must perform flawlessly and can continuously reach target dry-air quality when properly designed and maintained.



More expensive pilot-operated valves have delivered consistent pressure and flow rates when used.

Simple, inexpensive mechanical valves have created variable downstream pressure and flow rates at some plants.

Figure 4-25 Common pressure-reducing valves at LOX-fed ozone systems

Supplemental Air for Nitrogen Addition

A LOX-fed ozone system is optimized by adding nitrogen molecules to the generator feed-gas oxygen supply. The author has observed 10% to 20% improvement in generator efficiency; the degree of improvement is variable among ozone generator suppliers. Nitrogen addition has been part of LOX-fed ozone system design since the mid-1990s when medium-frequency high-concentration (8 %wt to 12 %wt) ozone generators were introduced. The operating nitrogen concentration ranges between 0.3 %vol and 12 %vol, although concentrations between 1 %vol and 3 %vol are more common (consult the ozone system supplier). Efficiency improves using the following design and operating strategies:

1. Efficiency improvement is generally unchanged over a range of nitrogen concentrations, such as 1 %vol to 5 %vol. Supplemental air feed is typically controlled manually. Sophisticated programmable control logic is unnecessary. The schematic in Figure 4-19 depicts a simple rotameter for airflow measurement.
2. Efficiency improvement continues for a period of time (several hours) after nitrogen feed (i.e., air feed) is stopped. Moisture breakthrough has occurred from malfunctioning heatless desiccant dryers. Dew point temperature on the supplemental air line is measured to alarm and shut down supplemental air feed in case of excess moisture conditions. System operation continues with LOX feed only. Dew point temperature is measured on the feed-gas line to the generators and is used as a backup alarm and to stop power to the ozone generator in case of excess moisture conditions.

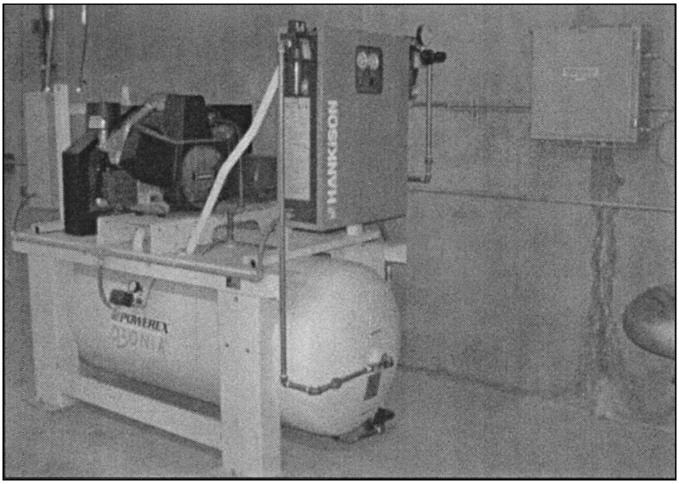


Figure 4-26 High-pressure supplemental air-feed system in use at LOX-fed ozone system

Point 3 in Figure 4-19 displays operating values from the supplemental air system. Airflow rate is 3.1 scfm_{68F}, which is 2% of the total feed-gas supply. Airflow rate is often controlled manually in small- to medium-sized ozone systems (e.g., <1,000 lb/d) and is usually controlled automatically in larger installations. Manual control is selected to minimize installation (and maintenance) costs and/or when operating conditions allow for a fixed airflow rate for several weeks or months at a time (i.e., airflow rate can be constant and still maintain acceptable nitrogen feed percentage).

Equipment used to achieve a dry air supply is similar to the high-pressure air-fed ozone system discussed earlier in this chapter. Design and operating features for maintaining successful performance must be included, especially with respect to low moisture content in the air supply. A supplemental air-feed system that is currently in operation is shown in Figure 4-26.

Point 4 follows supplemental air in the process schematic in Figure 4-19. Feed-gas flow rate is 157.0 scfm_{68F} to the ozone generator. Supplemental air feed has introduced nitrogen molecules (and a negligible quantity of argon), with oxygen and nitrogen concentrations at 98.6 %wt and 1.4 %wt, respectively. Dry feed-gas is verified with a dew point meter that alarms and shuts down the generator at dew point temperatures above –76°F (–60°C). Feed-gas is filtered (0.1 µm) to capture debris that might flake off from the walls of the stainless steel piping or otherwise enter the feed-gas supply. Although debris quantity is negligible and filter clogging is infrequent (several years between replacement), filtration is necessary because the high ozone-concentration oxygen-fed ozone generator has a very small dielectric

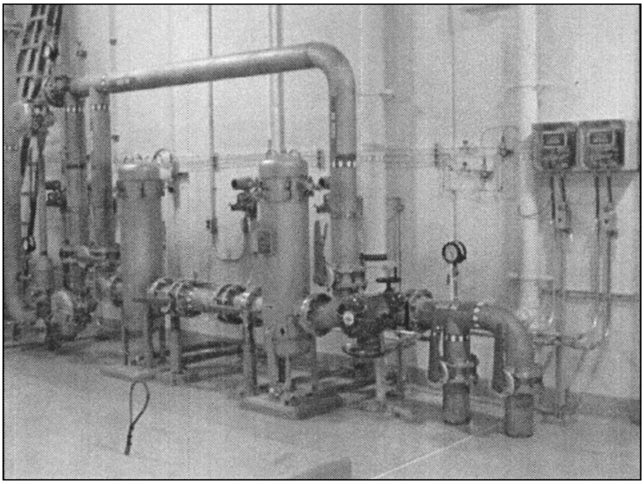


Figure 4-27 Oxygen feed-gas filters and pressure-reducing station in use at LOX-fed ozone system

gap width (e.g., between 0.3 and 0.5 μm). Figure 4-27 shows an oxygen-feed filter and pressure-reducing station in operation at a LOX-fed ozone system.

Ozone Generator

Point 5 in Figure 4-19 is after the ozone generator and before the ozone contactor. The oxygen concentration decreased to 90.6 %wt from 98.6 %wt and ozone concentration increased to 8 %wt. Nitrogen and argon concentrations are unchanged. Gas flow rate is lower at 152.9 $\text{scfm}_{68\text{F}}$ instead of 157.0 $\text{scfm}_{68\text{F}}$. The mass (pounds per minute) flow rate is unchanged, but volumetric flow (ft^3/min) is reduced when three oxygen molecules combine to form two ozone molecules. Gas flow change is considered in research studies and performance testing activities but is usually ignored in field-system design and operation.

The ozone product-gas temperature after the generator is shown as 120°F, a possible value when the generator is operating at 100% power. Generator outlet gas temperature is most affected by cooling water temperature, level of applied power, and operating ozone concentration. Operating ozone concentration is an offshoot of the feed-gas flow rate through the generator and the level of applied power. A reduction in gas flow will decrease gas velocity through the dielectrics, increase product-gas ozone concentration, and increase gas detention time within the generator. The net effect is a decreased ozone production rate, primarily because gas temperature is increased when flow-through velocity is reduced. Figure 3-14 (chapter 3) indicates that the ozone production rate might decrease by 20% simply by reducing gas flow, which raises operating ozone concentration from 8 %wt to

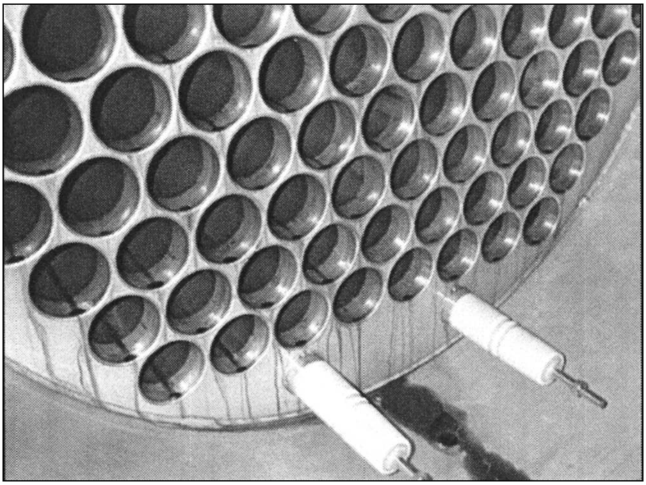


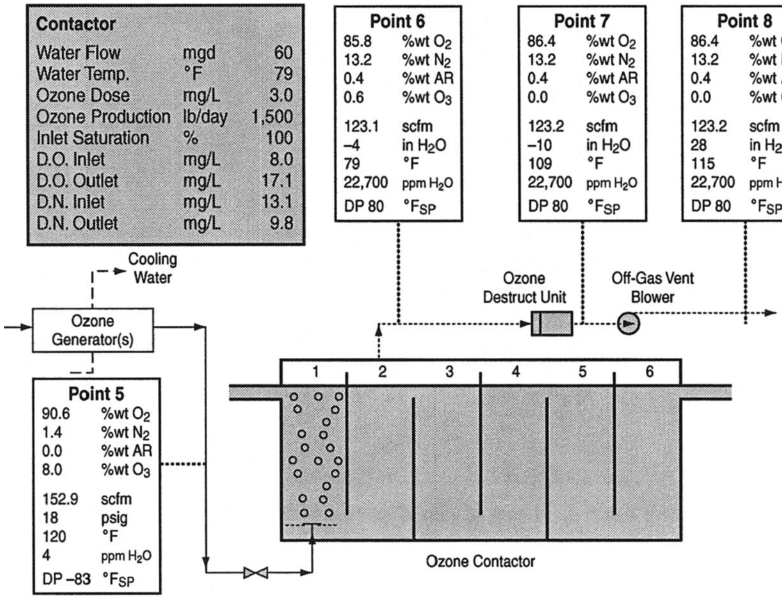
Figure 4-28 Excessive nitric acid in a LOX-fed ozone generator resulting from improper operation

10 %wt. However, optimized operating ozone concentration depends on the combined costs for LOX and energy; this is discussed in chapters 3 and 5.

The DP_{SP} value for point 5 is shown as –83°F in Figure 4-19, which is higher than the inlet DP_{SP} of –100°F. In this example, hydrocarbons, which might be converted to water vapor during ozonation, were assumed to exist in the LOX supply. Hydrocarbon concentration will vary in LOX supplies depending on the location of LOX production site, the degree of air pollution during LOX production, and the location within the LOX supply tank where the supplier draws LOX into the delivery truck. Water utilities have minimized hydrocarbon-moisture contamination inside their ozone generators by limiting the hydrocarbon concentration in their LOX supplies to <20 ppm_{vol} (i.e., by contract with the LOX supplier).

Moisture loading and nitric acid formation inside oxygen-fed ozone generators are significantly less problematic than for air-fed ozone generators for two primary reasons. First, nitrogen concentration is much lower, and second, and more important, the likelihood of moisture contamination is significantly lower. Indeed, the major component of an air-fed ozone system is the moisture-removal equipment, which is not the case for oxygen-fed ozone systems.

Air-fed ozone generators are cleaned more frequently (e.g., once per year) than are oxygen-fed ozone generators (e.g., once every 5 years). However, oxygen-fed ozone generators can develop significant quantities of nitric acid if designed or operated improperly. Figure 4-28 shows excessive nitric acid that formed in an oxygen-fed ozone generator because the generator outlet valve remained open



Contactor		
Water Flow	mgd	60
Water Temp.	°F	79
Ozone Dose	mg/L	3.0
Ozone Production	lb/day	1,500
Inlet Saturation	%	100
D.O. Inlet	mg/L	8.0
D.O. Outlet	mg/L	17.1
D.N. Inlet	mg/L	13.1
D.N. Outlet	mg/L	9.8

Point 5	
90.6	%wt O_2
1.4	%wt N_2
0.0	%wt AR
8.0	%wt O_3
152.9	scfm
18	psig
120	°F
4	ppm H_2O
DP −83	°F_{SP}

Point 6	
85.8	%wt O_2
13.2	%wt N_2
0.4	%wt AR
0.6	%wt O_3
123.1	scfm
−4	in H_2O
79	°F
22,700	ppm H_2O
DP 80	°F_{SP}

Point 7	
86.4	%wt O_2
13.2	%wt N_2
0.4	%wt AR
0.0	%wt O_3
123.2	scfm
−10	in H_2O
109	°F
22,700	ppm H_2O
DP 80	°F_{SP}

Point 8	
86.4	%wt O_2
13.2	%wt N_2
0.4	%wt AR
0.0	%wt O_3
123.2	scfm
28	in H_2O
115	°F
22,700	ppm H_2O
DP 80	°F_{SP}

Figure 4-29 Contactor and off-gas process schematic for LOX-fed ozone system

during ozone system shutdown. The opened outlet valve allowed moisture to migrate back into the generator from the ozone contactor. Consider that the desired moisture content is about 1 ppm_{wt} within the ozone generator and about 30,000 ppm_{wt} at the gas-liquid interface at the ozone contactor. Upon restart, generator purging was insufficient to remove the excessive moisture before power was applied and nitric acid was formed. The important point is that, just as with air-fed ozone systems, potential sources of moisture loading to the ozone generators must be minimized by: (1) maintaining positive pressure in off-line generators and (2) purging the generators (i.e., a few minutes if bottled up and several hours if opened) with dry oxygen gas before power is applied to the dielectrics (consult with ozone system supplier).

Ozone Contactor

The ozone contactor schematic shown in Figure 4-29 is a bubble-diffuser over-under baffled basin, which is the most common ozone contactor configuration. However, sidestream injector ozone dissolution systems are now competitive systems because of their ability to operate at higher ozone concentration (e.g., 12 %wt), which results in a significant reduction in gas flow rate. Sidestream systems are gaining popularity and are discussed later in this chapter.

As shown in Figure 4-29, ozone is delivered into the first chamber of the contactor, which is the most common application point. Refer to chapters 2 and 3 for discussion of cases or operating conditions when ozone might be added to chambers other than chamber 1. Ozone production rate is 1,500 lb/d in the example, which is an ozone dose of 3.0 mg/L at water flow rate of 60 mgd. The example assumes that the contactor inlet DO and DN levels are at 100% saturation, or 8.0 and 13.2 mg/L, respectively, for water temperature of 79°F and plant elevation of 1,200 $\mathrm{ft_{MSL}}$. The outlet DO level is increased significantly to 17.1 mg/L, because gas applied to the contactor has a high oxygen content (i.e., 90.6 %wt). The DN level is decreased from 13.2 mg/L to 9.8 mg/L, because applied gas nitrogen content is very low (1.4 %wt).

Water utilities that operate oxygen-fed ozone systems have considered that problems could develop by operating at a supersaturated DO level. One problem might be filter gas binding (e.g., sometimes called air-binding), which also might occur for air-fed ozone systems (see also chapter 5). Another problem is an increased potential for corrosion and/or an increased potential for biological regrowth in the distribution system. Fortunately, reported problems are rare or are manageable with attention to good operating practices that include the following (see also chapter 5):

1. Always operate water treatment plant filters under positive-head conditions, which is consistent with good filter operating practice.
2. Maintain or implement a corrosion control program.
3. Maintain or implement good distribution system operating practices (e.g., minimize detention time in the distribution system, maintain chlorine or chloramine residual).

Ozone Off-Gas and Destruct

Ozone contactor off-gas parameters are displayed at point 6 in Figure 4-29. The off-gas ozone concentration is 0.6 %wt, which implies 93% ozone transfer efficiency (i.e., 0.6 %wt ~ 0.07 × 8 %wt). Typical transfer efficiency for high ozone-concentration oxygen-fed systems is 95%, whereas typical transfer efficiency for low ozone-concentration air-fed systems is 85%, each with 20-ft diffuser depth. More information about contactor, diffuser, and gasket design and ozone transfer efficiency is presented later in this chapter. Information about diffuser operation and maintenance and the importance of gasket integrity is presented in chapter 5.

The off-gas (point 6) oxygen, nitrogen, argon, and ozone concentrations are 85.8 %wt, 13.2 %wt, 0.4 %wt, and 0.6 %wt, respectively. The off-gas flow rate is 123.2 $\mathrm{scfm_{68F}}$, which is about 20% lower than the contactor inlet-gas flow rate (152.9 $\mathrm{scfm_{68F}}$). The off-gas flow rate for oxygen-fed ozone systems is significantly lower than that for air-fed ozone systems, because the ozone concentration is higher (i.e., lower feed-gas flow rate is needed) and overall gas dissolution into the water is greater (i.e., oxygen transfer is greater than nitrogen stripping). However, ozone destruct and vent blower sizing should also consider that the off-gas flow rate might increase dramatically during short periods of time due to changes in water level within the ozone contactor. The vent blower must be sized to handle the extra off-gas flow that results from water level changes or, as a minimum, the off-gas pressure/vacuum relief valve should be sized to relieve excessive pressure/vacuum that might develop when, or if, the water level changes.

Design and operation of the off-gas destruct system and off-gas exhaust blower for oxygen-fed ozone systems is similar to design and operation for air-fed ozone systems. Refer to the previous discussion of the low-pressure off-gas destruct and blower for information and considerations concerning design and operation of this equipment. One additional consideration is that the off-gas flow rate is significantly lower for the oxygen-fed ozone system. This suggests that the potential exists for tunneling or short-circuiting of off-gas through the catalyst. To address potential problems, ozone destruct system design might include recycle piping that maintains minimum gas flow through the catalyst bed. However, most ozone destruct systems do not include this provision. Consult the catalyst supplier or the ozone system supplier for details.

VACUUM-PRESSURE SWING ADSORPTION OXYGEN-FED OZONE SYSTEM

The VPSA oxygen-fed ozone system schematic is similar to the LOX-fed ozone system schematic, except that the high-purity oxygen feed-gas is produced on site. Such a system is known as either a VPSA or a VSA on-site oxygen production system. There are multiple manufacturers that supply on-site oxygen equipment used in industrial applications that require oxygen for purposes other than ozone generation. The VPSA (and VSA) technology is applied in a few large ozone installations in the United States.

Las Vegas, Nevada, has two water treatment plants with ozone and VPSA on-site oxygen production facilities. Plant design criteria are shown in Table 4-1. On-site oxygen production was selected instead of LOX feed based on economics and practical operational considerations. Practical operation was based on a LOX delivery requirement to support operation at design conditions. LOX delivery-truck capacity ranges from 4,500 to 6,000 gal. The larger-capacity truck delivers about 30 tons of oxygen (i.e., 6,000 gal at 9.52 lb/gal). Several truck deliveries per day were considered impractical.

Economic considerations involved the cost of purchasing and operating a VPSA on-site oxygen production facility versus the cost of LOX. The author conducted power-production tests on the installed VPSA system and observed oxygen production specific energy values of 11 kWd/ton at 100% design output

Table 4-1 Selected Design Criteria for Southern Nevada Ozone Systems

Design Parameters	Alfred Merritt Smith WTP	River Mountains WTP	Units
Plant capacity	600	300	mgd
Ozone dose	3.2	3.2	mg/L
Ozone production	16,000	8,000	lb/day
Ozone concentration	8.0	8.0	%wt
VPSA design criteria			
Installed capacity	100	50	tons/day
	200,000	100,000	lb/day
	1,663	832	$\text{scfm}_{68\text{F}}$
Oxygen/nitrogen/argon	92/4/4	92/4/4	%vol

and 17 kWd/ton at 50% design output. Reasons for the lower specific energy value at reduced output are discussed later. As an example, at a $0.10/kWh energy price, the unit price of oxygen production is $26/ton to $41/ton at 11 kWd/ton to 17 kWd/ton (e.g., $26/ton = 11 kWd/ton × 24 hr/d × $0.10/kWh), respectively. In Las Vegas, the purchase price of LOX was $150/ton. However, the author noted that the LOX purchase price ranged from $60/ton to $80/ton at other locations across North America. The LOX price differential at Las Vegas plus remote delivery (i.e., LOX trucked in from Los Angeles) were contributing factors that justified the selection of VPSA on-site oxygen production facilities.

The VPSA system has molecular sieve media that adsorbs water, hydrocarbons, and nitrogen molecules, thereby drying the gas and increasing its oxygen concentration. Figure 4-30 shows that the air blower delivers atmospheric air into the adsorbent bed and that enriched oxygen gas is delivered to the product-oxygen storage tank. This is one of seven steps (about 10 sec in duration) in the approximately 50-sec VPSA operating cycle. Figure 4-31 shows the same air blower drawing vacuum in the adsorbent bed. Adsorbed moisture, hydrocarbons, and nitrogen molecules are desorbed and vented to atmosphere during this approximately 20-sec step. The other five steps are transition steps between the major pressure and vacuum steps.

The adsorbent bed outlet pressure is variable, ranging from 3 psig to 7 psig. Higher ozone system operating pressure, between 12 psig and 14 psig, is achieved by the booster compressor; it is called a base-load oxygen compressor (BLOC) in Figure 4-31. Equipment for the 50-ton capacity VPSA system at the Alfred Merritt Smith Water Treatment Plant in Las Vegas is shown in Figure 4-32.

At least twice in 50 sec the flow-direction valves (shown in Figures 4-30 and 4-31) either open or close. This valve cycling frequency creates significant wear of

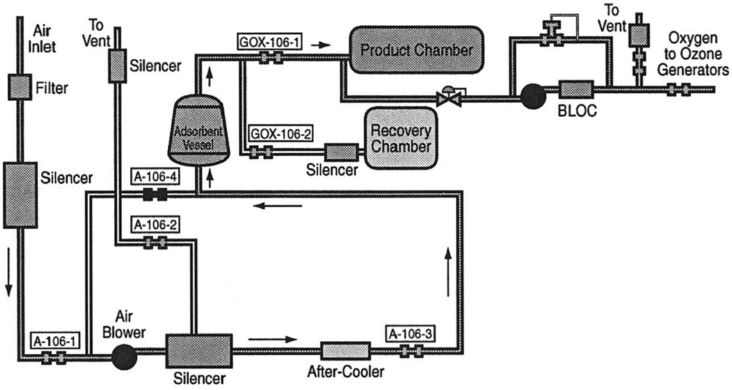


Figure 4-30 VPSA pressure-operating step where water and nitrogen are adsorbed onto the molecular sieve media

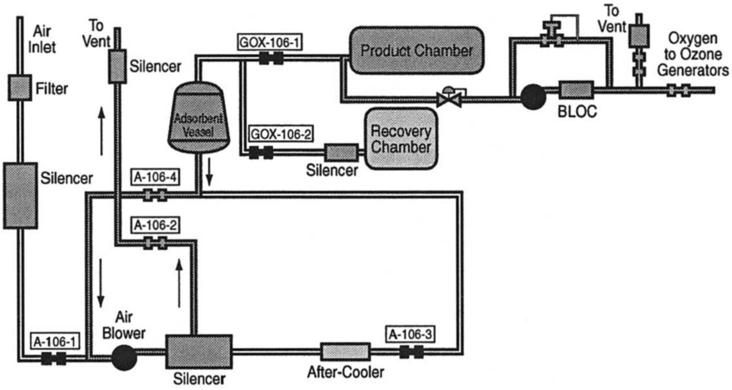


Figure 4-31 VPSA vacuum-operating step where water and nitrogen are desorbed from the molecular sieve media

valve seats and valve actuators. Consequently, maintenance is significant for VPSA and VSA systems. Large plants can and must support the level of maintenance required to sustain continuous operation. When maintained properly, VPSA and VSA systems support successful operation of the ozone system.

At Las Vegas, LOX is available as backup in case the VPSA unit(s) shuts down. When inlet pressure to the ozone generator falls below a preset value, LOX is supplied automatically. In other large plants that use VPSA or VSA systems, the VPSA or VSA unit is sized to operate at 100% capacity under normal operating conditions, with supplemental LOX added during short-duration events when peak ozone production is required. This approach reduces the capital cost of the

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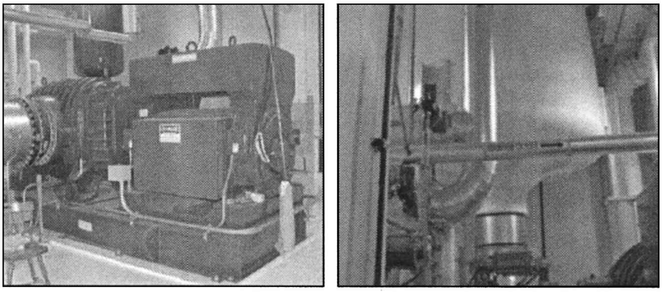
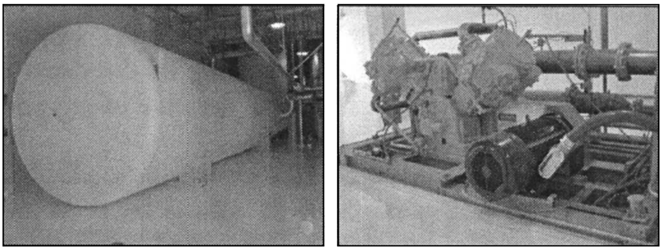


Air Blower

Adsorbent Vessel



O_2 Product Tank

Booster Compressor

Figure 4-32 VPSA equipment at the 600-mgd Alfred Merritt Smith Water Treatment Plant, Las Vegas, Nevada

VPSA or VSA system and ensures that the unit will operate most efficiently, i.e., near or at design output capacity.

PRESSURE SWING ADSORPTION OXYGEN-FED OZONE SYSTEM

PSA on-site oxygen production is an alternative to LOX feed-gas supply in very small, small, and medium-sized ozone systems. PSA technology preceded and is similar to VPSA and VSA technology in terms of adsorption of water, hydrocarbons, and nitrogen molecules during pressure operation and desorbtion of water, hydrocarbon, and nitrogen molecules at lower pressure (see previous description of the VPSA system for more detailed explanation). The PSA system has less equipment (e.g., does not require a booster compressor), but energy requirements and operating costs are greater than for VPSA or VSA systems (e.g., specific energy value approaching 15 kWd/ton, or higher, versus 11 kWd/ton). However, the simplicity of PSA lends itself to small plant applications. Alternatively, the lower operating cost of VPSA and VSA systems justifies its more complex equipment arrangement at large-scale applications.

Figure 4-33 shows a process schematic for a PSA oxygen production system. The air compressor operating pressure is typically 90 psig for small-capacity PSA systems. The heatless desiccant dryer is installed to remove excess moisture from

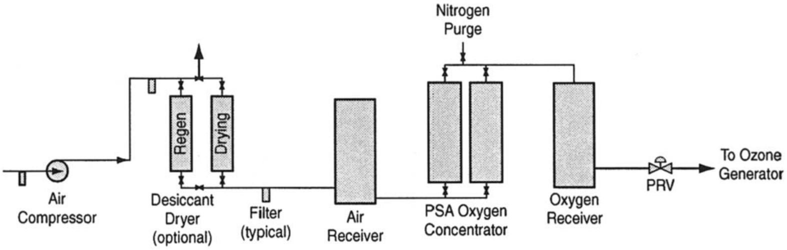


Figure 4-33 PSA schematic for on-site oxygen at small and medium-size ozone systems

the air stream. Molecular sieves are used to adsorb water, hydrocarbons, and nitrogen molecules, but excessive moisture loading to the sieves will decrease nitrogen adsorption capacity and result in a decrease of oxygen production capability.

Figure 4-34 shows a skid-mounted PSA system for small plants. Oxygen-enriched gas (~95% O_2) output might be 25 scfh_{68F} for these units, which is 0.25 ton/d (0.25 ton/d = 25 $\text{ft}^3/\text{hr} \times 24\ \text{hr/d} \times 0.0838\ \text{lb/ft}^3$). At 8 %wt ozone concentration and 0.25 ton/d gas flow (500 lb/d), the ozone production rate is 40 lb_{O_3}/d. The associated plant water flow rate is 1.6 mgd at an assumed ozone dose of 3 mg/L. Ozone system suppliers provide on-site PSA oxygen/ozone systems as a package unit.

OZONE CONTACTOR

Ozone dissolution features define the two main categories of ozone contactors. Bubble-diffuser ozone contactors dissolve ozone into the water via a porous stone diffuser that creates small bubbles. Following dissolution, the ozonated water continues through the contactor for oxidation and disinfection reactions. Sidestream ozone systems dissolve ozone into a sidestream flow via an injection setup or in the main process flow stream in some sidestream arrangements. The sidestream flow is subsequently mixed with the main process flow stream, which is directed to a reaction tank or pipeline for oxidation and disinfection reactions. Historically, bubble-diffuser ozone contactors have been common in drinking water treatment applications. Currently, sidestream-injection systems are gaining in popularity. Both systems are discussed in the following paragraphs.

Bubble-Diffuser Dissolution Ozone Contactors

Common features of bubble-diffuser contactors are depicted in Figure 4-35 and discussed here. In most situations, at least two contactors are installed. Information concerning contactor size and layout is discussed in chapter 3 and information concerning disinfection and log-inactivation calculations is presented in chapter 2.

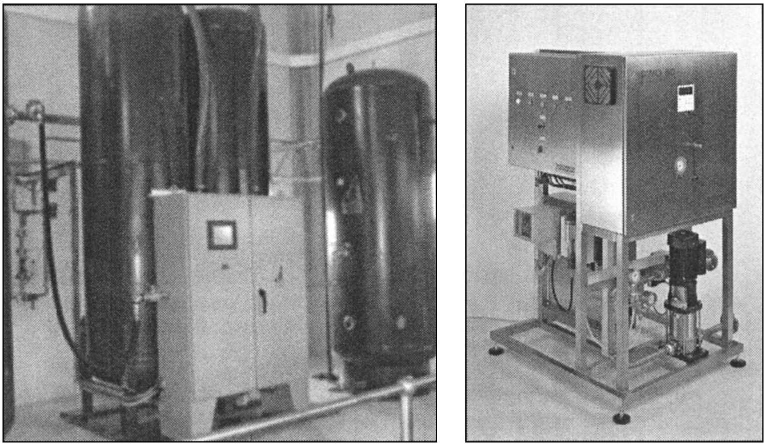


Figure 4-34 PSA oxygen production unit (Photos courtesy of Oxygen Generation Systems Inc. on the left and AirSep Inc. on the right)

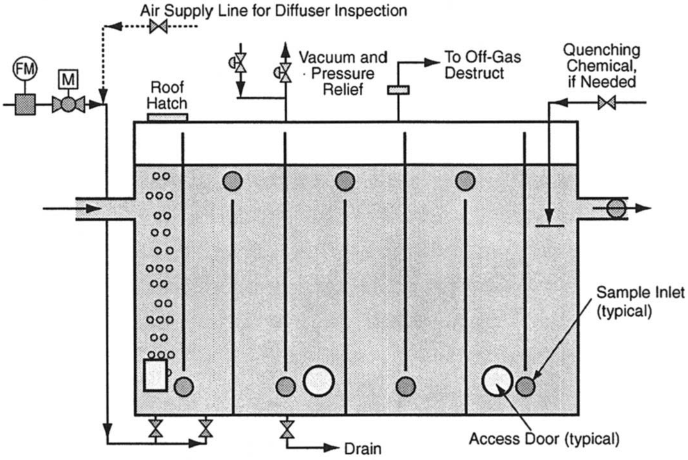
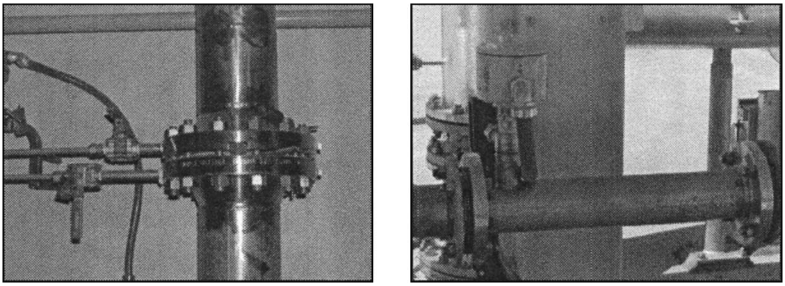


Figure 4-35 Features typical in an over-under baffled bubble-diffuser ozone contactor

Ozone piping to each contactor includes a flowmeter/indicator/transmitter and motorized control valve (see Figure 4-35). These devices are critically important because they control gas flow rate and overall ozone treatment performance. Ozone process control and automation is presented later in this chapter. The control valve and actuator must be sized correctly and capable of precise control over a broad range of gas flow. Butterfly valves and standard ball valves are generally insufficient for precise control. V-port ball valves or similar



Orifice-plate flowmeter with differential pressure taps and DP transmitter located on ozone generator inlet feed-gas inlet piping.

Mass flowmeter located on inlet piping to ozone contactor.

Figure 4-36 Thermal mass flowmeter and V-port valve flow control arrangement on ozone contactor inlet pipe and orifice-plate flowmeter on ozone generator inlet pipe

precision-control valves are used to successfully control ozone gas flow. Thermal mass flowmeters are commonly used to measure contactor gas flow. Figure 4-36 shows a thermal-mass flowmeter. Also shown is an orifice plate, which is installed on the ozone generator inlet piping to field-verify accuracy of the thermal mass flowmeter. Types of gas flow measurement devices used in ozone systems and flow measurement accuracy are discussed in chapter 8.

Ozone gas is dissolved into the water by bubble diffusion using rod- or dome-shaped ceramic porous stone diffusers, as shown in Figure 4-37. Rod-shaped diffusers are common in air-fed applications that use a higher gas flow rate, which ranges between 2 and 6 ft^3/min per diffuser. Dome-shaped diffusers are common for the oxygen-fed applications where the gas flow rate is lower. Dome diffuser gas flow rate typically ranges between 0.5 and 2 ft^3/min per diffuser. An important design detail is dissolution chamber floor area and diffuser spacing to achieve good coverage of gas bubbles. A rule-of-thumb for diffuser spacing is ~4 ft^2/diffuser, or less.

Diffusers consist of ceramic porous stones, 316 stainless steel holders, and gasket seals. Gaskets are susceptible to deterioration (see Figure 4-38). Hypalon gaskets generally perform well in low-ozone-concentration air-fed systems and perform poorly in high-ozone-concentration oxygen-fed systems. Next-generation Viton gaskets have increased longevity in high-ozone-concentration oxygen-fed systems. However, Viton gaskets come in varying grades; it is important to use the best grade Viton possible. New-generation expanded Teflon gaskets (trade name Gortex or Garlon) have been used recently in ozone applications to improve gasket longevity. Initial feedback is good. Expanded Teflon is significantly more expensive than Viton; therefore, Viton gaskets remain a competitive alternative.

Annual diffuser inspection (see Figure 4-37) is needed to minimize coarse-bubbling and maintain maximum ozone transfer efficiency. Inspection reveals gasket

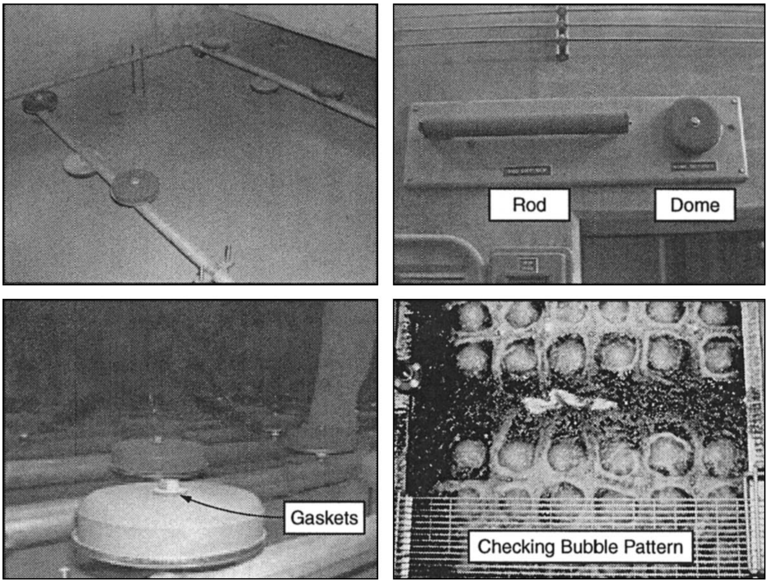
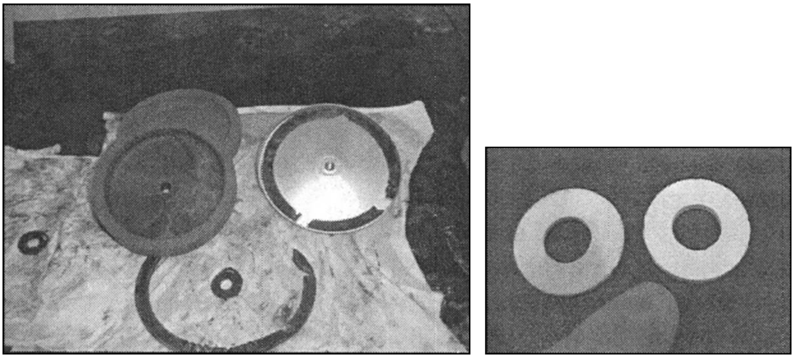


Figure 4-37 Ozone diffusers in a bubble-diffuser ozone contactor



Hypalon diffuser gaskets after 2 years of service in a high-ozone-concentration (8 %wt) oxygen-fed ozone application.

Alternative expanded-Teflon gaskets that are gaining popularity for use in oxygen-fed ozone applications.

Figure 4-38 Ozone diffuser gaskets in a bubble-diffuser ozone contactor

failure and, in some cases, diffuser clogging when manganese is present in the raw water. Diffuser inspection is facilitated by side-door entrance into the approximately 20-ft-deep tank. Example side and roof hatches are shown in Figure 4-39. Provision for draining and entry into ozone contactors must be carefully considered during the design phase because the contactor is a confined space. Provisions include drain

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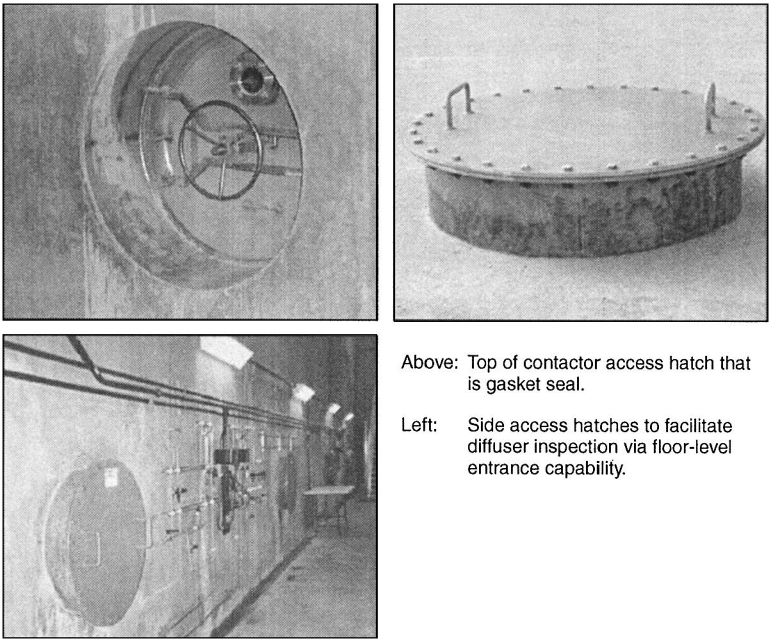

Above: Top of contactor access hatch that is gasket seal.

Left: Side access hatches to facilitate diffuser inspection via floor-level entrance capability.

Figure 4-39 Bubble-diffuser ozone contactor hatches to facilitate diffuser inspection and repair

line(s), side access, roof hatches, ventilation fans, and air supply source for diffuser inspection, as depicted in Figure 4-35.

Ozone transfer efficiency is affected by design and maintenance decisions (Rakness et al., 1988). Diffuser depth, which is the most important design decision, has been optimized at between 18 ft and 22 ft. The value for maximum transfer efficiency is approximately 85% for low-ozone-concentration (i.e., 1 %wt to 2 %wt) air-fed ozone systems and 95% for high-ozone-concentration oxygen-fed (i.e., 8 %wt to 10 %wt) ozone applications (Rakness et al., 1995). Other parameters affect transfer efficiency marginally, such as water temperature and ozone residual (i.e., range of residual in drinking water treatment). Ozone transfer efficiency decreases when diffuser gaskets leak or stones are broken and coarse bubbling develops. Diffuser maintenance is required to sustain fine-bubble operation. Monitoring transfer efficiency is effective in identifying diffuser problems and is discussed in chapter 5.

Ozone residual sample lines are shown in Figure 4-35 at the outlet of each chamber of the over-under baffled contactor. Chapter 7 discusses residual sampling set up to optimize performance. Vacuum-pressure relief and off-gas ozone destruct systems were discussed previously in relation to the ozone system schematics. Residual quenching is seen as an optional ozone treatment system in limited applications and is discussed in chapter 5.

The number and size of chambers in a bubble-diffuser contactor depend on performance objective. For oxidation reaction only (i.e., no disinfection), two or four chambers are used. For disinfection to achieve *Giardia* and virus inactivation credits (see chapter 2), six or eight chambers are common. For disinfection to achieve *Cryptosporidium* inactivation credit, 10 or more chambers are used. However, the dissolution chamber might be of smaller size to obtain good coverage of gas bubbles (see previous discussion). The benefit of multiple chambers is reduced short-circuiting and improved T_{10}/T ratio.

Roustan and colleagues (1993) evaluated and modeled the T_{10}/T ratio for multi-baffled bubble-diffuser ozone contactors. Their model estimates that T_{10}/T ratios for 6-, 8-, and 10-chamber contactors is 0.52, 0.58, and 0.63, respectively. Bellamy (1995) established a rule-of-thumb equation (see Eq. 4-1 below) to estimate the T_{10}/T ratio for over-under baffled bubble-diffuser ozone contactors. In Eq. 4-1, L is length of the chamber in the direction of water flow and D is water depth.

$$T_{10}/T = 0.91 - 0.52 \times \frac{L}{D} \qquad \text{(Eq. 4-1)}$$

Full-scale tracer testing is used to determine the actual T_{10}/T ratio (Teefy et al., 1996). Some contactor designers have considered that tracer testing will be implemented at startup and have incorporated special design features to accommodate the test, such as tracer chemical feed piping to a well-mixed application point at the contactor inlet and sample piping at the contactor outlet. Other samples could also be collected at residual sample taps along the contactor.

Sidestream Injection Ozone Dissolution

Ozone dissolution with sidestream injection is a viable alternative to bubble diffusers. Sidestream injection systems typically have lower maintenance costs, considering the expense involved with diffuser inspection and repair due to clogging and gasket leakage. Also, there is greater flexibility in contactor layout, because dissolution is separated from reaction. However, operating cost might be slightly higher, because of pumping cost related to the sidestream flow. Design considerations for efficient operation at design flow and under turndown conditions are discussed here.

The ozone reaction zone (i.e., contactor) in sidestream systems is designed independent of dissolution. An example of dependent design is the bubble diffuser ozone contactor. With bubble diffusers, the dissolution cell must be approximately 20 ft deep to optimize ozone transfer efficiency. The reaction zone is usually of similar depth. In contrast, all sidestream injection components are outside of the

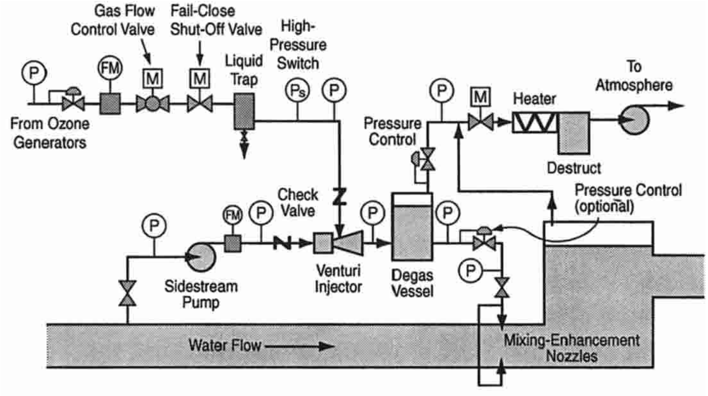

Figure 4-40 Simplified schematic of sidestream ozone dissolution system with degas vessel

contactor, which allows independent design of the ozone reaction zone. As such, the reaction zone is generally a pipeline contactor or shallow-depth tank with either vertical or horizontal baffles (i.e., up and down or back and forth water flow). Also, all equipment components are available for maintenance while ozone contactors remain in service.

Sidestream injection has gained popularity since development of medium-frequency ozone generators that produce high-concentration ozone gas (10 %wt to 12 %wt). High-concentration ozone has significantly reduced the operating gas flow rate. In turn, reduced gas flow has lowered sidestream capital and pumping costs to achieve required gas:liquid (G:L) ratios. The denominator, L, is the water flow rate that is pumped through the injector. Water flow (L) can be lowered when gas flow (G) is reduced for a given G:L ratio. There are two items of note for the G:L ratio. First, volumetric units of expression are used for both parameters, such as ft^3/min or m^3/hr. Second, gas flow should be expressed in standard temperature and pressure (STP) units, such as G_{68F}/L for STP of 68°F and 1 atm pressure. See appendix A for more information concerning STP.

Sidestream systems are installed in two basic configurations. One process schematic is a venturi injector located in front of a degas vessel, shown in Figure 4-40. In this schematic, the sidestream ozone residual is elevated significantly and off-gas that is collected in the degas vessel is directed to ozone destruct. In some cases, the degas vessel is pressurized sufficiently to direct off-gas through the destruct unit, without aid of an exhaust blower. However, only off-gas is directed to the destruct catalyst, not water. A small amount of off-gas might develop at the top of the ozone contactor, which should be directed to a separate ozone destruct unit. The injector-degas-vessel schematic is typically used to (a) minimize the DO level of the ozonated water, as discussed later; or (b) minimize gas bubbles in the downstream

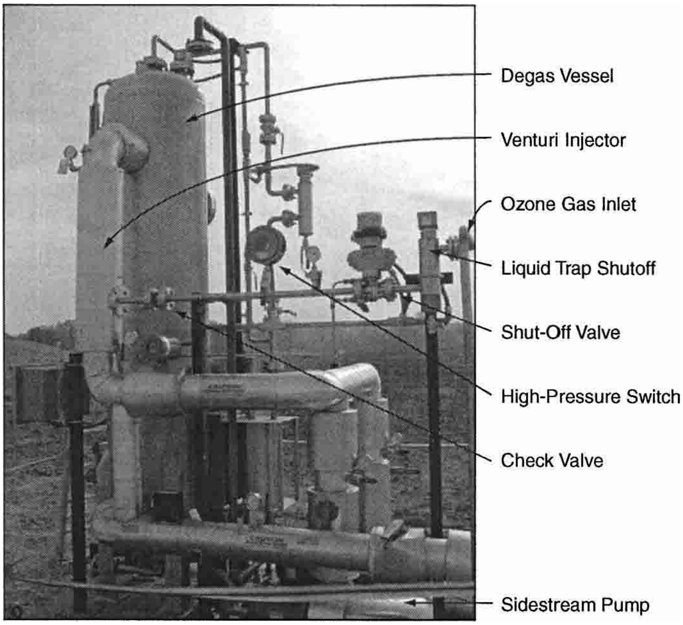

Figure 4-41 Skid-mounted sidestream ozone dissolution system with degas vessel

reactor (e.g., pipeline). The operating G:L ratio is usually lower (in the range of 0.1) for the injector-degas-vessel schematic.

In the injector-degas-vessel schematic the sidestream water flow, with elevated ozone residual, is directed to a pipeline and mixed with process water (i.e., the water to be treated with ozone), which is raw water, settled water, recycled water from the backwash-water treatment process, or other. The mixed sidestream-plus-process water is then directed into a contacting zone for further oxidation and disinfection. A skid-mounted injector and degas vessel unit is shown in Figure 4-41. In this application, recycle water from the backwash-water treatment process is ozonated. The purpose of the installation is to provide an extra level of disinfection protection for the recycle water and to carry ozone residual to the main flow for pre-oxidation.

The other sidestream process configuration eliminates the degas vessel, as shown in Figure 4-42. This is an injector-only schematic, which typically operates at higher G:L ratios (in the range of 0.3 to 0.5 and even up to 0.7). Some dissolution occurs within the sidestream itself. Undissolved gas bubbles that are co-mixed with the sidestream flow are directed to the main process flow stream where additional ozone and oxygen transfer occurs, with sufficient sidestream-mainstream mixing to achieve stable ozone residual. Undissolved gas coalesces in the pipeline and releases into the contactor. The off-gas is collected in the contactor headspace and piped to the ozone destruct unit.

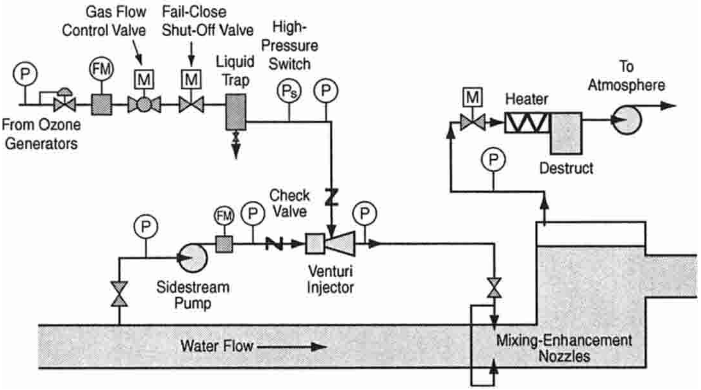

Figure 4-42 Simplified schematic of injector-only sidestream ozone dissolution system with direct pipeline injection

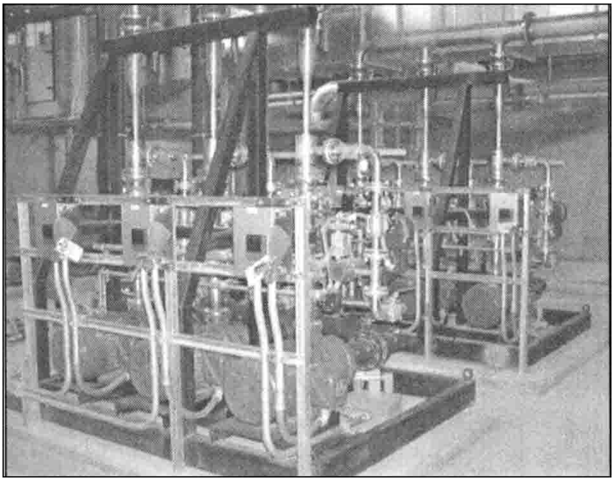

Figure 4-43 Two skid-mounted sidestream ozone dissolution systems with multiple pump/eductor units to facilitate economical operation at turndown

Two skid-mounted sidestream injection units are shown in Figure 4-43. Each skid is dedicated to an ozone contactor, which is sized for 50% of the design water flow rate. Four pump-injector systems operate (two on each skid) at design flow. The third pump-injector system on each skid serves as standby. Reduced operating cost at turndown conditions is a major advantage of this multi-pump-injector system configuration. Pump-injector units are turned on, as needed, to meet current plant flow rates. Additional information concerning system configuration is provided later in this chapter.

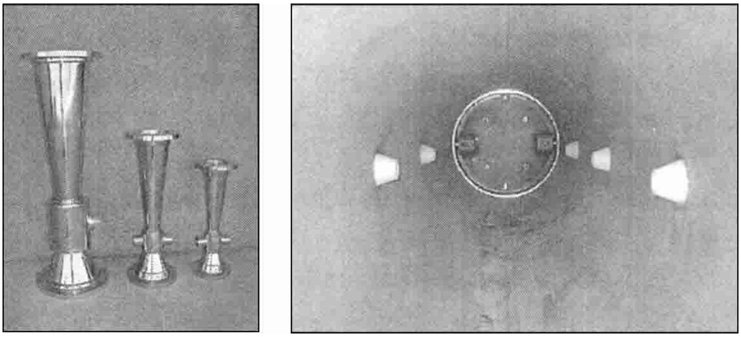

Figure 4-44 Sidestream injectors on the left are sized to meet design criteria. Nozzle injectors on the right promote good mixing between the sidestream flow and main process water flow. (Photos courtesy of Mazzei Injector Corporation)

Figure 4-44a shows three different sizes of injectors. The manufacturer selects the size of venturi injector that will meet site-specific design criteria. Figure 4-44b shows a sidestream-mainstream mixing zone. The mainstream nonozonated water flows through the inside of the pipe. The sidestream flow enters at the side of the pipe via several nozzles that are strategically placed to promote thorough mixing. Mixing is further enhanced by action of the nozzles that accelerate the velocity of the sidestream flow as it meets the main process flow. Mixing action shears coalesced bubbles that develop within the sidestream piping, which increases gas-liquid interface surface area thereby improving ozone mass transfer. Thorough mixing also develops stable ozone residual throughout the mainstream water flow.

The venturi injector is the central point of the sidestream system where ozone gas is mixed with sidestream water flow (see Figures 4-40 and 4-42). Important design and operating considerations, which promote reliable sidestream operation and good control of process performance, include the following:

1. Provide devices that protect the ozone generator from backflow of water or water vapor while maintaining optimal pressure in the ozone generator ahead of the low-pressure condition at the injector throat.
2. Provide controlled flow rates of ozone to each ozone contactor.
3. Provide pressure gauges at strategic locations along gas and liquid piping to assist in process troubleshooting activities (see Figures 4-40 and 4-42).
4. Select the sidestream schematic configuration based on overall plant needs.
    a. Considerations for selecting an injector-degas-vessel schematic include:
        1) DO level of the ozonated water can be minimized.

    2) Gas bubbles entering the main process reaction zone (e.g., pipeline contactor) can be minimized.
    3) NOTE: Detention time in the degas vessel plus sidestream piping should be minimized to prevent excessive decay that might increase applied ozone dose.

b. Considerations for selecting an injector-only schematic include:

    1) Capital and operating cost is minimized due to operation with a higher G:L ratio, which minimizes sidestream flow rate.
    2) NOTE: The ozone reaction zone should be designed with due consideration that additional ozone transfer must occur in the ozone contactor. For example, operating pressure at the sidestream-mainstream mixing point might be similar to the pressure (e.g., 7 to 10 psig) that exists in bubble-diffuser contactors (e.g., 18 to 23 ft diffuser depth).

The sidestream system operates in the following way: Water is pumped through the venturi injector to create a vacuum that draws in ozone gas. Some designs call for operation with positive pressure, instead of negative pressure, at the injector. During normal operation, a controlled volume of ozone gas is directed to the sidestream injector. However, during abnormal operation or system shutdown, a number of conditions exist that might cause water to back up into the ozone generator or cause water vapor to enter the generator. Keeping water and water vapor away from the ozone generator is critically important. Several design features that are used to achieve this objective are described in the following paragraphs.

Backflow protection devices are installed on the ozone gas supply line to prevent water backflow into the generator. Backflow occurs when the sidestream pump shuts off causing the venturi effect to stop and positive water pressure to build in the main flow pipeline. In this situation, the water pressure in the sidestream piping is greater than the pressure in the gas piping that is located between the generator and venturi. A single check valve on the gas line is insufficient to prevent water or water vapor from entering the ozone generator. In addition to a check valve, a shut-off valve (e.g., ball valve) must be closed. Two backflow-protection devices are shown in Figures 4-40 and 4-42, in addition to a check valve. A high-pressure switch that detects abnormal pressure and closes the shut-off ball valve should be used. In addition, a liquid trap that detects water and closes the shut-off ball valve should also be installed.

Off-line ozone generators must have closed outlet valves to prevent water vapor from entering the generator and creating nitric acid when the generator is restarted. For example, if the gas valves between the ozone generator and the sidestream injector are open and the sidestream pump is operating, the generator

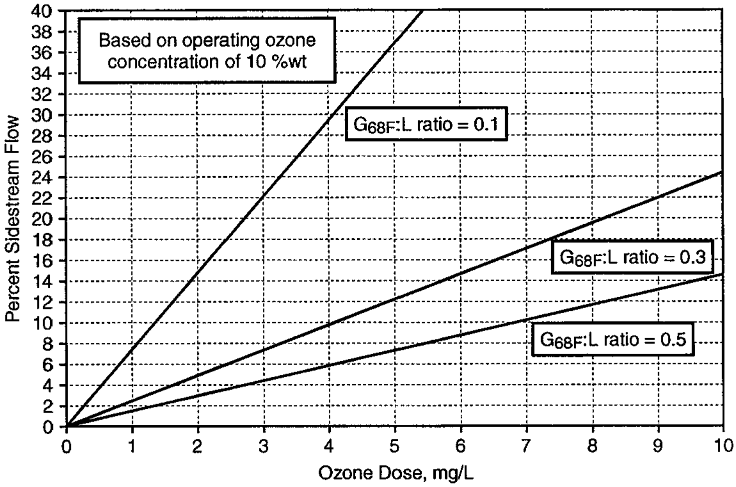

Figure 4-45 Relationship between ozone dose and sidestream water flow rate at variable G_{68F}:L ratio

vessel might be in a state of vacuum. In this negative-pressure condition, water vapor from the ambient air will find its way into the ozone generator. Ozone generators must be very dry (preferably with a dew point < –100°F, which is a moisture content of 1 ppm_{wt}). Ambient air moisture content might be 10,000 to 30,000 ppm_{wt}. Given this large differential, even minimal air leakage into the ozone generator will produce moisture contamination of the unit. A possible leak source is the ozone concentration meter, which typically remains in service while the generator is off-line. One way to minimize the potential of moisture contamination is to close the outlet valve on nonoperating ozone generators. This practice also applies to bubble-diffuser installations.

Constant-speed pumps or, in some instances, adjustable frequency drive pumps are used to deliver a controlled sidestream flow rate at constant pressure. Sidestream pump flow rate is a function of design ozone dose, G:L ratio, and ozone concentration. Pump size and operating conditions (e.g., flow rate, operating pressure, and power demand) are established in the design phase and are unchanged during operation. The relationship among the three design parameters (ozone dose, G_{68F}:L ratio, and ozone concentration) is summarized in Figure 4-45. The figure shows the percentage of sidestream water flow (i.e., percent of mainstream process water flow) to meet design conditions for ozone dose, G_{68F}:L ratio, and ozone concentration. The chart is developed for constant ozone concentration of 10 %wt, variable ozone dose, and three different G_{68F}:L ratios of 0.1, 0.3, and 0.5. The lower G_{68F}:L ratio of 0.1 is representative of operating conditions for the injector-degas-vessel schematic, where ozone and oxygen transfer occurs primarily within the sidestream workings. The higher G68F:L ratios are representative of operating conditions for the injector-only schematic, where some ozone and oxygen transfer occurs in the sidestream workings and additional transfer occurs after the sidestream combines with the main process water flow stream. Figure 4-45 shows that sidestream pump flow is ~4.5% of the mainstream process water flow rate at design ozone dose of 3 mg/L and G68F:L ratio of 0.5. Sidestream pump flow is ~22% of the mainstream process water flow rate at a G68F:L ratio of 0.1 and the same design ozone dose of 3 mg/L.

Sidestream flow percentage for noncharted conditions can be calculated using the following steps. For example, assume that the design ozone concentration is 12 %wt instead of 10 %wt. In these steps, an increase in design ozone concentration will decrease sidestream flow rate.

1. Find sidestream percent flow for design ozone dose and a selected G68F:L ratio from Figure 4-45, e.g., 4.5% at ozone dose of 3 mg/L, G68F:L ratio of 0.5, and ozone concentration of 10 %wt.
2. Adjust sidestream percent flow for selected design ozone concentration (e.g., 12 %wt). In this example, sidestream percent flow is 3.7% (i.e., 3.7% = 4.5% × 10 %wt ÷ 12 %wt).

   Another design choice is G:L ratio. For example, assume that the design G68F:L is 0.4 and design ozone concentration is 12 %wt. A decrease in design G68F:L ratio will increase sidestream flow rate.
3. Adjust sidestream percent flow for the design G68F:L ratio of 0.4, instead of 0.5 from step 2 above. In this example, the sidestream percent flow is 4.6% (i.e., 4.6% = 3.7% × 0.5 ÷ 0.4), where 0.5 is the selected G68F:L ratio in steps 1 and 2.

Operating pressure at the injector-discharge location is a typical design parameter. Design pressure value is usually established based on downstream pressure conditions, including pressure at the mixing point of the sidestream and mainstream flows, nozzle entrance losses, and friction loss. In some situations, the design pressure value is selected and controlled using a pressure control valve, as shown in Figure 4-40. The pressure control valve is used to develop higher operating pressure that will maximize ozone transfer efficiency. Ozone (and oxygen) transfer is discussed later in this section.

Sidestream pump size and operating power demand are largely determined by operating flow and pressure. Pressure at the pump discharge will be determined based on selected design pressure at the injector discharge location, pressure loss through the venturi injector, and friction loss of the piping between the pump and injector. Injector pressure loss is variable among venturi injector suppliers and is also a function of design gas and liquid flow rate and operating pressures. The

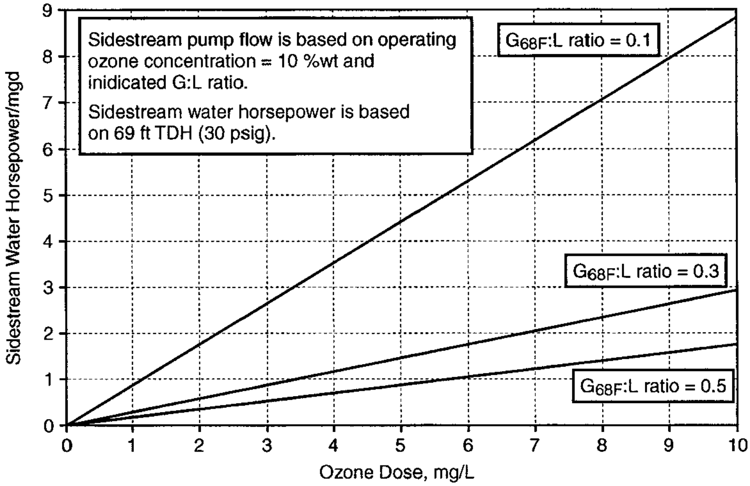

Figure 4-46 Relationship between ozone dose and sidestream pump water horsepower per million gallons per day (mgd) of mainstream process flow at variable G_{68F}:L ratios

sidestream pump boost pressure (i.e., pump outlet pressure minus pump inlet pressure) might be 10 psig, 20 psig, 40 psig, or other.

Figure 4-46 shows unit-flow water horsepower values (Whp/mgd) for variable ozone doses at G_{68F}:L ratios of 0.1, 0.3, and 0.5. The flow rate (mgd) is the mainstream process water flow rate that is being ozonated. In Figure 4-46, the sidestream water flow rate is based on indicated ozone dose (horizontal axis) and ozone concentration of 10 %wt. The pump boost pressure value is 30 psig, which is 69 ft total dynamic head (TDH). Figure 4-46 shows that unit-flow water horsepower is 2.7 Whp/mgd at an ozone dose of 3 mg/L and a G_{68F}:L ratio of 0.1. The operating power demand and resulting energy cost depend on pump and motor efficiency. For example, at pump efficiency of 75% and motor efficiency of 90%, the unit-flow power demand is 3.0 kW/mgd (i.e., 3.0 kW/mgd = 2.7 Whp/mgd ÷ 0.75 ÷ 0.90 × 0.748 kW/hp).

Operating conditions other than those indicated in Figure 4-46 will proportionally change unit-flow water horsepower values. For example, if the design value for operating ozone concentration is 12 %wt, unit-flow water horsepower is 2.25 Whp/mgd (i.e., 2.25 Whp/mgd = 2.7 Whp/mgd × 10 %wt ÷ 12 %wt). The unit-flow water horsepower value is lower because sidestream pump design flow rate is lower when design ozone concentration is higher. If pump design operating pressure is increased to 80-ft TDH, in addition to increasing design ozone concentration to 12 %wt, unit-flow water horsepower is 2.61 Whp/mgd (i.e., 2.61 Whp/mgd = 2.25 Whp/mgd × 80 ft_{TDH} ÷ 69 ft_{TDH}).

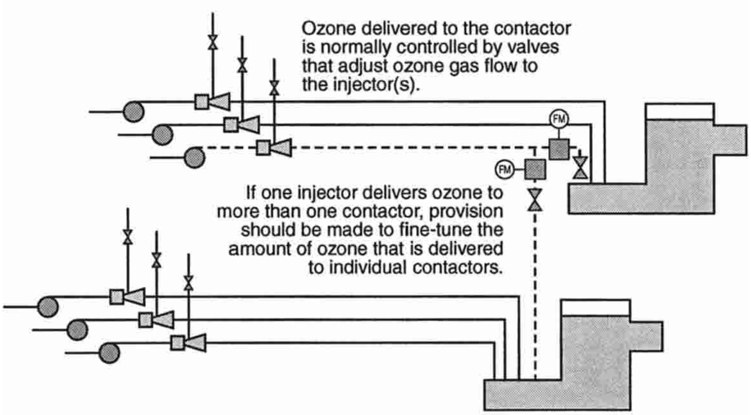

Figure 4-47 Illustration of sidestream layout with flexibility for reducing power demand at turndown plant flow and turndown ozone dose

The number and size of sidestream pump-injector units affect operating efficiency at turndown water flow rates, because sidestream pumps always operate at design sidestream flow (L) and design pressure. At design conditions, the G:L ratio is at design value, because gas flow (G) is at design value. At turndown ozone dose or water flow conditions, however, the G:L ratio is lower, because gas flow rate (G) is reduced while sidestream liquid flow (L) is unchanged. Fortunately, process performance is unaffected or improves, because ozone transfer is similar or better at lower G:L ratio. Unfortunately, unit-flow energy cost (kW/mgd) increases unless design flexibility is provided in number and size of sidestream pump-injector units or, in some instances, if variable frequency drives are installed.

Efficient operation at turndown water flow and turndown ozone dosage is an important consideration for sidestream system layout. Figure 4-47 illustrates a sidestream layout that provides for efficient operation and good control at turndown operating conditions. Efficient operation at turndown is achieved by choosing a multiple pump-injector design, such as four units in operation (two on each skid) at design dose and flow, with standby available on each skid. At turndown conditions, pump-injector units can be removed from service, yet stay below the design G:L ratio. For example, if the design G:L value is 0.3, the number of pump-injector units in service is such that the G:L ratio is as high as possible, yet below the 0.3 design value.

Ozone control is an important consideration for ozone system design in general and for sidestream design in particular. Design features that promote good ozone control are discussed in detail later in this chapter. One feature is direct control of the amount of ozone that is delivered to individual ozone contactors. The simplest ozone control strategy is to adjust the amount of ozone gas being delivered to each sidestream-contactor combination. If contactor performance indicators (e.g., the performance ratio; see chapters 2 and 5) call for a different amount of ozone to each contactor, more or less ozone can be delivered to each contactor by adjusting the gas flow control valve(s). In this way, optimum performance for each contactor is achieved (no underdosing and no overdosing).

The layout in Figure 4-47 illustrates one additional feature for reduced operating cost at extreme turndown condition. In this layout (dotted line in Figure 4-47), two ozone contactors are in service despite the fact that water flow is very low. In this example, long detention time (e.g., disinfection in cold water) is desired while the ozone dose is much lower than design, such that the G:L ratio is below design value with only one pump-injector unit on line. In this configuration, a gas flow adjustment to the single injector will change the quantity of ozone that is delivered to both contactors. Because it is likely that the individual contactors will require different amounts of ozone, flowmeters (ozone-residual resistant meters) and control valves are placed on the sidestream water flow piping. This allows for fine adjustment of the amount of ozone delivered to individual ozone contactors.

Optimum ozone transfer efficiency (>90%) in sidestream systems is achieved differently for injector-degas-vessel systems than for injector-only systems. For an injector-degas-vessel system, the design criterion for the G:L ratio must be in the range of 0.1 to maximize ozone transfer efficiency (i.e., >90%) within the sidestream unit (Jackson et al., 1999). The final design G:L value depends on site-specific conditions, such as operating pressure. The injector-only system operates at G:L ratios of 0.3 to 0.5 (and even up to 0.7). Excess gas bubbles in the sidestream are directed into the main-flow mixing zone (and ozone contactor), which provides for additional ozone and oxygen transfer. The reported ozone transfer efficiency for injector-only systems is >90% when the operating pressure in the mixing zone is 5 to 10 psig, good mixing intensity is available, and the sidestream G:L ratio is <0.5 (Mazzei et al., 1995; Neemann et al., 2002; Csalovski et al., 2001).

Ozone transfer within the sidestream is affected by the G68F:L ratio and saturation capacity of the sidestream water, which is displayed in Figure 4-48. The saturation capacity of the sidestream water is the maximum possible ozone residual value for the operating conditions and is a function of Henry's law, operating pressure, ozone concentration, and water temperature. The ozone transfer rate slows as the sidestream residual value approaches saturation capacity and stops altogether when saturation capacity is reached.

In Figure 4-48, the maximum possible ozone residual of the sidestream water flow is shown for G68F:L ratios of 0.1, 0.3, and 0.5. These values were obtained by assuming that 100% of the ozone in the gas (G) is transferred to the water (L), ignoring saturation capacity. These residuals can be compared to the saturation

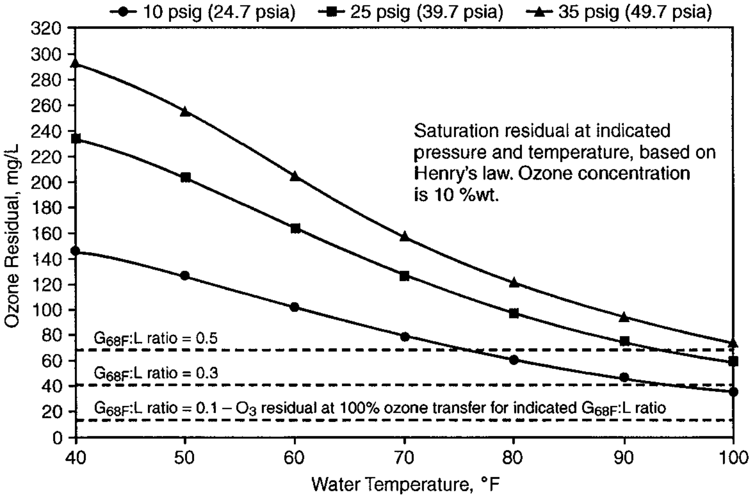

Figure 4-48 Saturation ozone residual at indicated temperature and pressure versus maximum residual possible at indicated G:L ratio

values for ozone, which are a function of water temperature, operating pressure, and ozone concentration. The saturation capacity increases as temperature decreases, pressure increases, and/or ozone concentration increases. The rate of ozone transfer is enhanced when the saturation capacity is high and maximum residual value is low (i.e., at higher delta value). From values shown in Figure 4-48, the following items are noted:

1. The maximum residual is lowest for a G_{68F}:L value of 0.1, which maximizes the delta value between maximum residual value and saturation capacity. This condition, in turn, elevates ozone transfer efficiency within the sidestream. This explains why the G:L ratio is lower in injector-degas-vessel systems.
2. At elevated water temperature, it might be necessary to increase operating pressure and/or lower the G:L ratio to optimize ozone transfer efficiency in injector-degas-vessel systems. As such, site-specific conditions should be used to optimize design.
3. The maximum residual is highest for a G_{68F}:L value of 0.5, which minimizes the delta value between the residual value and saturation capacity. This condition decreases ozone transfer efficiency within the sidestream works. The undissolved ozone in the gas bubbles is directed to the main process water within the sidestream-mainstream mixing zone for additional ozone transfer within the contact basin itself.

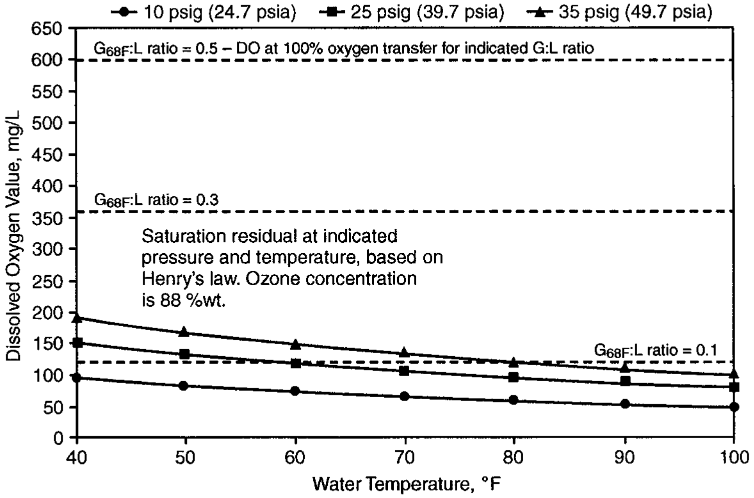

Figure 4-49 DO at indicated temperature and pressure versus maximum DO possible at indicated G:L ratio

Oxygen is transferred into the sidestream along with ozone. The quantity of oxygen that is transferred is unimportant and ignored during design of most ozone applications, regardless of the type of ozone dissolution system implemented. However, some plants want to minimize the DO concentration of the ozonated water. One approach is to strip oxygen from the ozonated water by diffusing air into the water at the end of the ozone contactor. This approach requires air compressors, diffusers, and additional contactor volume at about 20-ft water depth. Another approach is to use an injector-degas-vessel sidestream system.

The capability for oxygen transfer in the sidestream is similar to the capability for ozone transfer that was discussed above. In Figure 4-49, the maximum possible oxygen residual of the sidestream water flow is shown for G68F:L ratios of 0.1, 0.3, and 0.5. As with ozone, these values were obtained by assuming that 100% of the oxygen in the gas (G) is transferred to the water (L), ignoring saturation capacity. Saturation values for oxygen are a function of water temperature, operating pressure, and oxygen concentration. In Figure 4-49, the oxygen saturation values are much higher than those under atmospheric conditions, because operating pressure is elevated and oxygen concentration is high (e.g., about 90 %wt when ozone concentration is 10 %wt). The important point is that oxygen concentration in the sidestream water cannot exceed the saturation value. The following items are noted from data shown in Figure 4-49:

1. The saturation DO level is below the maximum possible DO value for all cases shown when the G68F:L ratio is 0.3 and 0.5. This means that in the

injector-only system, undissolved oxygen in the gas bubbles will be transported to the sidestream-mainstream mixing zone and ozone contactor. Additional oxygen transfer will occur in the ozone contactor. In practice, the contactor effluent DO values are similar for the injector-only and bubble-diffuser ozone systems.

2. The saturation DO level is in the same range as the maximum possible DO value when the G68F:L ratio is 0.1. This means that oxygen transfer is hindered as the DO value approaches the saturation value and is stopped altogether at the saturation value. With the injector-degas-vessel system, undissolved oxygen in the gas bubbles will be removed via the ozone destruct system. This means that the mainstream DO level will be increased only by the DO that is developed in the sidestream flow.

The ozone contactor effluent DO value is minimized using the degas-vessel-sidestream system, because oxygen-containing off-gas is directed to ozone destruct and away from the ozone contactor. The DO that is directed to the mainstream flow is limited by the amount of oxygen transfer in the sidestream flow. However, ozone transfer efficiency remains optimized, as discussed previously.

There is the potential for elevated bromate formation via high ozone residual in the sidestream piping of the sidestream system (Coffey, 2000). Ozone residual is elevated significantly in the sidestream unit process and oxidation reactions proceed rapidly, such as bromate formation if bromide is present in the sidestream water flow. Bromate that is formed will be diluted in the mainstream process flow, but the potential for too much bromate from the sidestream process should be evaluated.

Static Mixer, Sidestream Venturi Injection With Downflow Tube, and Aspirating Turbine Mixer Ozone Contacting

Two common types of ozone dissolution-reacting contactor arrangements are the bubble-diffuser ozone contactor (combined dissolution and reaction tank) and sidestream ozone dissolution system followed by a tank or pipeline reactor. Other contacting options have been implemented successfully and are discussed elsewhere (Langlais et al., 1991). In this section, three ozone-contacting arrangements that have been implemented recently—static mixers, sidestream venturi injection with downflow tube (SVI-DT), and aspirating turbine mixers—are discussed.

Static Mixers. Static mixers contain flow-mixing elements that are located inside a pipe (tube). Liquid that contains gas bubbles is mixed thoroughly within the static mixer, which is located on the sidestream piping, the mainstream piping, or both. Mysore and colleagues (2003) conducted an in-depth study, "Improvement of the Ozonation Process Through the Use of Static Mixers," at pilot-scale and full-scale plants. In England, full-scale plants with static mixers were evaluated, including those at the Egham and Walton water treatment plants with source water from the River Thames; the Chertsey Water Treatment Plant that treats surface water from North Burway and groundwater from Abbeymeads; and the Clay Lane groundwater treatment plant. The following observations were made:

1. Transfer efficiency was 96% to 99% at G:L ratios of 0.06 to 0.15 and liquid velocity of 0.7 to 1.6 m/sec, which corresponded to a pressure drop of 1.5 to 2.9 kPa (1.5 to 2.9 psi).
2. Although no microbial inactivation was measured within the static mixer itself, the static mixer provided the necessary starting conditions for efficient inactivation in the overall contacting system, including:
   a. Rapid and efficient dissolution of gaseous ozone and
   b. Generation of a homogeneous dissolved ozone solution that created high initial residual value within a short period of time.
3. Static mixers were very effective in destroying pesticides such as atrazine, inactivating microorganisms, removing color, and eliminating tastes and odors, all within a few seconds.
4. Static mixers produce a homogeneous ozone solution, have no moving parts, are easy to retrofit, require minimal maintenance, have low capital and operation and maintenance costs, have low energy consumption, are adaptable to automatic process control, are simple to operate, and have no small holes that could be gradually plugged.

Sidestream Venturi Injector With Downflow Tube. An SVI-DT, a specialized ozone dissolution system, is installed at the Gwinnett County Georgia Lanier and Shoal Creek water treatment plants (Schulz et al., 1995; Kim et al., 1998). A major advantage of this patented device is consistent ozone residual at the outlet of the first chamber, as opposed to highly variable residual that occurs with the bubble-diffuser ozone contactor (Schulz and Bellamy, 1999). An SVI-DT installation with a J-tube downflow tube arrangement is shown in Figure 4-50; this system is installed at the Shoal Creek Water Treatment Plant. Ozonated water in the sidestream enters the J-tube device via mixing nozzles (see also Figure 4-44). The J-tube is positioned within the first chamber of the over-under baffled contactor (i.e., the J-tube downflow tube is used in chamber 1 instead of bubble diffusers). The bottom depth of the J-tube is similar to that of a bubble diffuser (about 20 ft) to maximize ozone transfer efficiency.

Turbine Mixers. Turbine mixer ozone contactors are operated under positive-pressure or negative-pressure (i.e., aspirating) conditions (Langlais et al., 1991). The more common application in North America is negative-pressure conditions,

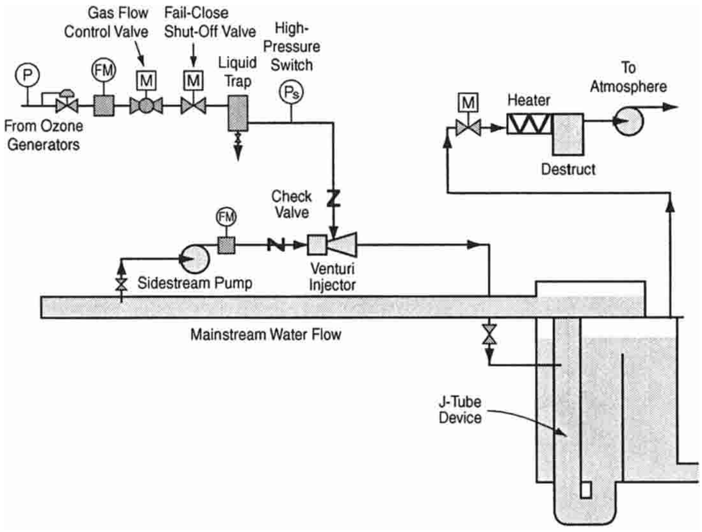

Figure 4-50 Sidestream process schematic with J-tube ozone dissolution device (Schulz et al., 1995)

whereby the ozone gas is drawn into the aspirating turbine mixer (Norton et al., 1999). An application at Abbotsford, Wisconsin (population 2,000), treated well water contaminated with trichloroethylene, benzene, radon, and bacteriological contaminants (3-log *Giardia* inactivation was required). A major advantage of the negative-pressure system involves gas pipe leakage. If a leak occurs, air leaks into the pipe rather than ozone leaking into the room (Norton et al., 1999). Also, the system has an excellent maintenance history based on use at three plants that were operated by a sister agency (Sturgeon Bay, Wisconsin). Ozone Technology, Inc., provided a pilot-scale system as well as the full-scale process (Norton et al., 1999).

INSTRUMENTATION FOR MONITORING, CONTROL, AND ALARMS

Instrumentation relates to equipment used in operations and for personnel safety. Personnel safety instrumentation is discussed in chapter 1. Equipment-related instrumentation is discussed in this section.

Instrumentation is used to monitor equipment operation and sound an alarm or shut down equipment to prevent damage. Instrumentation is also used to monitor ozone process operation and performance to ensure that treatment objectives are met without overdosing. In addition, instrumentation is used to monitor ozone equipment operation to provide insight into equipment operating characteristics that assist in troubleshooting potential operating problems. Some instruments are unique for specific feed-gas options, such as air-fed, LOX-fed, or

Figure 4-51 Dew point probe made of porous metal compound

on-site oxygen-fed ozone systems. Instruments are much the same for the ozone generator, contactor, and destruct units, because they are common to all feed-gas options. Ozone system suppliers provide additional instrumentation that is unique to their ozone generator and PSU. Commonly provided instrumentation is discussed in the following paragraphs.

Ozone generators will shut down when equipment or processes malfunction. Three primary alarm conditions are listed here. Secondary alarm conditions are also discussed.

1. *High dew point temperature:* DP_{SP} is typically above –76°F, which represents a moisture content value of 6.7 ppm_{wt}. Preferable operating dew point temperature is less than –103°F, which is a moisture content value below 0.8 ppm_{wt}. The dew point probe (Figure 4-51) is made of a porous metal compound that adsorbs moisture and registers moisture content as dew point temperature. Chapter 8 discusses the relationship between and conversion of moisture content to dew point temperature value. The probe gradually loses the capacity to absorb moisture and is generally replaced annually. The probe is usually wet when initially installed and will register an inaccurate, high dew point reading until it dries out. Also, the probe will take several hours or days to dry out after becoming wet. Probes can be sent back to the factory for reconditioning.

2. *Low cooling water flow rate.* The ozone system supplier determines the low limit value for cooling water flow rate, below which water-flow short-circuiting might occur within the ozone generator vessel. Conventional instrumentation for measuring cooling water flow rate is used, such as orifice plates or magnetic flowmeters.
3. *Low gas flow rate.* Two considerations are involved in determining the alarm value for gas flow rate:
    a. The alarm value for low gas flow rate must be sufficient to achieve an even distribution of gas flow through all ozone generator dielectrics. This is assessed using pressure-drop readings across the ozone generator (i.e., maintaining the minimum pressure-drop value suggested by the ozone system supplier). Pressure drop is affected by discharge-gap width (and gas flow rate), which is different among ozone system suppliers.
    b. Frequently, the selected value for low gas flow rate is the minimum rate at maximum applied power. However, this value might be too high and lead to inefficient operation at startup (i.e., before the plant reaches design flow). Water flow rate and ozone dose are often at minimum values during the early months or years of operation, thus requiring a low ozone production rate. Gas flow is set at the minimum flow rate, but operating ozone concentration is generally well below the optimum operating value (e.g., 3 %wt versus desired value of 8 %wt). Because ozone production is in a reduced state for extended periods of time, the plant staff may want to lower operating cost by operating at a lower gas flow rate. This is accomplished by changing the low-gas-flow set-point to a lower number and at the same time placing an upper limit on maximum power demand for the generator. As a result, the gas flow rate is lowered without applying too much power at a minimum gas flow rate. However, the minimum gas flow rate selected should be confirmed by the ozone manufacturer to ensure that gas flow is distributed to all dielectrics.

The following are secondary alarm conditions that might occur during unique operating conditions, such as failure of a primary alarm instrument.

- High generator outlet gas temperature.
- High generator outlet cooling water temperature.
- High temperature inside the PSU cabinet.

Four key instruments are used to monitor process performance. The dissolved ozone residual analyzer monitors disinfection process performance. Gas flow and ozone gas concentration meters are used to calculate ozone production. And,

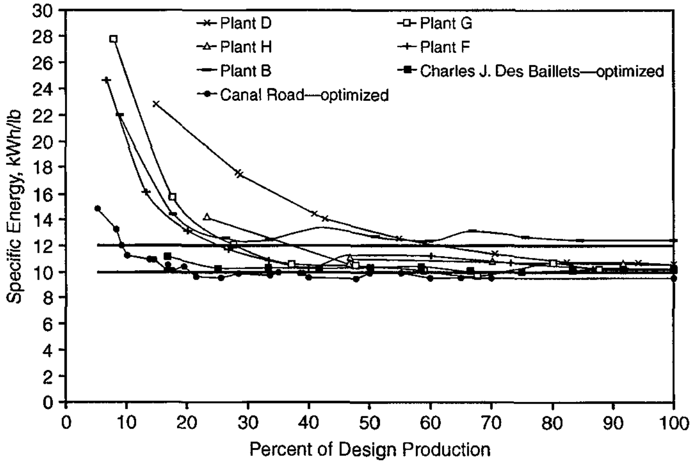

Figure 4-52 Measured total system specific energy value at full-scale air-fed ozone facilities (Rakness and DeMers, 1998)

ozone generator power demand is used to assess operating cost and efficiency. Ozone residual analyzers must be installed properly, calibrated routinely, and serviced periodically, as discussed in chapter 7. Chapter 2 explains disinfection performance calculations, and gas flow instrumentation and accuracy verification are discussed in chapter 8. Chapter 6 discusses ozone concentration meter installation, operation, and accuracy verification. Conventional power metering instrumentation (i.e., current and power transformers) is installed on the incoming electrical lines to the PSU.

TOTAL SYSTEM ENERGY EFFICIENCY

Several factors affect the operating costs of ozone systems. Labor and parts replacement account for about 20% to 35% of the total operational cost (Langlais et al., 1991). Remaining costs are for energy and LOX in LOX-fed ozone facilities. Energy consumption is assessed as specific energy, or kWh per pound of ozone produced (kWh/lb_{O_3}). Operation is optimized at the lowest possible specific energy value for air-fed ozone systems. For LOX-fed ozone facilities, both the LOX cost and the energy cost must be included in the assessment. In this case, operation is optimized when combined energy and LOX cost ($\$/lb_{O_3}$) is at the lowest possible value.

Specific energy data for air-fed ozone systems are summarized in Figure 4-52 (Rakness and DeMers, 1998). Data are normalized to percent design flow. The data indicate several important considerations regarding design and operation of air-fed ozone systems.

1. Above 30% design production, most air-fed ozone systems achieve a total system specific energy value between 10 and 12 kWh/lb.
2. The total specific energy value increases dramatically below 30% design production, except for optimized air-fed ozone facilities.
3. As illustrated, plant B has the highest specific energy at design. However, plant B was a high-pressure system with a heatless desiccant dryer that was operating at 90 psig. High-pressure air-fed ozone systems are typically used at small ozone installations where the extra cost of energy is offset by lower installation cost.
4. Two air-fed ozone systems had excellent efficiency at design and at turndown production. The Charles J. Des Baillets Water Treatment Plant in Montreal, Quebec, and the Canal Road Water Treatment Plant in Somerset, New Jersey, had low specific energy values at both design and extreme turndown conditions.
    a. Low design specific energy values were achieved by selecting a design operating pressure between 11 and 15 psig, instead of 20 to 25 psig. Desiccant dryer size was increased proportionally at these plants, because upstream moisture removal is affected by operating pressure (see earlier discussion concerning low-pressure air-fed ozone systems).
    b. In addition, the ozone systems were designed with flexibility in their air feed-gas systems to reduce power demand in proportion to gas flow by using either variable-speed compressors or load-unload compressor operation.

Specific energy data for oxygen-fed ozone systems that produce oxygen on site are summarized in Figure 4-53 (Rakness and DeMers, 1998). Here, too, data are normalized to percent design flow and indicate the following aspects of on-site oxygen-fed ozone systems.

1. PSA on-site oxygen generation resulted in a slightly higher operating specific energy value than with a VPSA system. As such, recent large-scale ozone systems use VPSA on-site oxygen concentration equipment. However, small-scale ozone systems use PSA equipment, as discussed earlier in this chapter.
2. VPSA plant 2 in Figure 4-53 has two VPSA units, each sized for 100% design ozone production. This means that the VPSA units at plant 2 will often operate at turndown conditions. The specific energy value increases at reduced ozone production at plant 2, due to less efficient operation of the oxygen production facilities at turndown operation (see Figure 4-54). When oxygen gas flow is reduced, the specific energy value increases for each unit of oxygen production (i.e., kW/ton/d or kWd/ton).

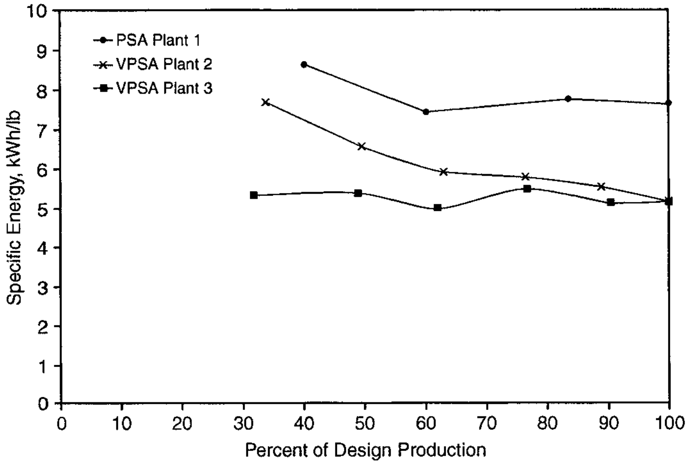

Figure 4-53 Measured total system specific energy value at full-scale on-site oxygen generation oxygen-fed ozone facilities (Rakness and DeMers, 1998; Rakness et al., 2004)

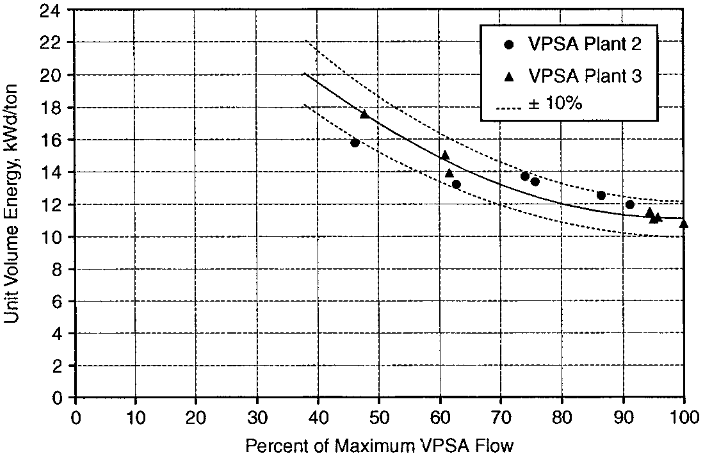

Figure 4-54 Measured total system specific energy value (kilowatts per ton per day) at full-scale on-site oxygen generation facilities (Rakness et al., 2004)

3. VPSA plant 3 in Figure 4-53 also has two VPSA units, but each is sized for 50% design ozone production. LOX is the backup oxygen supply in case of VPSA unit malfunction. At plant 3, the VPSA units operate at full production rate most of the time (i.e., not in turndown mode). VPSA units operate most efficiently at the full production rate (see Figure 4-54).

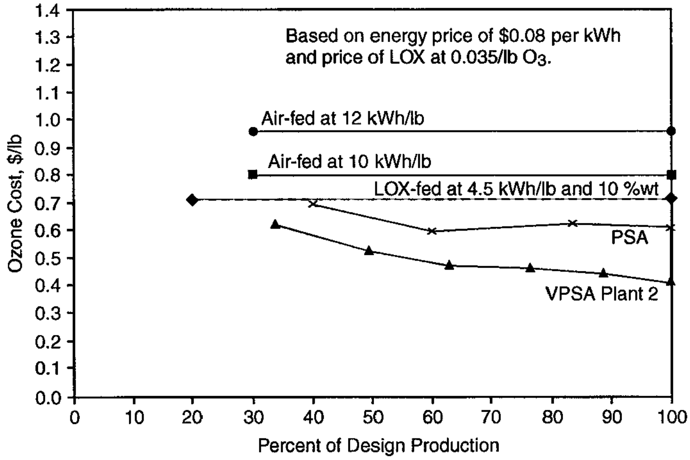

Figure 4-55 Energy and LOX operating cost at full-scale ozone facilities (Rakness and DeMers, 1998; Rakness et al., 2004)

The unit cost for producing ozone is summarized in Figure 4-55 for air-fed, LOX-fed, PSA oxygen-fed, and VPSA oxygen-fed ozone systems. Energy cost is \$0.08/kWh and LOX cost is \$0.035/lb O_2. The least expensive operating cost is for the VPSA oxygen-fed ozone system, followed by PSA oxygen-fed ozone facilities. VPSA oxygen-fed ozone systems are used in large facilities only, where energy cost savings offset the amortized equipment capital cost plus increased maintenance cost of operating the VPSA equipment. PSA oxygen-fed systems, which are used frequently in small ozone systems where oxygen and ozone generation are supplied together as a package unit, also require capital and maintenance expenses. Operating cost for air-fed ozone systems is higher than for LOX-fed ozone systems at the energy and LOX prices indicated. The lower operating cost for LOX-fed ozone systems, coupled with reduced equipment and maintenance costs for these units, results in the current widespread application of LOX-fed ozone facilities.

LOX-fed ozone system energy and oxygen operating costs depend primarily on the ozone generator specific energy value and the price of LOX. Energy consumption of other system components is typically 5% to 10% of the energy consumption for the ozone generator. Figure 4-56 summarizes LOX-fed ozone system specific energy values that were obtained during performance testing at the time of installation (Rakness and Hunter, 2002). The solid line through the data represents the capabilities of current ozone system suppliers, even at an elevated cooling water temperature of 95°F. (Note that 95°F cooling water goes to the generator vessel and PSU, but the PSU contains an internal air conditioner, thus, the PSU temperature had to be <95°F.)

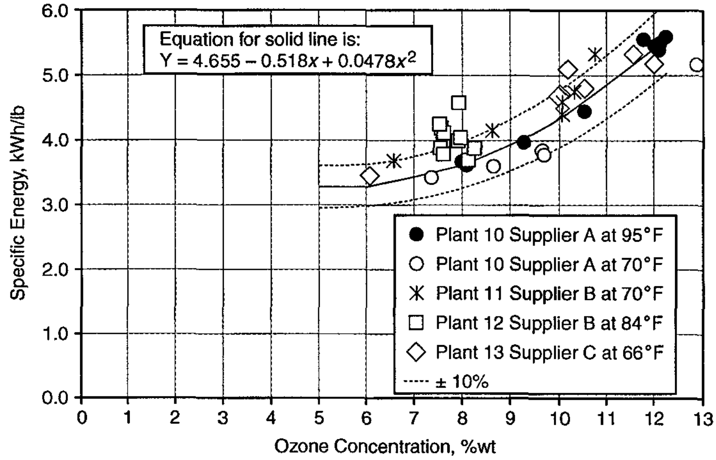

Figure 4-56 LOX-fed ozone system specific energy value at full-scale ozone facilities (Rakness and DeMers, 1998; Rakness et al., 2004)

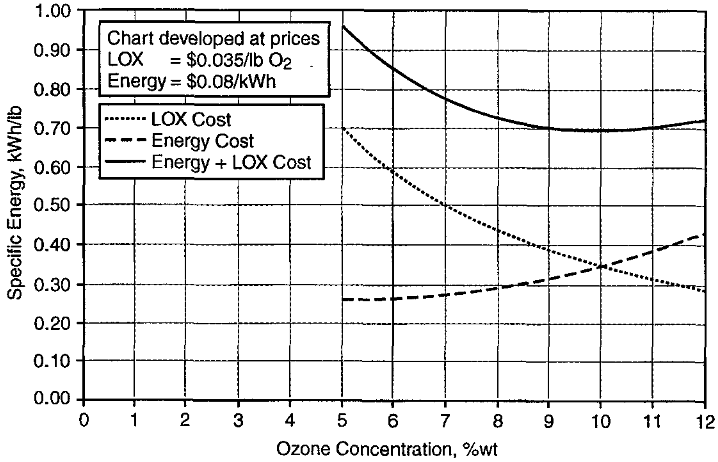

Figure 4-57 LOX-fed ozone system operating cost at average specific energy value shown in Figure 4-56

The optimum operating ozone concentrations for LOX-fed ozone systems are illustrated in Figure 4-57. These values are based on average specific energy values from Figure 4-56 and energy and LOX prices of \$0.08/kWh and \$0.035/lb O_2, respectively. The optimum value is 9 %wt or 10 %wt for the indicated conditions, but operation between 8 %wt and 12 %wt results in economical operation as well. The point is that optimum ozone concentration is achieved over a range of ozone

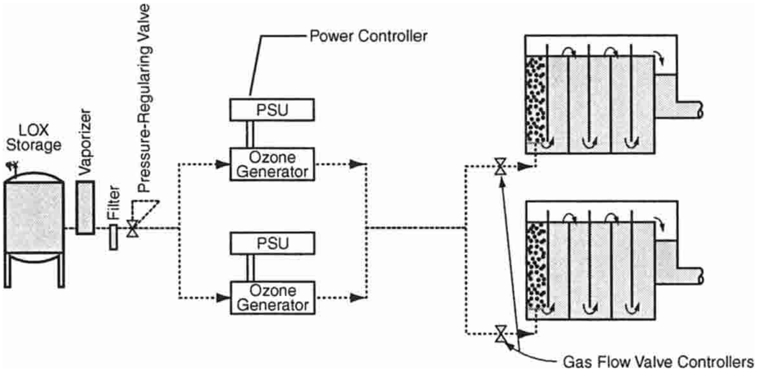

Figure 4-58 Simplified schematic of LOX-fed ozone system

concentration values, not just at one value. Operation over a range of ozone concentrations simplifies ozone control, as discussed in the next section. The optimum range shifts to the left if energy price increases or LOX price decreases, and vice versa. As such, the optimum operating ozone concentration is dynamic and should be assessed when prices change for energy or LOX.

OZONE PROCESS CONTROL AND AUTOMATION

On-line instrumentation is available for monitoring and controlling ozone system operation. Ozone systems are normally operated to obtain a measurable ozone residual and sufficient CT value to meet regulated disinfection inactivation credit. Electrical energy is used to generate ozone gas on site, and the ozone gas is then piped to the ozone contactor. The generator feed-gas is either dry air or gaseous oxygen. Vaporized LOX is becoming the preferred feed-gas. A simplified schematic of a LOX-fed ozone system is shown in Figure 4-58. Ozone production is controlled by adjusting gas flow and generator power.

The cost of generating ozone includes energy and LOX expenses, as discussed earlier. The unit-mass cost ($\$/\mathrm{lb}_{O_3}$) of ozone is lowest over a range of ozone concentration values (see Figure 4-57). The optimum concentration range is unique to each installation and depends on the price of energy, price of LOX, ozone generator efficiency, and cooling water temperature. In manual or automatic control, the objective is to always operate within the optimum concentration range.

Several ozone systems operate successfully in manual control (Rakness and Hunter, 2000a). During manual control, generator power adjustments are made in response to small changes (±20%) in water flow rate or ozone dose. Gas flow is changed only when a large change in water flow rate and/or ozone dose occurs. Steady-state ozone residual performance has been documented with this constant flow-control operating strategy (Rakness and Hunter, 2000a).

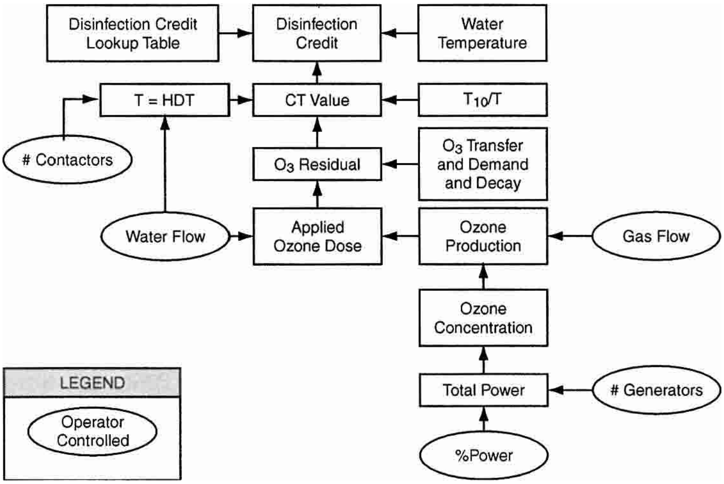

Figure 4-59 Relationship among ozone process parameters for manual ozone control

Automated control has been successful at some installations but unsuccessful at others (Rakness and Hunter, 2000a). The most common complaints are unsteady operation and slow response time. Constant-ozone-concentration control is the most common automation strategy. To work successfully, precise control-loop tuning adjustments are needed to achieve steady-state performance without lengthy response times. Constant-ozone-concentration control is described later in this section. An alternative automatic control strategy is constant-range-concentration control, which adopts the positive attributes of manual operation. Specifically, gas flow is held constant over a range of operating ozone concentrations (Rakness and Hunter, 2000a and 2000b). Constant-range-ozone-concentration control is also discussed later in this section. Each control strategy has advantages and disadvantages. Obviously, automatic control has an advantage over manual control because staff involvement is minimized. On the other hand, automation must be functional.

Manual Ozone Control

Figure 4-59 shows the relationship among ozone parameters for manual ozone control. Disinfection credit is the ultimate performance indicator. Disinfection credit is determined by knowing measured CT value, measured water temperature, and the credit allowed by regulation from disinfection CT-lookup tables (see chapter 2 for more information on calculating CT value and disinfection credit). The CT value (see Figure 4-59) is obtained from ozone residual, C, and T_{10} time (i.e., hydraulic detention time, T, multiplied by the contactor T_{10}/T ratio). Hydraulic detention time (HDT) is a function of water flow rate and number of contactors in service. The ozone residual value (see Figure 4-59) depends on applied ozone dose, ozone transfer efficiency, ozone demand, and ozone decay parameters. In manual or automatic process operation, applied ozone dose is the target parameter for controlling ozone system performance.

The applied ozone dose (see Figure 4-59) is determined by the relationship between the ozone production rate and the water flow rate. Ozone production is adjusted to maintain a target ozone dose for variable water flow rates. Ozone production is adjusted manually or is automatically controlled.

These five adjustments are made during manual control:

1. The number of ozone contactors in service is changed infrequently, such as seasonally when major changes occur in plant water flow rate.
2. The number of ozone generators in service is changed periodically, such as weekly or monthly when dramatic change occurs in ozone production due to variation in water flow rate or ozone demand.
3. The plant water flow rate is changed, as required, to meet water production needs.
4. The gas flow rate changes if the change in plant water flow rate is fairly large, e.g., >20%. The operator assesses the current operating ozone concentration and changes the gas flow rate if the measured ozone concentration is outside the optimum operating range.
5. Generator power is changed routinely during the day to maintain disinfection performance within a controlled range. Generator power is the one parameter that is adjusted most often.

Manual control is most successful when the following process and equipment features are present:

1. The primary gas flow control point is located at the inlet piping to each ozone contactor, where precise gas flow control is needed. Precise gas flow control is unnecessary at the generator. The ozone generator inlet valves are totally open. Alternatively, the generator inlet valves can be used as pressure control valves to control generator pressure via a programmable logic controller (PLC). The generator outlet valves are either totally open or totally closed, depending on which generators are in service.
2. The contactor gas flow control valves are precision control valves (e.g., V-port ball valves).
3. System operating pressure is stable, which allows gas flow to remain consistent when the control valve is in its final position.
4. Plant water flow rate and water quality are consistent for long periods of time, which means that stable disinfection performance occurs with infrequent changes to generator power.

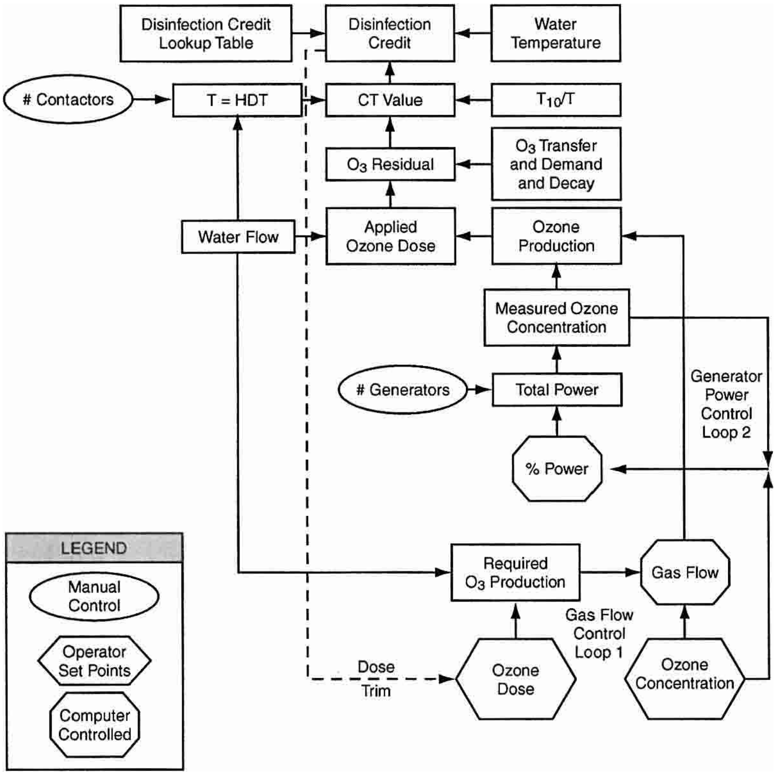

Figure 4-60 Relationship among ozone parameters for constant-ozone-concentration control

Constant-Ozone-Concentration Automated Control

Figure 4-60 shows the relationship among ozone parameters for constant-ozone-concentration automated control. Parameters between applied ozone dose and disinfection credit are the same as described for manual control. Parameters between applied ozone dose and generator gas flow and power are components of the constant-ozone-concentration automatic control strategy.

In constant-ozone-concentration control the ozone production rate is adjusted automatically to achieve the set-point ozone dose for variable water flow rate. The method for adjusting ozone production involves two control loops. Gas-flow control loop 1 (see Figure 4-60) calculates and sets the gas flow rate (i.e., adjusts gas flow control valve to the ozone contactor) based on required ozone production and operator-entered set-point ozone concentration. Generator-power-control loop 2 observes measured ozone concentration and adjusts generator power, as necessary, to maintain set-point ozone concentration.

At most plants the set-point value for the applied ozone dose is always an operator-entered value. However, at some plants an ozone-dose trim control feature is provided to automatically adjust the ozone dose set point to meet treatment objectives. The ozone-dose trim option observes the calculated value for disinfection credit and makes small adjustments to the ozone dose (e.g., 1% to 2% adjustment in dose) if measured disinfection credit is above or below a desired value. Small adjustments are made because minor changes in ozone dose create direct changes to the ozone residual value (i.e., ozone demand has been met), which can create large changes in CT value and disinfection credit.

The number of ozone contactors in service is always controlled manually. The number of generators in service is also controlled manually at most ozone facilities, because adding or removing generators from service is done infrequently and automatic change is unnecessary. Also, automation algorithms for bringing generators into service contain very involved control logic, because logic must include provision for purging the generator with dry gas before applying power. If present in the control logic, plant staff usually abandon this automation feature, because it often results in underdosing and causes disinfection noncompliance. Some installations have attempted to address the generator purging issue by directing purge gas to an off-gas ozone destruct unit. The goal is to start producing ozone with the formerly off-line generator (i.e., sending ozone to the off-gas destruct unit) so that the transition to ozone production delivery into the ozone contactors is smoother.

Constant-concentration control has been successful, especially when the following control components are present:

1. The primary gas flow control point is located at the inlet piping to each ozone contactor, where precise gas flow control is needed. Precise gas flow control is unnecessary at the generator. The ozone generator inlet valves are totally open or are used as pressure control valves via a PLC. The generator outlet valves are either totally open or totally closed, depending on which generators are in service.
2. The contactor gas flow control valves are precision control valves (e.g., V-port ball valves).
3. System operating pressure is stable, which allows gas flow to remain consistent at its computer-controlled set-point value. This means that the control valve is not continuously searching for a final set-point position.
4. Generator power change is fairly responsive. Responsive change is accomplished in two ways.
   a. Power will change immediately in response to sudden and large changes in measured water flow. This means that the ozone production rate can change abruptly to maintain the set-point value for ozone dosage. The

delay time is too long when gas flow must change in order for ozone concentration to change to finally activate generator power change.

   b. Ozone generator power is fine-tuned by responsive ozone concentration measurement. This means that the sample line must be short between the ozone concentration meter and ozone generator product-gas piping.

5. Control algorithm time delays are adjusted after startup based on existing operating conditions, which are likely different from predicted operating conditions. Wide swings in gas flow change and generator power change must be avoided.

Constant-Range-Ozone-Concentration Automatic Control

The constant-range-ozone-concentration automated control strategy is patterned after successful manual control. Specifically, gas flow is unchanged over a range of operating ozone production needs, such as ±20%. The constant-range-ozone-concentration control strategy can be implemented in all ozone installations and is especially beneficial when large changes in ozone production rate occur due to large fluctuations in plant water flow rate (Rakness et al., 2000). This is beneficial because ozone production is calculated and set using a feed-forward control strategy.

Figure 4-61 shows the relationship among ozone parameters for constant-range-ozone-concentration automated control. The operator manually selects and sets the number of contactors. The number of generators is also selected manually. Automatic generator control is described in more detail later in this section. Primary set points are water flow rate, ozone dose, and ozone concentration. Secondary set points are dose-tune multiplier, generator specific energy curve offset factor, and contactor disinfection-credit balance adjustment.

Gas-flow control loop 1 in Figure 4-61 fixes the gas flow rate via the three steps outlined below using set-point values for water flow, ozone dose, and ozone concentration. Gas flow is established using set-point values; therefore, gas flow is fixed until changes are made to set-point values.

1. The flow-control ozone production target is calculated from set-point water flow and ozone dose.
2. The fixed gas flow rate is determined using the flow-control production target and set-point ozone concentration.
3. Flow-control valve adjustments are made until measured gas flow equals the fixed gas flow rate. A dead-band control range is applied to lock in the position of the gas flow-control valve setting (i.e., keep the control valve from continuously making small adjustments).

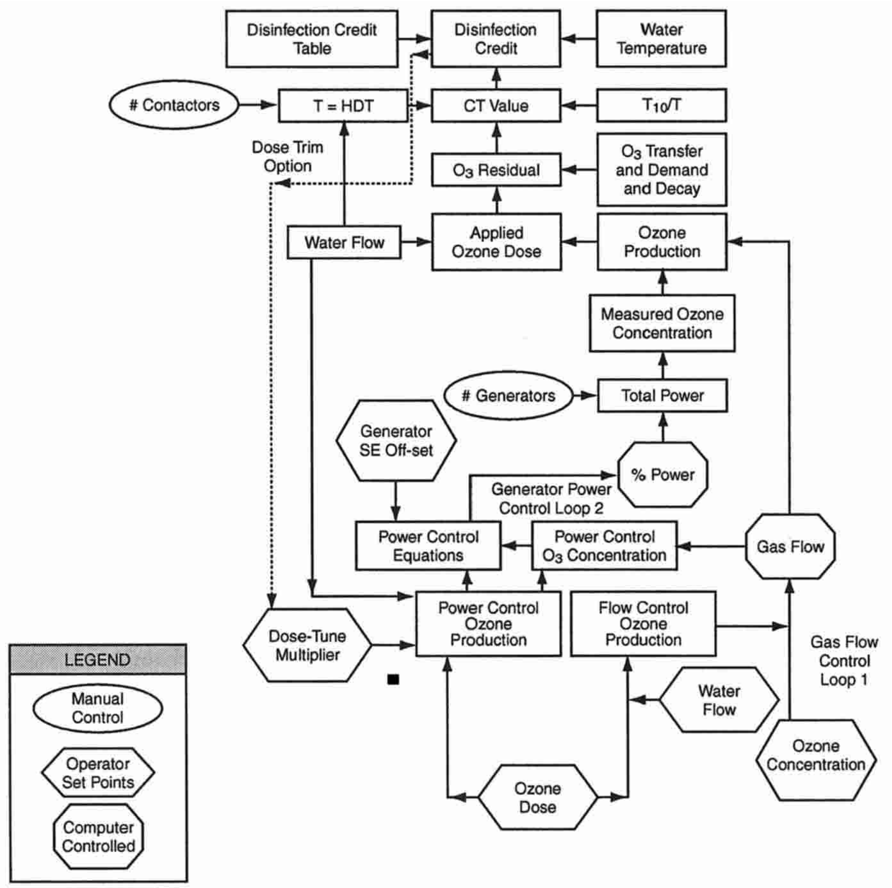

Figure 4-61 Relationship among ozone parameters for constant-range-ozone-concentration control

Generator power is calculated and set using measured water flow rate, set-point values for ozone dose, dose-tune multiplier (defined below), and generator specific energy (SE) curve offset factor (defined below), as outlined in the following steps:

1. The power-control ozone production target is calculated using measured water flow and the set-point values for ozone dose and dose-tune multiplier. The dose-tune multiplier is developed with the dose-trim logic (see discussion below).
2. The power-control ozone concentration is calculated from the power-control ozone production target value and fixed gas flow rate from gas-flow control loop 1.

3. Generator specific energy is calculated using the power control ozone concentration from step 2, an equation for generator specific energy such as the one shown in Figure 4-56, and the set-point generator specific energy curve offset factor. The offset factor adjusts for minor changes in the specific energy value that might occur due to changed generator efficiency (see discussion below).
4. Required generator power is calculated using the specific energy value from step 3 and power control production target from step 1.

The dose-tune multiplier is initially set at 1.0 but might be adjusted upward or downward based on assessment of disinfection performance. Dose-tune changes can be implemented manually or automatically. The dose-trim control logic views disinfection performance and adjusts the dose-tune multiplier by a small percentage (e.g., 1% or 2%) if performance of the weakest contactor (i.e., contactor with the lowest disinfection credit) is too low or too high.

The generator specific energy curve offset factor compensates for changes in generator performance due to dielectric cleanliness, water temperature, and other factors. The factor might change seasonally and generally ranges between 0.85 and 1.15. The purpose of the offset factor is to permit operating ozone dosage to match fairly closely the set-point ozone dosage. This occurs when the generator's operating ozone concentration matches the calculated power-control ozone concentration. A fine-tune control loop for ozone-concentration matching is incorporated into the control strategy in the following way. At periodic time intervals (e.g., every hour), the generator(s) operating ozone concentration(s) is automatically compared to the calculated power-control ozone concentration value and adjustments are made to the off-set factor(s) to compensate for differences that might occur. However, the overall control strategy automatically maintains disinfection performance via the dose-tune adjustment factor, even if the off-set factor is unchanged.

The constant-range-ozone-concentration automated control approach maintains a constant gas flow rate over a range of ozone productions. For example, the concentration range might be 8 %wt to 12 %wt (see Figure 4-56), which provides continuous, cost-effective operation. Concentration values beyond this range occur for one of two reasons. First, the dose-tune multiplier is too high, e.g., 1.22. Therefore, a limit is set for the dose-tune multiplier such that an alarm is activated and the operator modifies the set-point ozone dose, which will change gas flow range as well as generator power. Second, measured water flow is dramatically different from the set-point water flow rate value. However, this event is unlikely at most plants.

Constant-range-ozone-concentration control is implemented in Las Vegas where plant water flow changes significantly twice per day to take advantage of lower energy cost during the night (i.e., reduce raw water and treated water pumping cost) (Rakness et al., 2000). In addition, generators are brought into service automatically. For example, if water flow rate increases from 120 mgd to 600 mgd, the number of ozone generators in service might range from one to three. When an additional generator is brought into service, the generator outlet valve opens, the gas flow rate increases immediately, and the calculated total power demand is split among all generators in service. Generator purge is limited to just a few seconds in this application.

In summary, both constant-concentration and constant-range-concentration automated control work successfully at ozone facilities. The primary factors affecting successful application of either control strategy include:

1. The primary gas flow control point is located at the inlet piping to each ozone contactor, where precise gas flow control is needed. The ozone generator inlet valves are totally open or are used as pressure valves via a PLC. The generator outlet valves are either totally opened or totally closed, depending on which generators are in service.
2. The contactor gas flow control valves are precision control valves (e.g., V-port ball valves).
3. System operating pressure is stable, which allows gas flow to remain consistent when the control valve is in its final position.

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5

Optimizing Ozone Operation and Performance

The goal of optimizing ozone operation is to continuously achieve performance objectives at minimum operating cost. Optimization is accomplished through good operation and maintenance (O&M) practices, use of high-quality equipment, and proper design flexibility. Good O&M practices and troubleshooting considerations are described in this chapter.

Bottom-line optimization criteria include performance ratio (PR) (also called CT ratio [residual concentration times time] or inactivation ratio) and unit-volume operating cost ($/mil gal). Calculating, monitoring, and trending these two parameters documents optimization status and assists in quantifying improvement due to operational changes that might be made. Table 5-1 is a checklist of ideas for optimizing ozone operation and performance (Rakness and DeMers, 1998).

PR is the calculated value of measured disinfection credit divided by target credit. A PR of 1.0 means that the measured disinfection credit is equal to the target credit. A PR that is <1 means that required performance has not been achieved and the ozone dose must be increased. An elevated PR value, e.g., 5, means that measured performance is much greater than necessary, unless site-specific operating goals have targeted a high PR value. If the ozone system is operating much above the target PR value, the ozone dose and operating cost might be reduced, along with unwanted disinfection by-products such as bromate when the source water contains bromide. The Sebago Lake Water Treatment Plant in Portland, Maine, maintains tight control over PR (their PR ranges between 1.1 and 1.4) by controlling ozone residual and CT value (i.e., adjusting ozone dose), as shown in Figure 5-1 (Rakness and DeMers, 1998). As illustrated, the operating

Table 5-1 Ways to Optimize Ozonation

Consideration	Comment
1. Identify/select an optimization "champion" or optimization team.	A. The "champion" or team should lead the optimization effort. B. Plant administration and peer support should be solicited.
2. Identify a performance target that —Is related to water quality, —Is easy to measure, and —Provides instant feedback.	A. General and operations-related performance objectives are insufficient (see chapter 3). B. Disinfection performance criteria meet the conditions for an optimization performance target, since CT tables are available for determining *Giardia*, *Cryptosporidium*, and virus inactivation credit.
3. Monitor performance using performance ratio and select an operating safety factor.	A. Performance ratio is the ratio of measured disinfection versus target disinfection. B. Performance ratio must be greater than 1.0 at all times. C. An operating safety factor might be 1.2, 1.5, or another value to ensure the performance ratio is always greater than 1.0.
4. Develop reliable on-line residual analyzer performance and utilize analyzer readings to calculate CT value.*	A. Ensure analyzers are designed and installed correctly. B. Routinely standardize analyzers (e.g., weekly). C. Strategically locate analyzers to calculate CT value using an acceptable minimum number of meters, as discussed in chapter 2.
5. Verify accuracy of instrumentation used for determining unit-volume operating cost.	A. Gas flowmeter accuracy is discussed further in chapter 8. B. Ozone concentration meter accuracy is discussed further in chapter 6. C. Power demand meter accuracy might be verified using calibrated portable units.
6. Monitor optimization status using a spreadsheet-based monitoring program.	A. The monitoring program should calculate and report optimization status and provide flexibility to post individual data to a database from which trends in performance might be viewed. B. A monitoring program example is discussed in this chapter.
7. Implement optimization techniques as needed. Obtain ideas from several sources.	A. Consider conducting a formal ozone facility evaluation (DeMers et al., 1998). B. Develop and discuss optimization ideas internally and solicit ideas from other operating utilities.

Source: Rakness and DeMers, 1998.

* See chapter 2 for additional information concerning calculation of CT value and disinfection credit. See chapter 7 for information regarding ozone residual measurement and analyzer calibration.

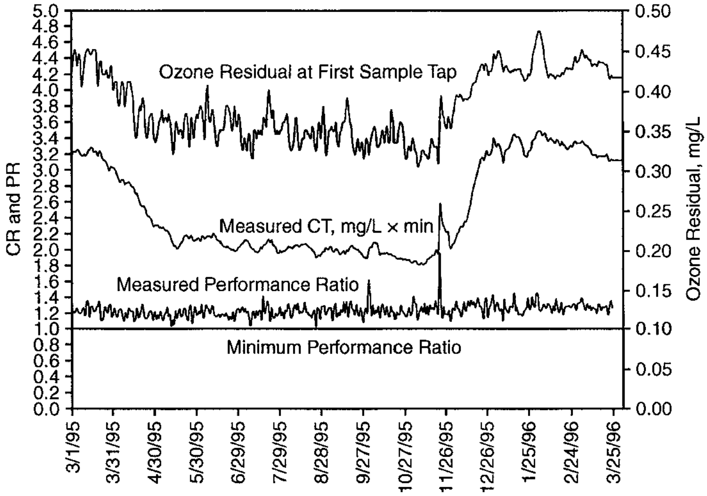

Figure 5-1 Ozone residual, CT, and PR instantaneous daily values during a 1-year period at the Sebago Lake Water Treatment Plant, Portland, Maine

CT value changes during the year due to changes in water temperature. Methods to calculate CT value and disinfection credit are described in chapter 2.

Unit-volume operating cost ($/mil gal) is calculated as unit-mass cost of ozone ($/lb) multiplied by ozone dose (lb/mil gal, which is ozone dose in mg/L × 8.34 lb/gal). Unit-mass cost of ozone includes specific energy (kWh/lb$_{O_3}$); price of energy ($/kWh); oxygen usage (lb$_{O_2}$/lb$_{O_3}$, which is the inverse of ozone concentration in %wt); and price of liquid oxygen (LOX) ($/lb$_{O_2}$). Implementing optimization strategies is likely to lower unit-volume operating cost. The Canal Road Water Treatment Plant, Somerset, New Jersey, lowered their unit-volume operating cost from $20/mil gal to $12/mil gal by making changes in the operation of their ozone system, as shown in Figure 5-2 (Rakness and DeMers, 1998).

OZONE SYSTEM MONITORING PROGRAM

Selected ozone system process data are used to calculate parameters that provide insight into ozone process performance and operation cost, such as PR and unit-volume operating cost. An example monitoring spreadsheet that provides information for daily review and weekly, monthly, and yearly reports and trend charts is described in this section. Example trend charts are used to illustrate desirable operating conditions.

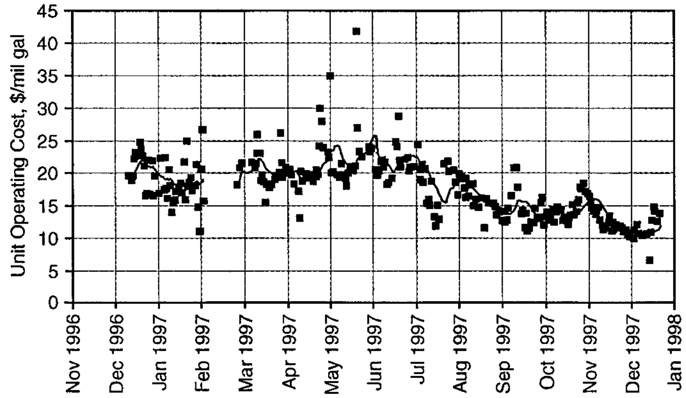

Figure 5-2 Unit-volume ozone operating cost at Canal Road Water Treatment Plant, Somerset, New Jersey

Parameter Calculations

Tables 5-2, 5-3, 5-4, and 5-5 were created using an electronic spreadsheet ozone data-monitoring program. Table 5-2 displays selected design and operating criteria that are used to complete process calculations. Energy and LOX prices are used to calculate operating cost. Load size for the LOX truck is used to calculate the number of days between LOX deliveries. (NOTE: From Table 1-1 (chapter 1), LOX density is 9.52 lb_{O_2}/gal.) The values for the T_{10}/T ratio, target *Giardia* and virus inactivation credits, and contactor volume are used to assess disinfection PR. Information on gas density is provided in order to convert gas flow volumetric information (scfm) to mass flow data (lb O_2/d).

Table 5-3 summarizes data collected from ozone system instrumentation readings. These data are used to calculate disinfection performance, ozone production, ozone dose, operating cost, etc. Table 5-4 summarizes input data from Table 5-3 and displays calculation results. Each calculated value is not described in specific detail, but the equations used to complete the calculations are shown in appendix A. Table 5-5 summarizes input data and disinfection calculations (i.e., CT calculations using the effluent method). Refer to chapter 2 for additional information concerning disinfection calculations.

Input and calculated data can be recorded, posted to a database, and used to develop operating charts and reports. Example reports and charts from full-scale ozone systems are described in the following paragraphs.

Residual Measurement Optimization

The Southern Nevada Water System (SNWS) inputs ozone data into an Excel spreadsheet from their supervisory control and data acquisition (SCADA) system

Table 5-2 Example Plant Ozone Design and Operating Criteria

Operating Variables			
Unit energy price	0.08	$/kWh	
Price of LOX	0.29	$/100 ft^3	
	69.83	$/US ton	
	0.035	$/lb	
LOX delivery truck size	4,500	gal/truck	
T_{10}/HDT ratio for O_3 contactors	60.0%	—	
Enter the target *Giardia* credit goal	0.5	Log	
Enter the target virus credit goal	2	Log	
LOX Supply			
Number storage tanks	1	#	
LOX tank size	13,000	gallons	
Total LOX storage	13,000	gallons	
Ozone Contactors			
Cell 1 volume	65,000	gallons	
Cell 2 volume	65,000	gallons	
Cell 3 volume	65,000	gallons	
Cell 4 volume	65,000	gallons	
Cell 5 volume	65,000	gallons	
Cell 6 volume	65,000	gallons	
Cell 7 volume	65,000	gallons	
Cell 8 volume	65,000	gallons	
Total volume/contactor	520,000	gallons	
Number basins	2	#	
Number diffuser in cell 1	40	#	
Feed-gas GMW	32	g/mol	
Molar volume	24.05	g/L	
Standard temperature	68°F		
	20°C		
Oxygen density	0.08305	lb/ft^3	1.3304 g/L

database. Imported data is "qualified" to ensure validity of calculated values. For example, the imported SCADA value for gas flow from an off-line ozone generator might be slightly above zero, even though the valve is 100% closed. The qualification calculation within Excel reports that value as zero, because it was less than an expected minimum value. The operators review the ozone residual profile chart

Table 5-3 Example Ozone Monitoring Data

Parameter		Value	Unit
Date		11/17/04	m/d/y
Water temperature		9	°C
Water flow rate		36	mgd
Nitrogen system—air flow		52	ft^3/hr (cfh)
Generator 1	Inlet gas flow	15	ft^3/min (scfm)
	Ozone concentration	10.1	%wt
	Generator power	32	kW
Generator 2	Inlet gas flow	14	ft^3/min (scfm)
	Ozone concentration	10	%wt
	Generator power	34	kW
Contactor 1	Gas flow rate	15	ft^3/min (scfm)
	Outlet residual cell 2	0.35	mg/L
	Outlet residual cell 3	0.12	mg/L
	Outlet residual cell 4	0.06	mg/L
	Off-gas ozone concentration	0.61	%wt
Contactor 2	Gas flow rate	16	ft^3/min (scfm)
	Outlet residual cell 2	0.33	mg/L
	Outlet residual cell 3	0.11	mg/L
	Outlet residual cell 4	0.06	mg/L
	Off-gas ozone concentration	0.72	%wt

created from these data (Figure 5-3). The expectation is that on-line meter reading values will be on the curve that is developed using first-order decay calculations (see chapter 2), which implies that all analyzers are working properly. An improperly working analyzer is illustrated in Figure 5-4; the second analyzer reading in contactor 2 is above the curve (i.e., the curve that was developed using analyzer readings taken from the first and third analyzers—using the k^*_{max} methodology discussed in chapter 2). A residual analyzer calibration check is conducted on all analyzers if one residual value is off the curve. See chapter 7 for residual testing and analyzer calibration procedure.

Generator Efficiency Optimization

The Metropolitan Water District of Southern California's H.J. Mills Filtration Plant is set up to input ozone data from the SCADA database into an Excel spreadsheet. Imported data are "qualified" to ensure validity of calculated values, similar to the procedure followed at SNWS (discussed previously). A generator specific-energy value is calculated using measured gas flow, ozone concentration,

Table 5-4 Selected Ozone Input and Calculated Data

Parameter	Unit	Data				Ozone Residual				
Date		11/17/04				Basin 1	Basin 2			
Ozone Generators	#	**Gen 1**	**Gen 2**		Cell 1					
Gas Flow	scfm	15.0	14.0		Cell 2	0.35	0.33			
Ozone Conc. Use	%wt	10.10	10.00		Cell 3	0.12	0.11			
Power Demand	kW	32	34		Cell 4	0.06	0.06			
Air Flow Rate (N_2 System)	cfh	52.0	or	3.0%	Cell 5					
Ozone Contactors		Total	**Basin 1**	**Basin 2**	Cell 6					
Water Temperature	°C	9.0			Cell 7					
Gas Flow	acfm	31	15	16	Cell 8					
Water Flow Rate	mgd	36.0	18.0	18.0						
Off-Gas Ozone Conc	%wt		0.61	0.72						
Transfer Efficiency	%		94%	93%						
	Ozone Generation System Performance						**Energy**	**LOX**	**Total**	
Parameter	**Unit**	**Total**	**Gen 1**	**Gen 2**		$/lb$O_3$	0.36	0.34	0.70	
Generator Inlet Gas Flow	scfm	29.0	15.0	14.0		lb O_3/day			349	
O_3 Concentration	%wt	10.05	10.10	10.00		$/day	127	117	244	
Ozone Production	lb/day	349	181	167		mgd			36	
Generator Power Demand	kW	66	32	34		$/MG	3.52	3.26	6.78	
Measured Specific Energy	kWh/lb		4.24	4.87	scfm O_2	scfm Total	Cscf/day	gal/day	gal/truck	days/truck
					28.1	29.0	405	353	4500	12.7
		Disinfection Results			**Gas Flow per Diffuser**					
Effluent Method	**Unit**	**Basin 1**	**Basin 2**		**Basin 1**	**Basin 2**				
CT-Value Effluent	mg-min/L	0.41	0.38	Cell 1	0.38	0.40	cfm/diff			
Virus PR—Effluent	—	1.3	1.3	Virus Target	2	Log				
Virus Credit Effluent	Log	2.7	2.6	*Giardia* Target	0.5	Log				
Giardia PR—Effluent	—	2.6	2.5	HDT	10.2	min				
Giardia Credit—Effluent	Log	1.3	1.3	Applied Ozone Dose	1.16	mg/L				

Table 5-5 Disinfection CT Value and *Giardia* and Virus Credit Using Effluent Method

T_{10}/T Ratio is	*0.60*	Range is 0.5 to 0.7				
Water Flow	*18.0*	mgd/basin	*12,500*	gpm		
Water Temp.	*9.0*	°C				
		Measured C	HDT	C for CT	T for CT	CT
		mg/L	min	mg/L	min	mg/L × min
Cell 1			1.28			
Cell 2		0.35	1.28	0.35	0.77	0.269
Cell 3		0.12	1.28	0.12	0.77	0.092
Cell 4		0.06	1.28	0.06	0.77	0.046
Cell 5			1.28		0.77	
Cell 6			1.28		1.54	
Cell 7			1.28		2.30	
Cell 8			1.28		3.07	
		SUBTOTAL FOR MEASURED CT				0.407
	Virus Direct Credit	Virus Inactivation Rate	From CT*	Virus Inactivation Credits Total	Required	Virus PR
	Log	k_V	Log I	Log I	Log I	—
	1.0	4.09	1.67	2.67	*2.0*	1.33
	Giardia Direct Credit	*Giardia* Inactivation Rate	From CT*	*Giardia* Inactivation Credits Total	Required	*Giardia* PR
		k_g	Log I	Log I	Log I	—
	0.50	1.97	0.80	1.30	*0.5*	2.61

and power demand. Also, the expected generator specific-energy value is determined from an ozone concentration versus specific energy curve (i.e., a curve similar to the one shown in Figure 4-56, chapter 4) that was developed during ozone system performance testing, which was conducted when the generators were new. The percent difference between measured and expected specific energy is determined. The anticipated result is minimal percent difference (e.g., ±10%), which means that the measured specific energy value is similar to the expected specific energy value. Two operating considerations are assessed from these results:

1. A sudden and large percent difference might indicate problems with instrumentation readings for measured gas flow, ozone concentration, or power demand. It is unlikely that a sudden and large change would occur with generator efficiency.

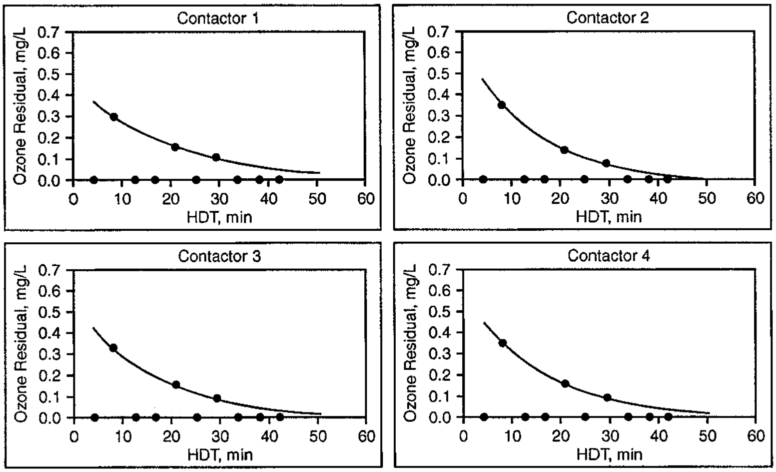

Figure 5-3 Expected ozone residual profile exists when the measured residual values from three analyzers are all on the first-order decay curve (River Mountains Water Treatment Plant, Las Vegas, Nevada)

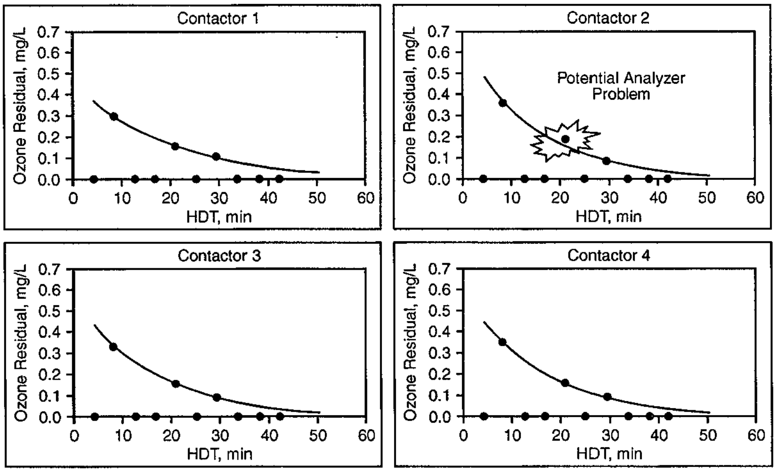

Figure 5-4 Unexpected ozone residual profile in contactor 2; three analyzer readings indicate potential problems with residual meter calibration

2. Generator efficiency might decrease gradually over time due to a slow buildup of nitric acid from the small amount of moisture that exists, even in "dry" gas. Figure 5-5 shows a month-to-month trend of specific energy percent difference. An expected normal-variation range is ±10%. Generator inefficiency is indicated when percent difference is sustained

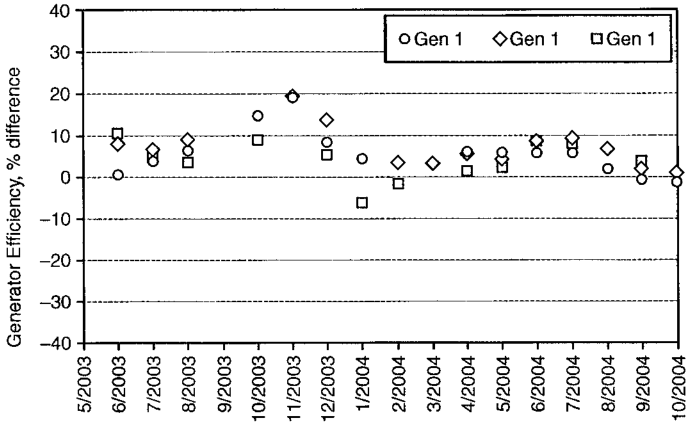

Figure 5-5 Ozone generator–measured specific energy compared to expected specific energy indicates trends in efficiency performance (H.J. Mills Water Treatment Plant, Riverside, California)

above 10%, as in October and November 2003 (see Figure 5-5). The ozone generators were cleaned at that time and specific energy percent difference returned to normal.

Disinfection Performance Optimization

Operators at the Helix Water District's R.M. Levy Water Treatment Plant in Lakeside, California, manually input ozone data into an Excel data-monitoring program. Data are collected at 4-hr intervals. The disinfection performance objective is virus credit. The regulated limit for virus credit is 2 log minimum. PR is the value obtained by dividing measured credit by regulated credit. The operating PR goal is 2.3, with an acceptable range between 1.5 and 3.0. The ozone dose is adjusted to control the PR value. Total automatic control is implemented, complete with full PR trim control (see automatic ozone control discussion in chapter 4). Figure 5-6 displays PR values for 186 data points that were collected at 4-hr intervals during October 2004. The PR value in contactor 2 was above 1.5 for every data point and above 3.0 only 15% of the time. In contactor 4, the PR value was also above 1.5 for every data point and above 3.0 only 1% of the time.

Note that the Portland (Figure 5-1) and Helix (Figure 5-6) plants were operating at different but, in both cases, optimized PR ranges for their site-specific installation. The operating PR range was 1.1 to 1.4 at Portland. At Helix, the operating goal was 2.3, with an acceptable range of 1.5 to 3. The site-specific difference is as follows: Portland's disinfection goal was a minimum 3-log *Giardia* inactivation credit, which required a CT value between 1.8 and 3.2 mg-min/L. Helix's disinfection goal was a minimum 2-log virus inactivation credit, which

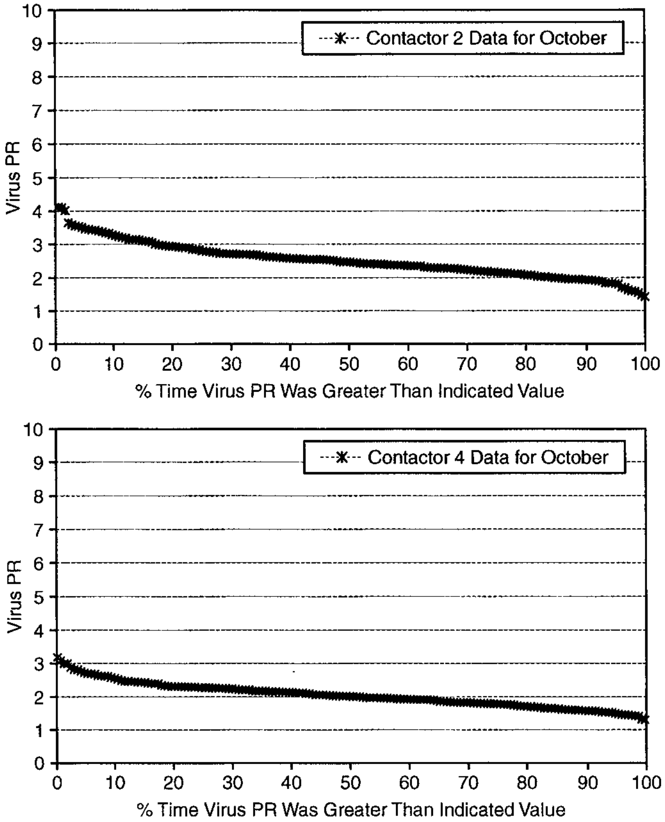

Figure 5-6 Virus PR for 186 data points during October 2004 (R.M. Levy Water Treatment Plant, Lakeside, California)

required a CT value (during October) between 0.4 and 0.6 mg-min/L. With such a low required CT value, the disinfection PR at Helix is much more sensitive to changes in ozone dose than at Portland. The point is that each plant must develop an operating range for PR that is suitable for their site-specific conditions.

Reports and Charts

The Helix Water District's ozone generation system monthly report (also includes weekly averages) is shown in Table 5-6. These data show example operating cost and other information that is part of an ozone system data-monitoring program. Table 5-7 shows the monthly summary report (also weekly averages) for the ozone contactor for October 2004. Ozone contactor detention time, residual values, disinfection credit, water flow, water temperature, and other information are displayed.

Table 5-6 Monthly Summary Report for Ozone Generation System Performance

		Monthly Average	Weekly Average for Week Begin Date				
Parameter	Units	October 2004	10/24	10/17	10/10	10/03	09/26
Water Flow Rate	mgd	35	24	30	41	42	48
Total Ozone Production	lb/day	354	222	307	425	448	614
Total System Power Demand	kW	59	39	50	70	73	117
Total Ozone Generator Power	kW	55	35	48	66	70	114
Energy Price	$/kWh	0.14	0.14	0.14	0.14	0.14	0.14
Liquid Oxygen Price	$/Ton	82	82	82	82	82	82
Total System Specific Energy	kWh/lb	4.05	4.33	4.02	3.93	3.92	4.51
Unit Mass Cost	$/lb	1.04	1.34	1.03	0.91	0.91	0.90
Unit Volume Cost	$/mil gal	10.24	11.63	10.37	9.43	9.64	11.38
Ozone Cost per Day	$/day	346	277	304	387	407	548
per Week	$/week	2,423	1,939	2,130	2,707	2,848	3,834
per Month	$/month	10,384	8,311	9,128	11,600	12,207	16,433
per Year	$/year	126,333	101,115	111,053	141,137	148,520	199,934
		Ozone Generator Evaluation					
Total Gas Flow	scfm	42	38	39	44	46	52
Total Ozone Concentration	%wt	7.00	4.91	6.65	8.10	8.10	9.79
		Ozone Generator No. 1					
Ozone Concentration	%wt						10.35
Measured Specific Energy	kWh/lb						4.43
Expected Specific Energy	kWh/lb						4.29
Percent Difference	%						3.3%
		Ozone Generator No. 2					
Ozone Concentration	%wt						10.99
Measured Specific Energy	kWh/lb						4.92
Expected Specific Energy	kWh/lb						4.58
Percent Difference	%						7.4%
		Ozone Generator No. 3					
Ozone Concentration	%wt	7.00	4.91	6.65	8.10	8.10	8.09
Measured Specific Energy	kWh/lb	3.78	3.90	3.73	3.73	3.73	3.84
Expected Specific Energy	kWh/lb	3.32	3.05	3.20	3.49	3.49	3.48
Percent Difference	%	14.4%	27.7%	16.9%	6.9%	6.9%	10.1%

Monthly data can be charted to show performance trends, as shown in Figure 5-7 for ozone dose and contactor detention time at the R.M. Levy plant. In Figure 5-8, ozone production, power demand, and specific energy trends are shown using data collected at the H.J. Mills Filtration Plant; disinfection PR and ozone dose data from the H.J. Mills Filtration Plant are shown in Figure 5-9. The

Table 5-7 Monthly Summary Report for Ozone Contactor Performance

		Monthly Average	Weekly Average for Week Begin Date				
Parameter	Units	October 2004	10/24	10/17	10/10	10/03	09/26
Water Flow Rate	mgd	35	24	30	41	42	48
Water Temperature	°C	21.6	19.9	21.2	22.3	22.7	23.7
Ozone Contactor							
Contactor HDT	min	21.7	29.7	24.2	17.2	16.6	15.2
Total Ozone Dose	mg/L	1.21	1.10	1.24	1.24	1.27	1.53
Ozone Contactor No. 1							
Residual at Cell 2	mg/L						
Residual at Cell 4	mg/L						
Half-life	min						
CT	mg/L × min						
Giardia Credit	Log I						
Virus Credit	Log I						
Ozone Contactor No. 2							
Residual at Cell 2	mg/L	0.29	0.27	0.30	0.28	0.32	0.40
Residual at Cell 4	mg/L	0.16	0.15	0.15	0.14	0.17	0.20
Half-life	min	6.0	9.2	5.6	3.9	4.4	4.7
CT	mg/L × min	0.46	0.60	0.49	0.33	0.40	0.41
Giardia Credit	Log I	2.3	2.6	2.4	1.7	2.3	2.6
Virus Credit	Log I	5.1	5.7	5.3	4.2	5.0	5.5
Ozone Contactor No. 3							
Residual at Cell 2	mg/L						
Residual at Cell 4	mg/L						
Half-life	min						
CT	mg/L × min						
Giardia Credit	Log I						
Virus Credit	Log I						
Ozone Contactor No. 4							
Residual at Cell 2	mg/L	0.38	0.33	0.39	0.38	0.39	0.49
Residual at Cell 4	mg/L	0.12	0.11	0.11	0.13	0.12	0.15
Half-life	min	2.9	4.0	2.9	2.5	2.3	2.1
CT	mg/L × min	0.35	0.44	0.36	0.30	0.28	0.32
Giardia Credit	Log I	2.0	2.1	2.1	1.9	1.8	2.2
Virus Credit	Log I	4.1	4.5	4.2	3.9	3.8	4.5

trend charts show the ozone dose values that were needed to control disinfection performance within a target operating range. Target range at the Mills plant was *Giardia* disinfection PR (called CT ratio) between 2 and 4, with a required *Giardia* disinfection credit of 0.5 log (e.g., a CT ratio of 2.0 is obtained when the measured *Giardia* credit is 1.0).

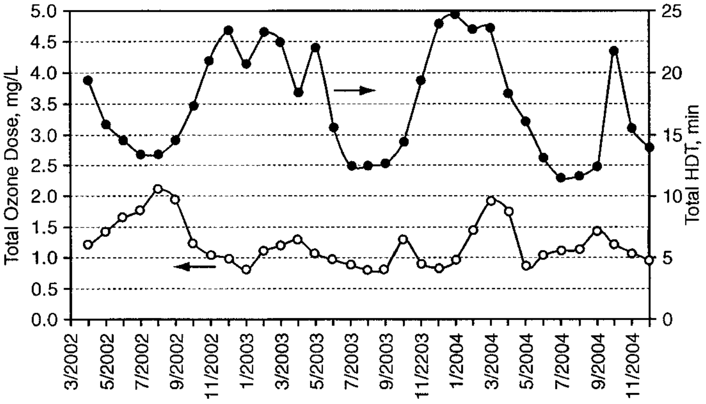

Figure 5-7 Ozone dose and contactor detention time trend charts from monthly average data in an ozone data monitoring program (R.M. Levy Water Treatment Plant, Lakeside, California)

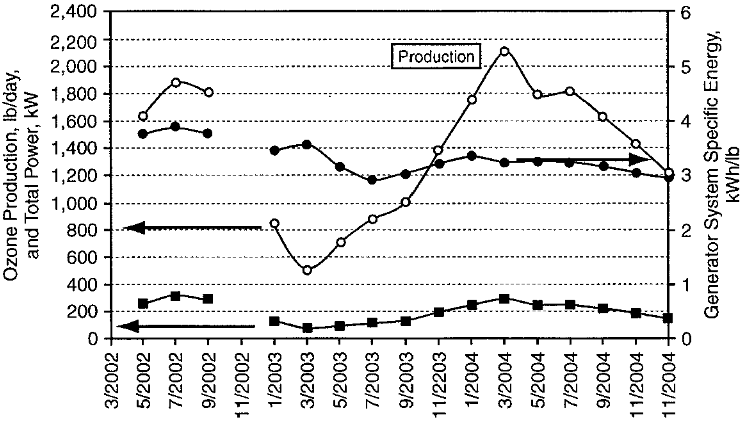

Figure 5-8 Ozone production, power demand, and specific energy trend charts from monthly average data in an ozone data monitoring program (H.J. Mills Water Treatment Plant, Riverside, California)

These trend charts were created using data collected at full-scale ozone installations that were designed and are operated to achieve specific disinfection targets that were based on *Cryptosporidium*, *Giardia*, or viruses. The data are used to track ozone performance so that best operating practices can be assessed. Another trend, ozone transfer efficiency, is shown in Figure 5-10. A reduction in ozone transfer efficiency implies that the ozone diffusers are not operating properly; this is discussed later in the chapter.

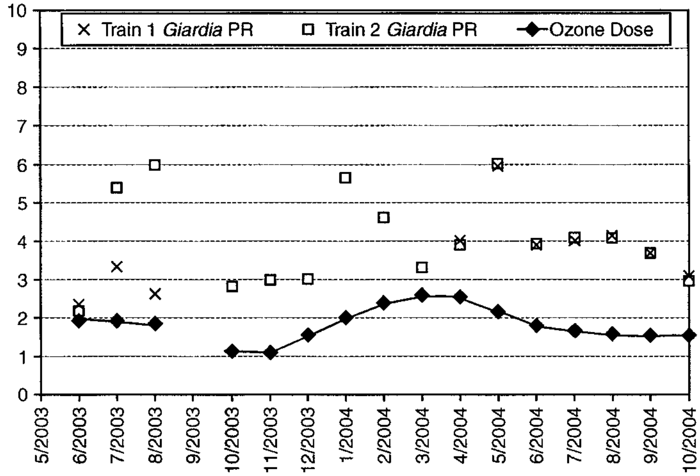

Figure 5-9 ***Giardia*** **disinfection PR and ozone dose trend charts from monthly average data in an ozone data monitoring program (H.J. Mills Water Treatment Plant, Riverside, California)**

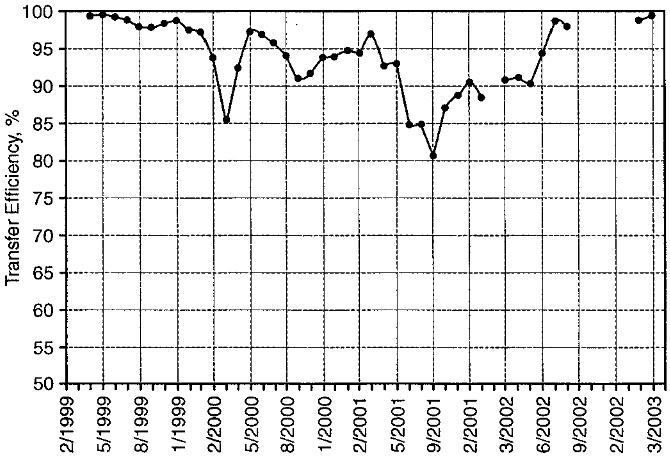

Figure 5-10 Concentration-based ozone transfer efficiency trend chart from ozone data monitoring program at Plant X

BIOLOGICAL FILTER OPERATION AND PERFORMANCE

Pre-ozone contactors are located before sedimentation and intermediate-ozone contactors are located after sedimentation. In both applications, ozonation is upstream of filtration and biological filtration occurs when chlorine addition is delayed until after filtration.

Background Biological Filtration

Biological activity in the filters develops naturally independent of the type of filtration media. Huck et al. (2000) studied biological filtration at pilot and full-scale ozone facilities. They (Huck et al., 2000) noted the following considerations for utilities that operate biological filters in the "background," i.e., biological filtration implemented without special consideration of filter design and operational practices.

1. Biological filters were consistently able to meet high standards of particulate removal. Turbidity levels <0.1 ntu were consistently attained.
2. Biological filters can be optimized for conventional filter performance parameters (e.g., head loss, length of ripening) without seriously compromising removal of biodegradable organic matter (BOM).

The following design and operation considerations were noted for utilities that wish to maximize biological performance with single-stage filtration, i.e., one-stage filtration that provides both particulate removal and biological oxidation, as opposed to two-stage filtration where particulate removal filters and biological filters are separate units (Huck et al., 2000).

1. Water temperature <5°C significantly impairs BOM removal. However, the potential for biological regrowth within the distribution system is also reduced at lower temperatures.
2. Acceptable removals of the easily biodegradable compounds (e.g., aldehydes and carboxylic acids), assimilable organic carbon (AOC), and biodegradable dissolved organic carbon (BDOC) can be achieved within the common range of design parameters (e.g., contact time) used for conventional filters. Longer contact time may be required for compounds that take longer to biologically oxidize and/or for very high BOM removal. AOC and BDOC values are obtained from special laboratory tests that report degree or extent of biochemical oxidation capacity of a water sample. Test methods are described in other publications (Huck et al., 2000).
3. Current design and operating practices of biological filters are hampered by the lack of generally accepted effluent criteria. Because biological filters feed another potential biological system (i.e., the distribution system), such criteria are likely to be site specific. Good distribution system operating practices, such as minimizing distribution system detention time, eliminating dead-end piping, maintaining chlorine or chloramine residual, and executing periodic flushing as required, should continue.
4. At water temperatures above 10°C, the choice of filtration media (anthracite or granular activated carbon [GAC]) was found to have no measurable impact on BOM removal. At lower temperatures, GAC media provided better performance than did anthracite media.

5. In full-scale installations and when the water temperature is above 10°C, BOM removal was insensitive to backwashing conditions, including presence of a disinfectant (chlorine or chloramine) or use of air scour. (NOTE: See chapter 2 for discussion of biological filtration and manganese removal and the need for chlorine-free backwash water for this application.) The potential impact of lower water temperature was not tested. At lower water temperature, the presence of chlorine in the backwash water and/or air scouring might negatively impact biological performance.

Monitoring Considerations

Parameters related to biological filters can be monitored to document biological performance. However, results are typically not useful for determining if changes should be made to filter-operating parameters, such as filter run time or backwash frequency. Operating parameters such as filter run time, rate of head loss, and backwash frequency are usually unchanged after biological growth has developed, unless the concentration of dissolved organic carbon is high (e.g., >6 mg/L). If filter run time is shortened due to biological growth, the filter can be backwashed with chlorinated water or chlorine can be added to the filter to control biological growth. A program for monitoring biological-related performance is likely to include one or more of the following parameters:

1. Heterotrophic plate count (HPC) following filtration is used to measure biological activity within the filter media. The HPC value is a function of multiple parameters including water temperature; type of media; concentration of BOM; length of time since startup, because biological growth develops over time; and presence or absence of chlorine or chloramine in the backwash water. The HPC value is highest in ozonated warm water that has elevated AOC or BDOC levels and that is filtered by GAC media that is backwashed with chlorine-free water. HPC is used in research studies to assess and document the effect of operating variables (e.g., media type, water temperature) on HPC value (Huck et al., 2000). For routine plant operation (i.e., nonresearch study), filter effluent HPC might be monitored to document variation in the HPC value over the course of a year. HPC is virtually eliminated when chlorine is added (Huck et al., 2000).
2. Total and fecal coliform density following filtration is a measure of possible coliform contamination within the biological filters. Contamination might be caused by recontamination following ozonation if the ozonated water is exposed to the atmosphere at the surface of the sedimentation basin or filters. A total and fecal coliform value is unlikely to be measured in the ozonated water. If total and/or fecal coliform is present in the filter effluent, it may be necessary to chlorinate the filter influent for several

hours or days (Nerenberg et al., 2000). Like HPC, total and fecal coliform is eliminated upon chlorine addition.

3. Huck et al. (2000) suggested that filter influent and effluent dissolved oxygen (DO) concentration can be used to assess biological filter performance. Like HPC, influent and effluent DO concentration (i.e., Δ DO value) is monitored to document variation in DO consumption over the course of a year. However, change in the DO concentration caused by possible filter gas binding (i.e., bubbles trapped in the filter) should be incorporated into the assessment. Filter gas binding potential is discussed later.
4. Measurement of AOC and BDOC is typically reserved for research studies. The information collected is not used to adjust filtration operating procedures, because of the long turnaround time needed to obtain sample results and the high cost for these analyses.
5. Also measured in research studies are aldehydes (formaldehyde, acetaldehyde, glyoxal, methylglyoxal), ketoacids (ketomalonic acid, pyruvic acid, and glyoxylic acids), and carboxylic acids (acetic, formic, and oxalic), which are measured to evaluate the ozonation by-products removed using biological active filters.

Water treatment plants that do not use ozone usually operate with nonbiological filters. Chlorine is added upstream of the filters (i.e., prior to sedimentation or prior to filtration) to provide a chlorine CT value that meets primary disinfection requirements. When ozone is used to meet disinfection criteria, chlorine addition is delayed until after filtration in an effort to minimize chlorine DBPs (i.e., TTHMs [total trihalomethanes] and HAA5 [sum of five haloacetic acids]) and promote biological filtration. The practical conclusions of the biological filter research study by Huck et al. (2000) indicate that it should be possible to implement biological filtration without change to historical filter operating practices, such as filter run time, frequency of backwash, and backwashing practices. Most plants report noticeable reduction in turbidity and improved particulate removal. If desired, enhanced biological oxidation can be implemented if biological action is protected using design and operation practices, such as use of nonchlorinated backwash water, replacement of anthracite with GAC, and increase in contact time.

Implementation Considerations

Biological filter effluent should be subjected to *free-chlorine disinfection* for at least 1-min contact time (perhaps even 2 to 5 min; see chapter 2) for one or more of the following reasons:

1. To quickly and effectively reduce HPC in the biological filter effluent.
2. To prevent rapid decay of chloramine residual in the distribution system when chloramination is implemented. Wilczak et al. (2003) determined

that free chlorine residual is necessary to maintain chloramine residual stability in the distribution system. Vokes confirmed the need (telephone conversation with Chuck Vokes, Interim Assistant Director of Utilities, Arlington, Texas, April 2004). Chloramine stability was improved when the biological filter effluent was subjected to free chlorine residual prior to ammonia addition.

Most plants are able to switch to biological filtration without incident. However, some plants have inadvertently discharged manganese that became attached to the filter media during operation for several years with chlorine addition. After years of operation with this "green sand" effect, manganese deposits developed and remained intact because chlorine oxidant was present. When prefilter chlorination is stopped, manganese no longer bonds to the media and soluble manganese is discharged into the filter effluent. Then, when subjected to post-filter chlorination, a manganese dioxide precipitate develops. When manganese is attached to the filter media and chlorine addition is stopped (i.e., a switch to biological filter operations made), one or more of the following special steps must be taken:

1. Remove and replace the filter media. This is the most common option.
2. Remove filters from service for an extended period of time and backwash these filters vigorously so that the manganese is detached and removed by backwashing.
3. Operate some filters with continued chlorine addition. Operate other filters biologically until the manganese is slowly released into the distribution system via a controlled sloughing operation.

Prior to implementing ozone some water treatment plants have been adding chlorine to the raw water and/or to the filter influent to meet disinfection CT requirements. The free chlorine residual in the flocculation and sedimentation basins and on top of the filters not only achieves disinfection but effectively prevents algal growth. After ozonation is implemented, the chlorine addition point is typically moved downstream of the filters so that biological filtration can be practiced. In doing this, algal growth may appear in the sedimentation basins and on top of filters that are exposed to sunlight. In some instances, strings of algae attach to the walls and extend across the surface of the basin. Algae growth is aesthetically unpleasant; however, it usually does not impact treated water quality. Algae growth can be minimized (not eliminated) using the following single or combined processes, and possibly in other ways as well.

1. Physically remove strings of algae growth and algal mats on a weekly or monthly schedule.
2. Add a small dose of chlorine to the rapid-mix (i.e., assume pre-chlorine application) to maintain a slight chlorine residual in the sedimentation

basin effluent (i.e., small enough to still maintain biological filter operation), assuming that compliance continues for chlorinated DBPs (i.e., TTHM and HAA5).

3. Periodically (e.g., weekly) add a heavy dose of chlorine (e.g., 4 mg/L) to the rapid-mix for a period of time (site specific) until chlorine residual begins to develop at the sedimentation basin effluent (i.e., small enough to still maintain biological filter operation).
4. Attach copper sheeting (copper is an algaecide) to weirs and along the sides of sedimentation basins (Lyford and Rakness, 2003).
5. Place floating covers, similar to swimming pool covers, on the surface of sedimentation basins and/or filters to control algae growth by minimizing sunlight exposure.

Filter Gas Binding

A possible (not common) side effect of ozonation that affects downstream filters is filter gas binding (commonly referred to as air binding). This occurs because the ozone contactor effluent is supersaturated with oxygen and also nitrogen when air is used as the feed-gas. However, most water treatment plants operate filters without the occurrence of air binding following ozonation. Edwards et al. (2004) studied factors that affect filter gas binding. They noted the following concerning design and operational practices that might explain why air binding is not an issue at most ozone plants.

1. A gas bubble can form when the dissolved gas pressure exceeds the local solution pressure.
    a. Bubbles can form due to cavitation, which develops near rapid-mix paddles that operate at high mixing rates.
    b. Bubbles can form within filter media when local pressure is below dissolved gas pressure, such as in filters that are operating in negative-head situations.
2. Bubbles that form during rapid-mix can attach to the coagulant floc, floating the floc to the surface in sedimentation basins. Bubble formation by cavitation is eliminated when the rapid-mix operation is adjusted to prevent cavitation action (e.g., slower mixing speed, deeper submergence).
3. Bubbles formed within the filter media can block pore spaces and thus create additional head loss (i.e., air binding). It is possible to eliminate negative-head operating conditions by increasing the depth of water above the media, backwashing at a lower loss-of-head value, minimizing filter plugging at the top of the media (e.g., algae or too high filter polymer dosage), or using other methods.

Practical conclusions from the air-binding research study (Edwards et al., 2004) indicate that good design and operation of a rapid-mix system are necessary to prevent bubble formation caused by cavitation. Conventional design and operational practices tend to discount occurrences of cavitation. These practices are applicable for both non-ozone and ozone system designs. Filter design and operation with positive head throughout the filter media are also good operating practices for non-ozone and ozone plants. However, existing systems that are on the verge of experiencing cavitation or air-binding might develop floating floc or air-binding problems following ozone implementation.

OZONE RESIDUAL QUENCHING

Ozone residual quenching is needed to maintain a safe working environment; it is not needed to improve water treatment process performance. An unsafe working environment can develop as the result of ozone off gassing, which occurs when water containing ozone residual is exposed to the ambient air. In some plants (i.e., those in northern regions), the ozone contactor effluent is open to ambient air inside the building that contains the rapid-mix, flocculation basins, sedimentation basins, and filters. Ozone residual in the water is released into the ambient air during rapid-mix or when the ozone-containing water is directed to the top of the filter. If the ambient-air ozone concentration becomes too high, an unsafe working environment is created. Safe ozone concentration levels are discussed in chapter 1. Elevated ozone residual does not adversely affect coagulation, flocculation, or biological filter performance. Therefore, maintenance of safe working conditions is the principal reason for implementing ozone residual quenching.

The ozone residual that remains in the contactor effluent is an operating issue at some plants and a nonissue at other plants. Ozone residual quenching is avoided in the following instances:

1. Minimal ozone residual exists in the contactor effluent. This occurs when *Giardia* and virus inactivation credit are the disinfection objectives. These objectives are achieved at relatively low ozone residual value and short detention time (i.e., detention time that exists within the first portion of an ozone contactor).
2. Tolerable ozone residual exists in the contactor effluent (e.g., 0.1 mg/L). This occurs when disinfection objectives are met with some level of residual in the contactor effluent, but the contactor effluent discharge surfaces to atmosphere in an outdoor setting and ozone off gassing *does not* cause unsafe working conditions (i.e., site-specific situation) or violate air quality standards.

Quenching chemicals include calcium thiosulfate and sodium bisulfite; hydrogen peroxide is used in some instances. The quenching reaction occurs within a few seconds with calcium thiosulfate and sodium bisulfite, assuming the quenching agent is mixed thoroughly in the ozone-containing process water. Alternatively, the hydrogen peroxide quenching reactions occur over several minutes (typically 3 to 5 min), depending on residual concentration, water temperature, water pH value, dissolved organic matter concentration, hydrogen peroxide dosage, and other factors. Hydrogen peroxide addition is an advanced oxidation process and is discussed further in chapter 2. An advantage of using hydrogen peroxide for quenching is its dual benefit of advanced oxidation reaction in addition to quenching. A disadvantage is that the quenching reaction is less controllable.

Sodium bisulfite and calcium thiosulfate can be fed directly (i.e., neat) or by carrier-water delivery. Direct feed is often used, especially when the quenching chemical can be mixed thoroughly with the ozone-containing process water. Carrier water is used for remote delivery or when additional mixing is necessary. Carrier water is filtered water (without chlorine residual) or plant service water that has chlorine residual. The preferred carrier water source does not contain chlorine residual, because the chlorine-quenching reaction consumes some of the chemical. The carrier water supply line should be inspected routinely, and the diffuser nozzles should be cleared of calcium carbonate or other deposits that might affect flow distribution and uniform chemical delivery.

Sodium Bisulfite for Ozone Residual Quenching

One mole of sodium bisulfite ($NaHSO_3$) will react with 1 mole of ozone ($SO_3^{2-} + O_3 = O_2 + SO_4^{2-}$). The molecular weight of 1 mole of ozone is 48 g (3 × 16). The molecular weight of 1 mole of sodium bisulfite is 104 g [23 + 1 + 32 + (3 × 16)]. Therefore, 104 g of 100% pure sodium bisulfite will treat 48 g of ozone, or 2.17 g/g (i.e., 2.17 = 104 ÷ 48). Sodium bisulfite is available in 25 %wt or 38 %wt solutions. The higher-strength product, 38% solution, is typically used; therefore, the quantity of sodium bisulfite product required to react with ozone is 5.7 g/g (5.7 = 2.17 × 100 ÷ 38). In practice, additional chemical might be required (e.g., 10% or more) to reduce ozone residual to acceptable levels. These levels will depend on site-specific factors such as mixing intensity of the quenching agent at the point of application and work-area sensitivity to even minor occurrences of ozone off-gassing.

The specific gravity of a 38 %wt sodium bisulfite solution is 1.33 g/mL, or 11.1 lb/gal. The sodium bisulfite feed rate is calculated in the following way: Assume the water flow rate is 1 mgd and ozone residual is 0.2 mg/L. The mass of ozone to be quenched is 1.67 lb/d (i.e., 1.67 lb/d = 1 mgd × 0.2 mg/L × 8.34 lb/gal). Because the quantity required for 38 %wt product is 5.7 lb/lb, the mass of 38 %wt sodium bisulfite solution that is required is 9.7 lb/d (i.e., 9.7 lb/d = 1.67 × 5.7). Since the weight of 38 %wt sodium bisulfite solution is 11.1 lb/gal, the solution feed rate is 0.87 gpd (i.e., 0.87 gpd = 9.7 lb/d ÷ 11.1 lb/gal).

Sodium bisulfite is a yellow liquid with a pungent sulfur dioxide gas odor. When sodium bisulfite is stored, sulfur dioxide fumes are released from solution and accumulate in the headspace of the storage tank (Walkowiak and Fraser, 1997). As such, storage tank ventilation is required and scrubbing may be necessary. Visible corrosion of adjacent structures and equipment, plus odors or hazardous conditions, develop unless scrubbing, using an acid-buffering agent (e.g., soda ash), is implemented (Walkowiak and Fraser, 1997). Tanks must be insulated to avoid elevated temperatures and excessive sulfur dioxide fumes. Also, insulation is necessary to keep sodium bisulfate product from crystallizing (freezing). Reported crystallization temperature is 15°C (60°F) (Richey et al., 2000). Sodium bisulfite product, which may or may not be listed as NSF Standard 60-compliant, is usually available from local chemical suppliers.

Calcium Thiosulfate for Ozone Residual Quenching

One mole of calcium thiosulfate (CaS_2O_3) will react with 4 moles of ozone ($S_2O_3^{2-} + 4O_3 + H_2O = 4O_2 + 2SO_4^{2-}$). The molecular weight of 4 moles of ozone is 192 g ($4 \times 3 \times 16$). The molecular weight of 1 mole of calcium thiosulfate is 152 g [$40 + (2 \times 32) + (3 \times 16)$]. Therefore, 152 g of 100% pure calcium thiosulfate will treat 192 g of ozone, or 0.79 g/g. Calcium thiosulfate is available in 24 %wt solution; therefore, the quantity of calcium thiosulfate product required to react with ozone is 3.3 g/g ($3.3 = 0.79 \times 100 \div 24$). In practice, additional chemical might be required (e.g., 10% or more) to reduce ozone residual to acceptable levels. These levels will depend on site-specific factors such as the mixing intensity of the quenching agent at the point of application and work-area sensitivity to even minor occurrences of ozone off-gassing.

The specific gravity of a 24 %wt calcium thiosulfate solution is 1.24 g/mL, or 10.3 lb/gal. The calcium thiosulfate feed rate is calculated in the following way. Assume the water flow rate is 1 mgd and ozone residual is 0.2 mg/L. The mass of ozone to be quenched is 1.67 lb/d (i.e., 1.67 lb/d = 1 mgd × 0.2 mg/L × 8.34 lb/gal). Because the quantity required for 24 %wt product is 3.3 lb/lb, the mass of 24 %wt calcium thiosulfate solution that is required is 5.5 lb/d (i.e., 5.5 lb/d = 1.67 × 3.3). Since the weight of 24 %wt calcium thiosulfate solution is 10.3 lb/gal, the solution feed rate is 0.53 gpd (i.e., 0.53 gpd = 5.5 lb/d ÷ 10.3 lb/gal).

Calcium thiosulfate (patent pending; BSP Captor NSF, Best Sulfur Products, Fresno, California) is a clear solution. It does not release sulfur dioxide fumes when the temperature is below its boiling point, which is 240°F (Richey et al., 2000). Consequently, scrubbing is unnecessary for storage tank ventilation systems. Crystallization temperature is reported to be 16°F. Use of insulation can eliminate the potential for crystallization but is not as important as with sodium bisulfite. Calcium thiosulfate can be obtained as a certified NSF Standard 60-compliant product.

OZONE PROCESS AND EQUIPMENT TROUBLESHOOTING

Ozone facilities have several components that work together to provide continuous, reliable performance. Experience indicates that routine preventive maintenance is necessary to minimize shutdown due to equipment failure. Selected areas for special O&M are discussed in this section, along with ideas and considerations for troubleshooting.

Desiccant Dryer Operation for Maximum Moisture Removal

Different types of desiccant dryers are used in ozone system operation, depending on the application. For example, heatless desiccant dryers are used in high-pressure air-fed ozone systems, and heat-reactivated desiccant dryers are used in low-pressure air-fed ozone systems. Heatless desiccant dryers are also used to supply a small quantity of nitrogen molecules (i.e., supplemental air) to liquid oxygen (LOX)-fed ozone systems. The role of the desiccant dryer is critical in minimizing moisture loading to the ozone generator.

The heatless desiccant dryer operates at high pressure (about 100 psig) with a cycle time of a few minutes (i.e., 4 to 6 min). As a result, the switching valves operate multiple times each day and need to be repaired or replaced periodically (e.g., annually). A major O&M consideration for the heatless desiccant dryer is the integrity of the tower-switching valves. If a valve malfunctions, moisture breakthrough to the ozone generator will happen immediately.

The heat-reactivated desiccant dryer operates at lower pressure and has more complex operating characteristics than the heatless desiccant dryer. Operating characteristics and design criteria are discussed in chapter 4. The bottom-line consideration is the desiccant's capability to continuously adsorb moisture. Moisture breakthrough is due to one or more of the following:

1. Reduced capability of desiccant to adsorb moisture because desiccant is:
    a. Too warm,
    b. Aged, or
    c. Reaching saturation.
2. Insufficient desiccant for the moisture-loading rate because the:
    a. Moisture loading rate has increased due to improper operation of upstream systems (e.g., refrigerant dryer) or
    b. Quantity of desiccant installed is insufficient for the drying time selected.

The heat-reactivated desiccant dryer has two towers. One tower dries the gas while the second tower is being regenerated. Regeneration consists of heating the desiccant so that the adsorbed moisture in the desiccant evaporates into the purge gas flow. Heating continues for 2 to 4 hours. The desiccant temperature remains steady at the boiling point of water as long as moisture is contained in the desiccant. When the moisture has evaporated, the desiccant temperature will increase fairly quickly. Elevated desiccant temperature signifies that the moisture has been removed.

The hot desiccant must be cooled in order for moisture to be adsorbed by the media. If the regenerated desiccant is returned to service too quickly, moisture breakthrough will occur, as evidenced by elevated dew point temperature (high dew point temperature spike). One troubleshooting activity is to monitor occurrence of moisture breakthrough when a regenerated tower is returned to service.

The process of desiccant heating and cooling gradually reduces the moisture-adsorbing capability of the desiccant. When the desiccant is new, a desiccant quantity of, say, 15 $lb_{desiccant}/lb_{H_2O}$ might be sufficient. The typical design value is 18 $lb_{desiccant}/lb_{H_2O}$, which is needed because the desiccant will lose its moisture-adsorbing capability over time. Eventually, the desiccant will need to be replaced. Desiccant replacement frequency is variable but is likely to be every 3 to 5 years.

The desiccant dryer has a specific operating cycle time, e.g., 24 hours. This means that one tower will be drying the process gas for 12 hours and will be in regeneration for 12 hours. During regeneration, the tower is heated for 2 to 4 hours and cooled for 10 to 8 hours. Ozone system desiccant dryers typically have a cycle time of 24 hours, but cycle time could be as short as 16 hours. A longer cycle time is beneficial because desiccant cooling occurs before the desiccant is returned to service. The quantity of desiccant required is determined by the moisture-loading rate (lb_{H_2O}/hr); the design value for unit mass of desiccant, such as 18 $lb_{desiccant}/lb_{H_2O}$; and the drying time, such as 12 hours or 8 hours. Therefore, a desiccant dryer with a 24-hour cycle time is a more expensive unit.

As the desiccant ages it loses its moisture-adsorbing capability, which is indicated by an increase in dew point temperature near the end of the drying cycle. One way to extend desiccant life is to reduce the cycle time. This can be done by changing the controller logic to implement a 20-hour cycle time instead of a 24-hour cycle time. However, the cycle time must be adequate to sufficiently cool the desiccant before it is returned to service.

Bubble Diffuser Maintenance to Maintain Ozone Transfer Efficiency

Small ozone bubbles emerge from well-operating ozone diffusers. These bubbles have a relatively large gas-to-liquid surface area, which maximizes ozone transfer efficiency. Ozone transfer efficiency is field-calculated as inlet ozone concentration (i.e., concentration from the ozone generator) minus off-gas ozone concentration divided by inlet ozone concentration. This transfer efficiency value provides an estimate of the true transfer efficiency and is termed *concentration-based transfer efficiency*. True transfer efficiency is mass-based and includes gas flow and ozone concentration. Concentration-based transfer efficiency is equal to mass-based transfer efficiency when inlet- and off-gas flow are identical. However, the off-gas flow rate is usually different from the contactor inlet-gas flow rate. Off-gas flow rate is sometimes lower due to the transfer of ozone and other gases (e.g., oxygen) into the water or is sometimes higher due to excessive vacuum draw and leakage of ambient air into the off-gas piping. Concentration-based transfer efficiency is generally sufficient to monitor changes in diffuser performance.

Ozone transfer efficiency decreases if diffusers are cracked and/or gaskets leak, which cause large bubbles to form (this is called *coarse bubbling*). Cracks in stone diffusers can develop, though gasket leakage is more common. Concentration-based ozone transfer efficiency can be monitored and trends developed to assess the relative extent of coarse bubbling, as shown in Figure 5-10. At the utility represented in the figure, Hypalon diffuser gaskets were installed in the plant's LOX-fed dome-shaped bubble diffusers. Operation at high ozone concentration caused gasket deterioration within 1 year. Transfer efficiency improved following gasket repair but deteriorated after another year of operation. Eventually, the diffusers were totally refurbished and high-grade Viton gaskets were installed, with the expectation that ozone transfer efficiency would be satisfactory for 2 to 3 years of service life. Other plants have replaced Hypalon with expanded Teflon (brand name Gortex and Garlon) gasket material, with the expectation (and initial operating evidence) that ozone transfer efficiency would be satisfactory for an even longer period of time. Unfortunately, a comprehensive study has not been completed to document gasket issues and considerations that would assist in choosing between high-grade Viton, expanded Teflon, or other ozone gasket material. Issues include cost, longevity, resilience (i.e., ability to stop leakage), and availability.

Figure 5-10 illustrates that monitoring of concentration-based ozone transfer efficiency is sufficient to assess the extent of coarse bubbling in the bubble diffuser. As such, it is unnecessary to measure the ozone off-gas flow rate to document true ozone transfer efficiency, unless the information is needed for research purposes. Issues and considerations for achieving continuous and accurate monitoring of off-gas ozone concentration include the following:

1. Ozone in a wet gas has a short half-life of about 80 min (Coffey, 2000). This means that some ozone will decay naturally within the ozone contactor's headspace. Placing the off-gas inlet piping directly above the diffusers will minimize headspace decay. Also, the sample piping should be short to minimize detention time prior to sample analysis.
2. The saturated off-gas will condense moisture within the sample line if cooled. This suggests that the sample line should be set up with a drip leg that allows condensed moisture to be drained either manually or automatically.

3. Over time, the wet off-gas fouls the sample cell of the ozone concentration meter. Consequently, the off-gas ozone monitor will need to be cleaned more frequently than the ozone generator's product-gas ozone concentration meter. The off-gas can be directed through a filter to help reduce sample-cell cleaning frequency. Consult the manufacturer of the ozone concentration meter for off-gas sample filter installation instructions and cleaning protocol to ensure that the sample gas-cleaning setup does not adversely affect the ozone concentration readings.

Ozone diffusers are installed in the contactor at 18- to 22-ft water depth. Maintenance of these diffusers is a routine activity that should be completed either annually or bi-annually. Maintenance involves field inspecting each diffuser for cracks, observing bubble pattern to determine if gaskets are leaking, and repairing or replacing diffusers and gaskets, as applicable. At some plants diffusers are removed and replaced with new or refurbished diffusers; removed diffusers are inspected and repaired at a later time using a maintenance bench setup.

Because an ozone contactor is classified as a confined space, safety considerations are an important part of standard operating procedures for draining, entering, and refilling the ozone contactor. The following safety precautions should be taken:

1. Prepare written operating procedures for draining and entering a contactor. Ideally, the procedures should be developed during the design phase of the project so that helpful design features can be incorporated into the setup, as applicable.
2. Ensure that the contactor is designed so that it is easily drained. Because air will displace the water when water is drained from the contactor, provisions should be made for ambient air to enter the contactor while the contactor is drained.
3. Ensure that the contactor is designed with side-entry access. Top-down access into a 20-ft plus deep tank is difficult, at best.
4. Perform bubble testing of diffusers using air.
5. Determine whether the contactor will be filled with disinfected water or not. Filling with disinfected water might be desired or required.
6. Carefully fill chambers that contain diffusers; exposed diffusers may break when water cascades directly on top of them. These chambers can be backfilled with water so that the water level is above the diffusers before water is directed into that chamber.

Ozone Generator Maintenance for Continuous Optimized Operation

Ozone generator maintenance includes generator dielectric and vessel cleaning; PSU maintenance; and generator shell cleaning if the cooling water is corrosive or has a tendency to cause scaling. Historically, dielectric and vessel cleaning was an expected and potentially frequent maintenance task, but cleaning frequency has been reduced in newer ozone systems. Issues concerning cleaning frequency are discussed below.

PSU maintenance consists of cabinet cooling-system and electrical system maintenance. Maintenance of the electrical system is usually infrequent and can be completed via contract with the ozone system supplier or other service provider.

Ozone generators will need periodic cleaning if energy efficiency deteriorates. Monitoring ozone generator energy efficiency was discussed earlier in this chapter and illustrated in Figure 5-5. Cleaning frequency is a function of moisture contamination. For example, air-fed ozone systems that have weak desiccant drying systems (i.e., frequent occurrence of elevated dew point temperature—elevated moisture loading) require annual cleaning, at a minimum. Alternately, air-fed ozone systems that have robust desiccant drying systems may require cleaning every 3 to 5 years. LOX-fed ozone systems require cleaning less often (e.g., 5 to 10 years, or longer), especially when:

1. Moisture does not backflow into the ozone generator from the ozone contactor. Backflow is minimized when the generator outlet valve is closed in off-line ozone generators.
2. Moisture-laden ambient air does not enter off-line ozone generators (i.e., off-line generators are always under positive pressure).
3. Moisture does not enter an operating generator via the nitrogen feed system due to malfunction of the supplemental-air desiccant dryer.

Cleaning ozone generators is a time-consuming task (i.e., 1 to 2 weeks is required) that necessitates expertise, experience, and strict procedural implementation. Figure 5-11 illustrates the cleaning process, which requires removing dielectrics, swabbing dielectric tubes, replacing dielectrics, rehooking up the electrical system, and other specialized tasks. Mechanical and electrical safety precautions are inherent in the process. Plants that clean generators annually should train their staff to perform the cleaning tasks. If generators require infrequent cleaning (e.g., every few years), cleaning can be contracted out. Consult the ozone system supplier concerning best-practice methodology for generator cleaning.

Generator vessel maintenance for corrosion or scaling is infrequent, though corrosion and scaling do occur. Cooling water that has a chlorine (not chloramine) residual and/or high chloride concentration has been implicated in corrosion occurrence (i.e., once-through cooling and not open-loop/closed-loop cooling arrangements). However, it is unclear whether the problems are a result of chlorine residual and/or high chloride or are associated with stopping cooling water flow when the ozone generator is off-line. Currently, many ozone generators are set up to maintain a low flow of cooling water through the generator vessel when the

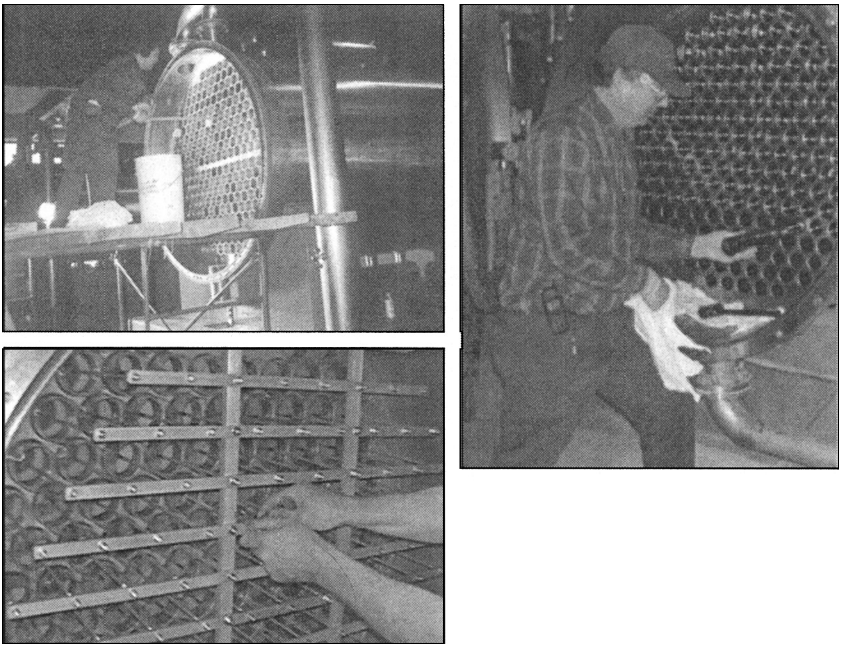

Figure 5-11 Ozone generator dielectric cleaning and replacement maintenance

generator is off-line (this is variable, and the ozone manufacturer should be consulted). Cooling water with the potential for scaling has resulted in scale buildup. "Boiler-water" scaling due to heat is unexpected, because the temperature differential is quite low (i.e., <10°F). Though most waters are non-scaling, scaling can occur (Figure 5-12).

Many ozone systems are designed with an open-loop/closed-loop cooling water system as a proactive measure to avoid corrosion or scaling (see Figure 3-13, chapter 3). Closed-loop water is noncorrosive, nonscaling conditioned water. Heat is transferred from the closed-loop system to the open-loop system in a plate-and-frame heat exchanger. Open-loop cooling water is treated or nontreated water, depending on the quality of the nontreated water source. The advantage of a closed-loop/open-loop system is that maintenance activities are confined to the plate-and-frame heat exchanger if the open-loop water is problematic.

Heat-Catalyst Ozone Destruct Unit Performance and Maintenance

The heat-catalyst ozone destruct unit consists of a heating element, manganese dioxide catalyst, and off-gas exhaust fan or blower. The heating element elevates the off-gas temperature slightly (e.g., 30°F) to prevent moisture condensation onto the catalyst pellets. If moisture condensation occurs, ozone contact with the catalyst

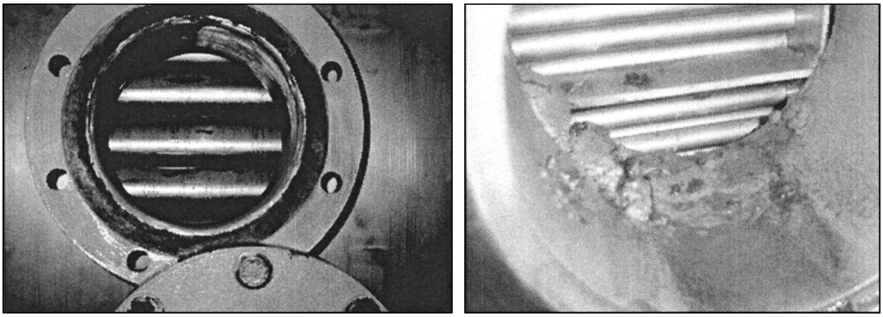

Figure 5-12 Ozone generator vessel corrosion and scaling occurs infrequently

media is prevented and the catalytic reaction is stopped. Wet catalyst can be removed, dried, and returned to service but might not be as effective as new catalyst. Alarms are provided to indicate malfunction of the heating element. Heating elements generally perform well, except when exposed to condensed moisture that has collected in the off-gas piping. Chapter 4 discusses the potential for moisture condensation inside the off-gas piping, including methods for moisture removal.

Ozone molecules are converted back to oxygen molecules by the manganese dioxide catalyst. Key ingredients needed for good catalyst performance are absence of chlorine, sulfur dioxide, or hydrogen sulfide gases that poison the catalyst, plus absence of condensed moisture by proper operation of the heating element. Catalyst capability degrades slowly over time due to reaction with hostile gases that are stripped from the water and collected in the off-gas. Under normal operation, catalyst life expectancy is several years (3 to 5 years or longer). In all plants, a demister (i.e., stainless-steel wire mesh) is installed on the off-gas line to coalesce water droplets and reduce moisture content of the off-gas. A few plants install spray nozzles when foaming is a potential problem.

The exhaust blower pulls the off-gas through the heating element and catalyst and discharges ozone-free off-gas into the ambient environment. Exhaust blowers perform well with customary preventative maintenance efforts.

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6

Measuring Ozone Concentration in Gas

Ozone concentration in gas is one of the most important parameters for operating an ozone system with respect to safety (chapter 1) as well as control (chapter 4) and monitoring (chapter 5) of process operation. In this chapter ozone concentration measurement techniques are discussed. Methods for calibrating in-plant ozone concentration meters are also discussed.

OZONE CONCENTRATION MEASUREMENT LOCATIONS

The values of ozone concentration in gas are high in the product gas from the ozone generator, medium in the off-gas from the ozone contactor, and low in the workspace or the vent-gas from the ozone destruct unit. Low concentrations, typically <0.1 ppm$_V$, are measured using principles of ultraviolet light (UV) absorbance by ozone molecules. Medium concentrations are usually >0.1 %wt (670 ppm$_V$) and high concentrations are usually > 1.0 %wt (6,700 ppm$_V$); both can be measured using wet chemistry methodology as well as by UV light.

Ozone Generator Product Gas

UV meters that measure high concentrations of ozone are located at the outlet of the ozone generator. Measurements are used to assess power-production efficiency, ozone production, ozone dosage, etc., and for ozone process control. The meters have short sample lines so that response is quick when ozone concentration changes. Wet chemistry testing verifies the accuracy of these meters. An example wet chemistry test setup is shown in Figure 6-1.

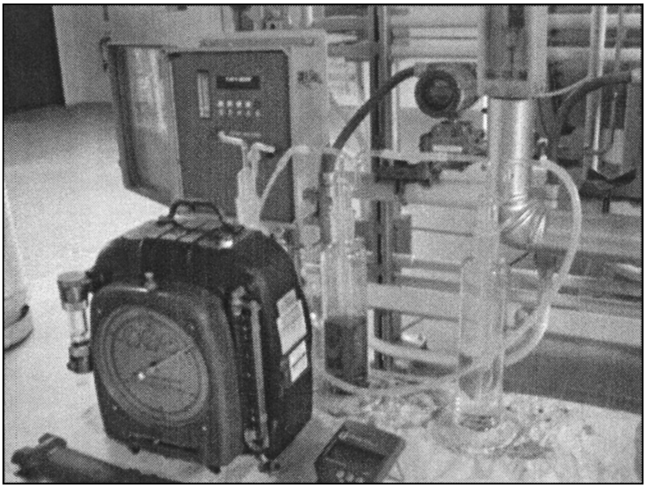

Figure 6-1 Ozone concentration meter (in the background) for measuring high-concentration ozone, with wet-chemistry testing setup in foreground

Ozone Contactor Off-Gas

The concentration of ozone off-gas in the contactor and the resulting ozone transfer efficiency is assessed with UV meters that measure a medium ozone-concentration value. The off-gas ozone concentration meters are used to monitor potential problems with ozone transfer. For example, an elevated off-gas ozone concentration from bubble-diffuser ozone contactors might indicate failure of the ozone diffuser gasket (see chapter 5).

Meters that measure off-gas ozone concentration in the contactor are similar to meters that measure generator product-gas ozone concentration, but the installation is different. Because generator product-gas ozone is pressurized, the ozone sample is pushed through the meter. In contrast, contactor off-gas is under vacuum and the ozone sample must be pulled through the meter with a vacuum pump (Figure 6-2). The meter setup includes the following important elements. An ozone destruct cartridge (mounted vertically to avoid short-circuiting) is located between the meter and the vacuum pump to protect the vacuum pump from ozone damage. Because the off-gas sample is saturated with moisture, off-gas moisture-conditioning units are installed on the sample line and meters are located close to the off-gas piping. Wet-chemistry testing is used for quality assurance checks of off-gas medium-concentration UV meters.

Ozone Destruct Vent Gas

Performance and regulatory compliance reporting requirements for the ozone destruct unit are assessed using UV meters that measure low ozone concentration.

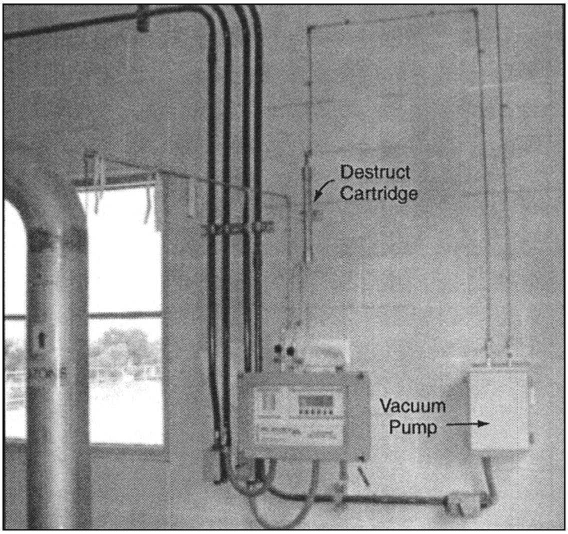

Figure 6-2 Installation of contactor off-gas ozone concentration meter and vacuum pump

Meters are located near the vent-gas piping where the ozone sample is pushed through the meter. Some installations have had problems with moisture condensation. It seems that the vent-gas sample cools sufficiently to form moisture droplets in the sample as it flows to the meter. Moisture-conditioning units are installed on the sample line in these installations. Another consideration is accuracy of the ozone destruct vent gas UV meter. Some plant discharge permits require quality assurance and quality control (QAQC) checks. A standard or reference meter can be used to implement QAQC checks; this meter is of the type used for ozone-in-air pollution monitoring programs.

Ambient Air

UV meters that measure low ozone concentration are used to detect ambient ozone concentrations and monitor the ozone installation for potential ozone leaks. Ozone production is stopped if the leakage is sizable. Wet-chemistry testing cannot be used to verify the accuracy of low-concentration UV meters. However, highly accurate ambient air monitoring is unnecessary because of the extreme differential in concentrations involved. Specifically, the ambient ozone concentration is <0.1 ppm_V, whereas the ozone generator product-gas concentration is several thousand ppm_V. This means that a major leak in the ozone system will be detected quickly, even if the UV meter is moderately accurate. The most important consideration for the ambient air UV ozone concentration meters is that they are responsive to low to moderate ozone concentration values (in the range of 0.1 to 0.2 ppm_V).

Ozone safety monitoring and alarms are discussed further in chapter 1. Some plants have experienced unnecessary plant shutdowns when a single meter reading has shut down the ozone system. At these plants, an alarm sounds if one concentration meter displays an elevated concentration value, but two meters must display an elevated reading before ozone production is stopped.

Ozone Measurement Using Ultraviolet Light

In this section, the theory, installation, and calibration of the UV ozone gas concentration meter is described. The UV meter, which is used extensively, is self-calibrating and generally reliable when properly installed. Proper installation can be validated (for high and medium ozone concentrations) using wet chemistry test results, which are also described in this chapter.

Theory

Gaseous ozone molecules absorb UV light, with maximum absorption occurring at 253.7 nm. The commonly accepted gas-phase absorption coefficient for ozone is 3,000 ±30 L mol^{-1} cm^{-1}, at 273 K and 101.3 kPa (Langlais et al., 1991; Duguet et al., 1986; Mauersberger et al., 1986; Molina and Molina, 1986).

Ozone concentration is determined using the Beer-Lambert law, as shown in Eq. 6-1. Optical density (Eq. 6-2) is obtained by rearranging Eq. 6-1, and ozone concentration (Eq. 6-3) is obtained by rearranging Eq. 6-2. The temperature (T) and pressure (P) of the absorption cell must be measured and incorporated into the calculations to display standardized (NTP or STP) concentration readings (C_{NTP} or C_{STP}), as shown by Eq. 6-4.

$$I = Io e^{-\varepsilon l C} \qquad \text{(Eq. 6-1)}$$

$$\varepsilon l C = OD = \ln\left(\frac{I}{Io}\right) \qquad \text{(Eq. 6-2)}$$

$$C = \frac{OD}{\varepsilon l} \qquad \text{(Eq. 6-3)}$$

$$C_{NTP} = \frac{OD}{\varepsilon l} \times \frac{P_{NTP}}{P} \times \frac{T}{T_{NTP}} \qquad \text{(Eq. 6-4)}$$

Where:

I_o = light intensity in the absence of ozone
I = light intensity in the presence of ozone
= 3,000 ±30 $M^{-1}cm^{-1}$
l = path length, cm
C = ozone concentration, moles per liter

OD = measured optical density

T = temperature of sample cell in R (459.7 + °F) or K (273.15 + °C)

T_{NTP} = normal temperature of sample cell that is specified by the manufacturer, R or K

P = absolute pressure inside sample cell, which is barometric pressure plus gauge pressure, psia

P_{NTP} = normal absolute pressure of sample cell that is specified by the manufacturer, psia

Operating Characteristics of Commercial UV Meters

Most commercial UV ozone meters operate similarly, but equipment features are frequently different. Every meter has a fixed sample-cell path length. Low-concentration meters have a path length of several centimeters to increase the amount of UV light absorbance for the lesser ozone concentrations. High-concentration meters have a path length of a few millimeters.

Commercially available gas-phase UV meters provide consistent, reliable, and accurate ozone concentration readings if they are suitably constructed and correctly installed. Wet-chemistry testing can be used to field-verify accuracy of an installed meter. Ozone concentration readings are displayed on a volumetric basis (e.g., g/m^3, mg/L, or ppm$_v$) or mass basis (e.g., %wt). Each UV ozone meter has a listed reference temperature, pressure, and gram molecular weight (GMW) of feed-gas supply (e.g., 32 g/mol for oxygen or 29 g/mol for air). Meter reading adjustments are made automatically (newer models) or manually (older models), according to Eq. 6-5.

$$\text{Adjustment Ratio} = \frac{P_s}{P_a} \times \frac{T_a}{T_s} \times \frac{GMW_s}{GMW_a} \qquad \text{(Eq. 6-5)}$$

Where:

P_s = meter's reference or standard pressure (absolute)

P_a = actual sample cell pressure (absolute)

T_a = actual sample cell temperature, R or K

T_s = meter's reference or standard temperature, R or K

GMW_s = meter's reference or standard gas GMW

GMW_a = actual feed-gas GMW

The ozone concentration value displayed on a UV meter is a temperature-and-pressure corrected reading or an uncorrected reading. Older UV meters require independent temperature and pressure measurements and operator-initiated calibration adjustments. Newer meters are constructed with internal temperature and pressure instrumentation and display corrected readings automatically. Meters that display the ozone concentration on a mass basis (e.g., %wt) must contain the correct GMW value in the preset adjustments.

Wet Chemistry Validation of Installed UV Meters

UV measurement is an absolute measurement that is accurate to ±1% in a precision laboratory under controlled situations (Rakness et al., 1996a). In field applications the accuracy has been shown to be within ±2% due to operating conditions that are not easily controlled (Rakness et al., 1996b). There is minimal interference from other gases, such as nitrogen oxides, found in the output of ozone generators.

The iodometric, wet chemistry method (otherwise known as the KI [potassium iodide] method) appears to have a standard deviation percentage of 2% when performed carefully using a prescribed procedure (Rakness et al., 1996b). The procedure outlined below addresses areas where special precautions are necessary, such as quality control checks of the normality of the titrant that is used to obtain the mass of ozone reacted with the KI and quality control checks of the totalized volume of process gas that passes through the gas washing bottle(s).

Ozone Wet Chemistry Testing

The KI wet chemistry method is based on the principle that iodide ion is oxidized by ozone to form iodine when ozone gas is bubbled through a solution of KI. When bubbling is stopped, the KI solution is adjusted with sulfuric acid to pH 2, or lower. The liberated iodine is titrated to a starch endpoint (i.e., clear color from a bluish color) using standardized sodium thiosulfate. The mass of ozone reacted is determined based on a theoretical ozone/iodine stoichiometry of 1.0.

Unfortunately, the ozone/iodine stoichiometry is not always 1.0—it can range from 0.65 to 1.5 (Birdsall et al., 1952; Boyd et al., 1970; Byers and Saltzman, 1959; Flamm, 1977; Gordon et al., 1989; Wood, 1987), depending on testing methodology. Factors that affect the stoichiometry include KI solution pH, buffer composition, buffer concentration, iodide ion concentration, sampling techniques, reaction time, and ozone gas flow rate. Because these factors influence the desired stoichiometry (i.e., 1.0), the wet chemistry test must be performed very carefully using a prescribed procedure (Rakness et al., 1996a).

The necessary one-to-one stoichiometry is as follows:

$$O_3 + 2I^- + H_2O = I_2 + O_2 + 2OH^-$$

The iodine formed in the above reaction is titrated directly with thiosulfate ion:

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

When ozone reacts with iodide ion, two moles of hydroxide ion are produced for each mole of iodine. The preexistence of hydroxide ion in the absorption solution and/or formation of hydroxide ion in the reagent solution creates an inherent problem with the iodometric determination of ozone, because the reaction of ozone with hydroxide ion constitutes the initiation step of the ozone decomposition process in aqueous solution (see discussion of advanced oxidation in chapter 2). The unbuffered KI method (KI), and the neutral buffered potassium iodide Europe method ($NBKI_e$), which includes weakly buffered KI solution (IOA Standardisation Committee, 1987a), are regarded as being better than other wet chemistry methods, because ozone decomposition and other side reactions are minimized or, at least, counterbalanced in the subsequent acidification step so as to achieve the desired 1:1 stoichiometry during the sodium thiosulfate titration step (Wood, 1987).

The detection limit of the KI and $NBKI_e$ methods is 0.1 mg/L. Specific chemical interferences include oxides of nitrogen, other oxidants capable of oxidizing iodide ion to iodine, and any inorganic impurities that might react with the iodine. Generally, the interferences are minimal at the outlet of commercial ozone generators and in the off-gas from drinking water ozone contactors.

Ozone Wet Chemistry Test Procedure

Results from the wet chemistry test are inherently variable due to the complex chemical reactions that occur during the test and due to the test's sensitivity to analytical procedures. A definitive procedure for conducting the wet chemistry test is presented here to enable the reader to obtain reasonably consistent results that have a 1:1 stoichiometry.

1. Equipment.
   1.1. One or two standard gas washing bottles, 500 mL capacity, *without* a fritted diffuser. A fritted diffuser is unnecessary and should be avoided because the frit may promote destruction of ozone as the ozone gas enters the KI solution, thereby leading to inaccurate results. NOTE: An additional gas-washing bottle with strong KI solution can be used to destroy ozone that is flushed through tubing prior to each test.
   1.2. One totalizer-type, wet-test gas meter equipped with integral manometer and thermometer capable of reading water temperature within ±0.2°C. The accuracy of the wet-test meter is critical to overall accuracy of the wet-test result. The volumetric accuracy of the wet-test meter should be within ±1%. Independent laboratories can calibrate the wet-test meter.

- 1.3. Tubing and connections of glass, stainless steel, aluminum, or Teflon. A small amount of Silicone or Tygon tubing may be used to facilitate connections to glassware.
- 1.4. The following pieces of lab equipment: One beaker (1 to 2 L); one digital scale (0.001 g accuracy); measuring tray and scoop; one or two 1-L volumetric flasks (i.e., for mixing potassium iodide solution and diluting 1*N* sodium thiosulfate to 0.1*N* or 0.2*N* solution); one 500-mL graduated cylinder; one 100-mL graduated cylinder; two 10-mL graduated cylinders (for adding acid following bubbling); several small plastic funnels; two 500-mL plastic squirt bottles (for distilled water and sodium thiosulfate); one 100-mL or one 200-mL squirt bottle (for starch solution); two 1-L plastic brown bottles (for potassium iodide solution); box of latex gloves; safety glasses; and white paper towels.

2. Reagents.
   - 2.1. Use either unbuffered KI or slightly buffered KI ($NBKI_e$). All other buffering formulations for KI are *not* acceptable.
     - 2.1.1. Unbuffered KI (used most often in North America). Potassium iodide stock reagent (2%): Dissolve 20 g KI in 1 L of distilled water. Store in a brown bottle and refrigerate.
     - 2.1.2. Slightly buffered KI ($NBKI_e$).

       Potassium iodide stock reagent (2%): Dissolve 20 g KI in 1 L of distilled water. Add 7.3 g of disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$) and 3.5 g of monopotassium dihydrogen phosphate (KH_2PO_4). Store in a brown bottle and refrigerate.
   - 2.2. Sulfuric acid (2*N*): Add 56 mL concentrated sulfuric acid to 944 mL distilled water. Store in a reagent bottle.
   - 2.3. Sodium thiosulfate ($Na_2S_2O_3$) stock solution (1*N*): Dissolve 250 g of pentahydrate sodium thiosulfate ($Na_2S_2O_3$–$5H_2O$) granules into 1 L of freshly boiled distilled water. Store in a brown bottle and refrigerate.

     NOTE: Sodium thiosulfate solution may be purchased directly from a chemical supplier rather than making up the product from granules (see steps 2.5, 3.1, and 3.2).
   - 2.4. Prepare starch indicator solution using one of the two following methods:
     - 2.4.1. Zinc chloride starch indicator: To 4 g soluble starch, add a little cold distilled water and grind to a thin paste. Disperse the paste into 100 mL of distilled water that contains 20 g of zinc chloride ($ZnCl_2$). Boil the solution until the volume has been

reduced to 100 mL. Dilute this solution to a total volume of 1 L and add 2 g of $ZnCl_2$. The indicator is stable for about 1 month when stored in the dark at room temperature.

    2.4.2. Starch indicator: To 5 g soluble starch, add a little cold distilled water and grind to a thin paste. Pour into 1 L of boiling distilled water, stir, and let settle overnight. Decant and refrigerate the clear supernatant.

2.5. Sodium thiosulfate ($Na_2S_2O_3$) (0.1*N*): Add 100 mL of 1*N* $Na_2S_2O_3$ stock solution to 900 mL distilled water. Standardize this solution each day, as discussed in steps 3.1.1 and 3.1.2. Other normalities can be used, as described in step 3.7.

2.6. Potassium dichromate ($K_2Cr_2O_7$) (0.1000*N*): Dissolve 4.904 g anhydrous $K_2Cr_2O_7$ (primary standard quality) in distilled water and dilute in a volumetric flask to 1 L. Store in a reagent bottle.

2.7. Potassium periodate (KIO_3).

2.8. Distilled water: Use 3 to 5 gal of distilled water, depending on the number of tests to be conducted. Conductivity shall be less than 10 µm/cm. Distilled water quality is critical to results. Consider that approximately 1.5 gal of distilled water is required to fill the wet-test meter.

3. Methodology.

3.1. Standardize the 0.1*N* sodium thiosulfate titrant using either method 3.1.1 or 3.1.2. This activity can be completed prior to the test and should be completed each day of the test. (NOTE: Standardizing is avoided when product is from a certified laboratory and is used before its expiration date.)

    3.1.1. To 150 mL distilled water in a 250-mL Erlenmeyer flask, add, with constant stirring, 1.0 mL concentrated H_2SO_4, 20.0 mL of 0.1000*N* $K_2Cr_2O_7$, and 2.0 g KI. Cover and let the mixture stand 6 min in the dark. Titrate with the approximate 0.1*N* $Na_2S_2O_3$ titrant until the yellow color is almost gone. Add 1.0 mL of starch indicator solution and continue titration until the blue color just disappears. The normality of $Na_2S_2O_3$ titrant = 2.0 ÷ $Na_2S_2O_3$ mL consumed.

    3.1.2. Weigh 0.5 g of potassium iodate (KIO_3) and dilute to 250 mL in a 250-mL Erlenmeyer flask. By burette, add 25 mL of this periodate solution to a 125-mL Erlenmeyer flask. Add 0.5 g KI, 50 mL of water, and 2 mL of 1*N* sulfuric acid. The iodine formed is titrated with the approximately 0.1*N* $Na_2S_2O_3$

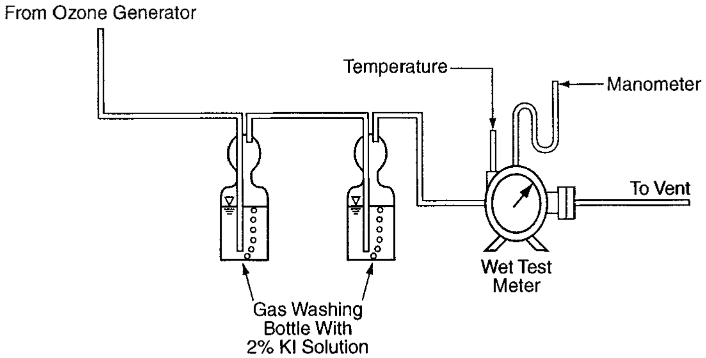

Figure 6-3 Ozone concentration wet test setup for ozone generator product-gas

titrant until the yellow color is almost gone. Add 1.0 mL of starch indicator solution and continue titrating carefully until the blue color just disappears. The normality of $Na_2S_2O_3$ titrant = 2.0 ÷ $Na_2S_2O_3$ mL consumed.

3.2. Fill a 50-mL class A burette with the $Na_2S_2O_3$ titrant that was standardized in steps 3.1.1 and 3.1.2. Fill the burette just prior to adding ozone to the gas-washing bottle (see step 3.6). Maintain fresh titrant in the burette (e.g., refresh daily).

3.3. Add 400 mL of 2% KI or $NBKI_e$ solution to each gas-washing bottle. Two bottles are suggested.

3.4. Level the wet-test meter.

3.5. Assemble the wet-test equipment for ozone product-gas measurements, as shown in Figure 6-3. The wet test setup for measuring ozone off-gas is slightly different, as shown in Figure 6-4. The off-gas must be pulled through the wet-test meter and only one gas-washing bottle is used.

3.6. Bubble ozone through the KI solution and start recording the volume that is bubbled through the KI using either step 3.6.1 or step 3.6.2.

3.6.1. Safely purge the tubing from the ozone-piping source to the gas-washing bottle with fresh ozone before connecting the tubing to the bottle (e.g., purge into an off-line gas-washing bottle). Then, connect the tubing that has been purged with ozone to the gas-washing bottles and immediately begin recording the wet-test meter volume.

3.6.2. Allow the gas inside the sample line to bubble through the test KI solution until the sample line is fully purged with sample

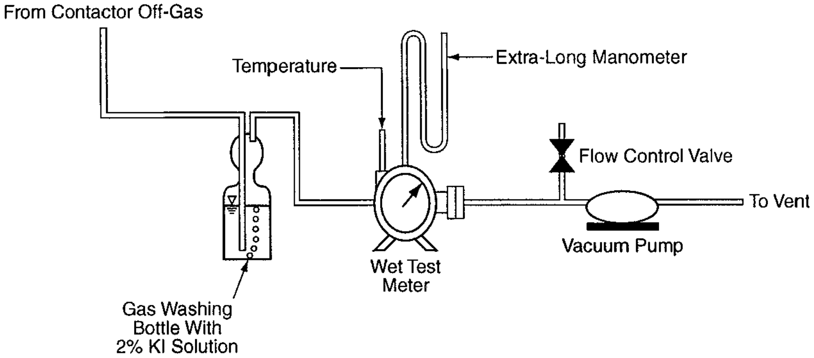

Figure 6-4 Ozone concentration wet test setup for ozone contactor off-gas

ozone gas. Begin recording flow on the wet-test meter as soon as a yellow color is noticed at the point of entry inside the gas-washing bottle.

3.7. Bubble 2 to 4 L of ozone gas through the bottles at a rate of about 1 to 2 L/min. Record the exact volume of the wet-test meter as the uncorrected volume on the data sheet. The recommended gas volume to be collected depends on ozone concentration, titration volume, and $Na_2S_2O_3$ normality (see Figures 6-5 and 6-6). Improved accuracy is obtained when the titration volume is at least 20 mL and the gas volume is at least 2 L. The normality of the $Na_2S_2O_3$ titrant can be adjusted to achieve these conditions, as discussed in step 2.5.

3.8. After bubbling has stopped, quickly add about 10 mL of 2*N* H_2SO_4 to each gas-washing bottle to lower the pH of the solution below 2.

3.9. Transfer the liquid from each gas-washing bottle to a 1- or 2-L Erlenmeyer flask (use 2 L for two gas-washing bottles). Thoroughly rinse the gas-washing bottles three times with distilled water, retaining all rinse water in the Erlenmeyer flask. When transferring contents, minimize splashing and aeration.

3.10. Read the initial volume of $Na_2S_2O_3$ titrant in the burette. (NOTE: The titrant should have been recently standardized, as described in steps 3.1.1 and 3.1.2. However, if the titrant is from a commercial laboratory, the solution can be used as long as the bottle has been stored properly and is within the expiration date listed on the container.) Continue titration with $Na_2S_2O_3$ until the solution turns a pale yellow color.

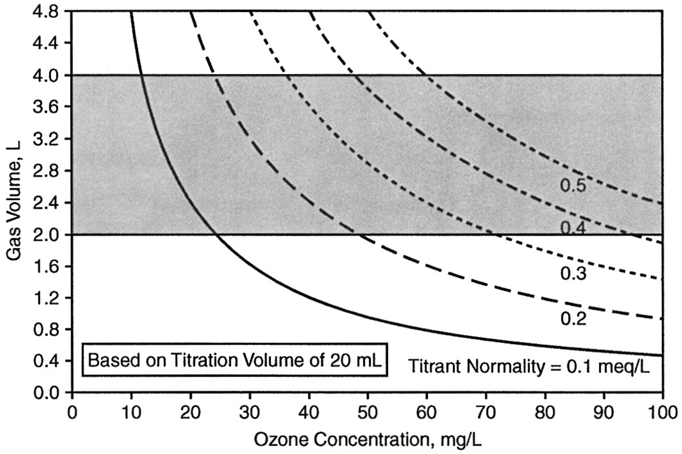

Figure 6-5 Relationship among wet test parameters for a titration volume of 20 mL

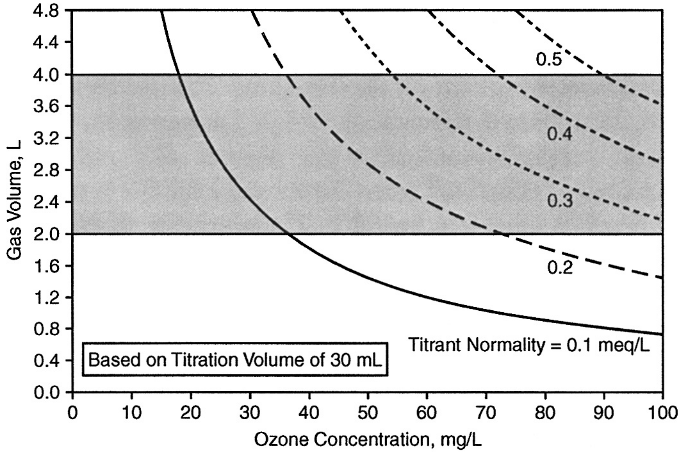

Figure 6-6 Relationship among wet test parameters for a titration volume of 30 mL

3.11. Add about 5 mL of starch solution to the flask. A bluish color will form. Carefully continue the titration, drop by drop, until the blue color just disappears and the solution is clear.

3.12. Record the final burette reading and determine the total volume of titrant used. Record the volume of titrant used and the exact normality of the titrant from steps 3.1.1 or 3.1.2.

3.13. Complete the calculations described in step 4.

4. Determination of ozone concentration from the wet chemistry test procedure discussed in steps 3.1 through 3.12.
   4.1. Find temperature-corrected and pressure-corrected gas volume using Eq. 6-6.

$$V_{STP} = V_a \times \frac{(P_a - P_v + P_m)}{P_s} \times \frac{T_s}{T_a} \qquad \text{(Eq. 6-6)}$$

Where:

V_{STP} = gas volume, in liters (L_{STP} or L_{NTP}), referenced to standard or normal temperature and pressure conditions (see appendix A for discussion concerning standard and normal temperature and pressure)

V_a = uncorrected gas volume, as measured by wet-test meter, L

P_s = reference standard (normal) pressure of 1 atm, which is 101.3 kPa or 760 mm Hg

T_s = reference standard (normal) temperature (Normal temperature is 273.15 Kelvin = 0°C and standard might be 293.15 Kelvin = 20°C, or other stated values.)

P_a = barometric pressure, kPa or mm Hg

P_v = vapor pressure, based on wet-test meter temperature, as shown in Table 6-1, kPa or mm Hg

P_m = manometer pressure of wet-test meter, kPa or mm Hg (NOTE: It may be necessary to convert from inches of water, using 1.868 mm Hg per inch of water and 0.1333 kPa per mm Hg. Typically, the wet-test manometer pressure is zero when testing the ozone generator product-gas. The manometer pressure is a negative number when testing the ozone contactor off-gas due to the vacuum condition developed within the meter.)

T_a = wet test meter temperature, K (temperature in °C + 273.15)

   4.2. Find mass of ozone trapped in KI or $NBKI_e$, using Eq. 6-7.

$$O3_{Mass} = 24 \times V_t \times N_t \qquad \text{(Eq. 6-7)}$$

Where:

$O3_{Mass}$ = mass of ozone trapped in KI or $NBKI_e$, mg

24 = conversion factor = 24,000 meq/L per 1,000 mL/L

V_t = volume of sodium thiosulfate titrant used, mL

N_t = normality of sodium thiosulfate, mg/meq

Table 6-1 Look-Up Table for Vapor Pressure (VP)

Temp. °C	VP mm Hg	Temp. °C	VP mm Hg	Temp. °C	VP mm Hg	Temp. °C	VP mm Hg	Temp. °C	VP mm Hg
10.0	9.21	15.0	12.79	20.0	17.53	25.0	23.76	30.0	31.82
10.2	9.33	15.2	12.95	20.2	17.75	25.2	24.04	30.2	32.19
10.4	9.46	15.4	13.12	20.4	17.97	25.4	24.33	30.4	32.56
10.6	9.58	15.6	13.29	20.6	18.20	25.6	24.62	30.6	32.93
10.8	9.72	15.8	13.46	20.8	18.42	25.8	24.91	30.8	33.31
11.0	9.84	16.0	13.63	21.0	18.65	26.0	25.21	31.0	33.69
11.2	9.98	16.2	13.81	21.2	18.88	26.2	25.51	31.2	34.08
11.4	10.11	16.4	13.99	21.4	19.11	26.4	25.81	31.4	34.47
11.6	10.24	16.6	14.17	21.6	19.35	26.6	26.12	31.6	34.86
11.8	10.38	16.8	14.35	21.8	19.59	26.8	26.43	31.8	35.26
12.0	10.52	17.0	14.53	22.0	19.83	27.0	26.74	32.0	35.66
12.2	10.66	17.2	14.71	22.2	20.07	27.2	27.05	32.2	36.07
12.4	10.80	17.4	14.90	22.4	20.32	27.4	27.37	32.4	36.48
12.6	10.94	17.6	15.09	22.6	20.56	27.6	27.70	32.6	36.89
12.8	11.08	17.8	15.28	22.8	20.81	27.8	28.02	32.8	37.31
13.0	11.23	18.0	15.48	23.0	21.07	28.0	28.35	33.0	37.73
13.2	11.38	18.2	15.67	23.2	31.32	28.2	28.68	33.2	38.15
13.4	11.53	18.4	15.87	23.4	21.58	28.4	29.01	33.4	38.58
13.6	11.68	18.6	16.07	23.6	21.84	28.6	29.35	33.6	39.02
13.8	11.83	18.8	16.27	23.8	22.11	28.8	29.70	33.8	39.46
14.0	11.99	19.0	16.48	24.0	22.38	29.0	30.04	34.0	39.90
14.2	12.14	19.2	16.68	24.2	22.65	29.2	30.39	34.2	40.34
14.4	12.30	19.4	16.89	24.4	22.92	29.4	30.74	34.4	40.80
14.6	12.46	19.6	17.10	24.6	23.20	29.6	31.10	34.6	41.25
14.8	12.62	19.8	17.32	24.8	23.48	29.8	31.46	34.8	41.71

NOTE: Multiply by 0.1333 kPa/mm Hg to convert from mm Hg to kPa.

4.3. Find concentration of ozone in mg/L$_{NTP}$ (Y_1) using Eq. 6-8.

$$Y_1 = \frac{\text{Mass from Equation (6-7)}}{V_{STP} \text{ from Equation (6-6)}} \qquad \text{(Eq. 6-8)}$$

4.4. End of wet chemistry test procedure

Validating the UV Meter With Wet Chemistry Tests

Ozone concentration is determined using iodometric wet chemistry as a way to confirm the trustworthiness of installed UV ozone meters. However, the UV meter reading should be established independently, meaning that the UV meter should be set up per manufacturer's instructions, with the span set at 1.0 (i.e., without bias).The wet chemistry test is then conducted such that the ozone concentration value is consistent during the test. This will allow use of both the meter and wet chemistry test to sample a product-gas (or off-gas) with the same (or very similar) ozone concentration value. The two results provide an independent comparison of the ozone concentration value. A comparative ozone concentration measurement that exceeds ±2% indicates that something may be wrong with the UV meter installation or with the wet chemistry test procedure, such as an inaccurate wet test meter or sodium thiosulfate solution that has a different normality. Both the UV meter and wet chemistry test procedures should then be reevaluated to ensure they are being performed correctly. The UV meter should be repaired or replaced if it is not functioning properly.

The procedure for completing a UV meter versus wet chemistry test comparison is as follows:

1. Arrange sample flow of the ozone generator product-gas to the UV meter and gas-washing bottles, as described below, so that truly comparative ozone concentration readings are obtained.
    - 1.1. Provide a sample tap to the gas-washing bottle from the same sample line that runs to the UV meter. If the UV meter reading *is not affected* when ozone is bubbled through the KI solution, simultaneously read the UV meter readings (several readings taken) while bubbling ozone. The UV meter reading *is not affected* when sufficient pressure exists to force gas flow to both the gas-washing bottles and the UV meter without affecting flow to the UV meter.
    - 1.2. If the UV meter reading *is affected* when ozone is bubbled through the KI solution, read the UV meter for a short period of time before and after bubbling ozone. It is important to confirm that the ozone generator production rate and associated ozone concentration do not change when switching from one test method to the other.
2. Confirm that the UV meter is displaying an ozone concentration that properly takes into account the sample cell temperature, pressure, and feed-gas composition (GMW). If the UV meter reading is not automatically adjusted for sample cell temperature and pressure, make calibration adjustments, as necessary.
3. Independently perform the wet chemistry test. Because the UV meter reading could change while ozone is being bubbled into the gas-washing bottle, collect several UV meter readings and average the results.

4. Determine percent difference between the UV meter ozone concentration value (average of several UV meter readings, if applicable) and wet chemistry ozone concentration value using Eq. 6-9. Be sure the ozone concentrations are properly determined, as discussed below.

$$\%\ \text{Difference} = \left\{\frac{\text{UV Concentration}}{\text{Wet Chemistry Concentration}} - 1\right\} \times 100 \qquad \text{(Eq. 6-9)}$$

4.1. If the UV meter reading is displayed in milligrams per liter, ensure that its reference temperature and pressure are the same as those used for determining the wet chemistry ozone concentration (e.g., mg/L_{STP}).

4.2. If the UV meter reading is displayed in weight-percent, use Eq. 6-10 to convert the wet chemistry reading from milligrams per liter to weight-percent. The weight-percent calculation must include the determination of ozone generator product-gas density in its denominator. In Eq. 6-10, the term ($0.5\ Y_1\ V_m/48$) effectively accounts for the fact that three oxygen molecules form two ozone molecules within the ozone generator, thus slightly increasing the product-gas density.

$$Y_1' = \frac{100\ Y_1}{W_{fg}\left(1{,}000 + \frac{0.5\ Y_1 V_m}{48}\right)} \qquad \text{(Eq. 6-10)}$$

Where:

Y_1' = ozone concentration, percent by weight
Y_1 = ozone concentration, mg/L_{NTP0C}
100 = conversion of mass ratio to percent expression
V_m = molar volume (22.411 L_{NTP0C}/mol)
48 = gram molecular weight of ozone, g/mol
W_{fg} = density of feed gas, g/L_{NTP}, as shown in Eq. 6-11

$$W_{fg} = \frac{(V_{O_2} \times GMW_{O_2}) + (V_{N_2} \times GMW_{N_2}) + (V_{AR} \times GMW_{AR})}{V_m} \qquad \text{(Eq. 6-11)}$$

V_{O_2} = oxygen concentration in feed-gas (~20.94% vol for air)
V_{N_2} = nitrogen concentration in feed-gas (~78.12% vol for air)
V_{AR} = argon concentration in feed-gas (~0.94% vol for air)
GMW_{O_2} = gram molecular weight of oxygen, at 32.00 g/mol
GMW_{N_2} = gram molecular weight of nitrogen, at 28.01 g/mol
GMW_{AR} = gram molecular weight of argon, at 39.95 g/mol

NOTE: Other gases present in air or in the feed-gas may be included if desired, but these gases typically would result in, at most, a minor adjustment.

Ozone Production Calculation Considerations

Ozone concentration is multiplied by gas flow rate to obtain ozone production rate. It is very important to use the correct gas flow rate with the ozone concentration reading of record, otherwise an incorrect ozone production rate will be obtained. Two approaches can be used, and these are described in the following paragraphs.

One approach involves recording/reporting ozone concentration on a volumetric basis as grams per cubic meter or milligrams per liter. In this approach, the volumetric flow rate of the ozone generator product-gas must be used as the gas flow rate reading of record (e.g., liters per minute or cubic meters per hour). The ozone generator feed-gas flow rate *cannot* be used; if it is, an incorrect ozone production rate will result. This approach to calculating ozone production is complicated, because the composition and density of the ozone generator product-gas are changed every time the ozone concentration value changes.

There is an easier method for accurately determining ozone production. This approach involves recording/reporting ozone concentration value in weight-percent. The conversion from milligrams per liter to weight-percent can be performed using Eq. 6-10, if necessary. In this approach the feed-gas mass flow rate is the reading of record, and ozone production is calculated as feed-gas mass flow rate (i.e., kilograms per hour or pounds per day) multiplied by the ozone concentration value in weight-percent. The second approach provides correct results, because the mass flow rate of the ozone generator feed-gas is equal to the mass flow rate of the ozone generator product-gas (i.e., mass flow is unchanged). The advantage of this latter approach is that the composition of the feed-gas is generally unchanged. Refer to appendix A for more information on calculating ozone production.

Example Wet Chemistry Validation

Examples of wet chemistry test results versus UV meter readings are shown in Table 6-2. During this test the ozone generator product-gas concentration was about 8 %wt. The average of the UV meter readings during the time ozone was bubbling through the KI solution was 7.994 %wt. The UV meter automatically corrected for sample cell temperature and pressure and displayed its readings in weight-percent. Oxygen was the feed-gas and the meter set point GMW was 32. The feed-gas was vaporized liquid oxygen with supplemental nitrogen addition at about 2 %vol. The meter span setting was adjusted to 1.0, which is the normal position for no additional correction to the displayed ozone concentration reading.

Table 6-2 Example Wet Chemistry Versus UV Meter Validation Test

Wet Chemistry Calculations and UV Meter Comparison				
Test Number	1		Input	
Meter	AIT-981-4		Input	
Date	03/22/2002		Input	
Time	13:43		Input	
Readings From UV Meter	8.01	%wt	Input	
	7.99	%wt	Input	
Take readings while ozone is bubbling into the KI solution.	7.99	%wt	Input	
	7.98	%wt	Input	
	8.00	%wt	Input	
	8.00	%wt	Input	
	7.99	%wt	Input	
Average UV Meter Reading	7.994	%wt		
Meter Span, Pressure and Temp.	1	Usually 1	Input	
Barometric Pressure	758.7	mm Hg	Input	
Wet Test Temperature	25°C		Input	
Wet Test Manometer	0	in water	Input	
Vapor Pressure at WT Temp	23.76	mm Hg		From Lookup Table
Total Pressure	734.94	mm Hg		
End Meter Reading	1.500	L	Input	
Start Meter Reading	0.000	L	Input	
Uncorrected WT Meter Volume	1.500	L		
Corrected Volume of Gas	1.329	L	At 0°C and 760 mmHg STP	
Volume of Titrant Used	32.1	mL	Input	
Normality of Titrant	0.201	mg/me	Input	
Mass of Ozone =	154.8504	mg		
Ozone Concentration =	116.5	mg/L_{pg}	At 0°C and 760 mmHg STP	
W_{fg} Density of Feed-gas	1.42433	g/L_{stp}	1424.3	mg/L_{stp}
Ozone Conc %wt = Y' =	7.964	%wt		
Comparison of Wet Test Meter to UV Meter				
Wet Test	116.524	mg/L		
Wet Test	7.964	%wt		
UV Meter	7.994	%wt, with adjustment		
Variation	0.38%	UV meter reads higher		
Spreadsheet Variables				
Feed-Gas Oxygen Concentration	98	%vol	Input	
Feed-Gas Nitrogen Concentration	2	%vol	Input	
Feed-Gas Argon Concentration	0	%vol	Input	
Total	100			
Feed-Gas GMW	31.919	g/mole		
Standard Temperature	0°C		Input	
Standard Volume	22.41	L		

NOTE: The UV meter span setting must be set to its normal position when validating the accuracy of an installed UV meter.

Table 6-2 indicates which entries are input and which are calculated. Correct gas volume is determined using Eq. 6-6.

$$V_{NTP} = V_a \times \frac{(P_a - P_v + P_m)}{P_s} \times \frac{T_s}{T_a}$$

$$1.329 = 1.5 \times \frac{(758.7 - 23.76 + 0)}{760} \times \frac{(273.15 + 0)}{(273.15 + 25)}$$

Where:

V_{NTP} = gas volume, $L_{NTP\ 0C}$, referenced to normal temperature and pressure conditions

V_a = uncorrected gas volume (1.5 L) measured by wet-test meter

P_s = normal, reference standard pressure (1 atm, which is 760 mm Hg)

T_s = normal, reference standard temperature (273.15 Kelvin)

P_a = uncorrected barometric pressure, at 758.7 mm Hg

P_v = vapor pressure at 23.76 mm Hg, based on wet-test meter temperature of 25°C (see Table 6-1)

P_m = wet test meter manometer pressure, at 0 mm Hg

T_a = wet test meter temperature (25°C), Kelvin (i.e., 273.15 + 25°C)

The mass of ozone trapped in the KI solution is calculated using Eq. 6-7.

$$O_{3Mass} = 24 \times V_t \times N_t$$

$$154.85 = 24 \times 32.1 \times 0.201$$

Where:

O_{3Mass} = mass of ozone trapped in KI solution, mg

24 = conversion factor = 24,000 meq/L per 1,000 mL/L

V_t = volume of sodium thiosulfate titrate used, at 32.1 mL

N_t = normality of sodium thiosulfate, at 0.201 mg/meq

The wet chemistry–based ozone concentration is determined using Eq. 6-8.

$$Y_1 = \frac{\text{Mass from Equation (6-7)}}{V_{STP} \text{ from Equation (6-6)}}$$

$$116.5 \text{ mg/L} = \frac{154.85 \text{ mg}}{1.329 \text{ L}}$$

The concentration in mass per volume must be converted into weight-percent using Eq. 6-10 and Eq. 6-11.

$$Y_1' = \frac{100\ Y_1}{W_{fg}\left(1{,}000 + \frac{0.5\ Y_1 V_m}{48}\right)}$$

$$7.965 = \frac{100 \times 116.5}{1.424 \times \left(1{,}000 + \frac{0.5 \times 116.5 \times 22.412}{48}\right)}$$

Where:

Y_1' = ozone concentration, percent by weight

Y_1 = ozone concentration, mg/L_{NTP0C}

100 = conversion of mass ratio to percent expression

V_m = molar volume (22.412 L_{NTP0C}/mol)

(NOTE: Molar volume must be adjusted if an STP is used that is different than NTP. For example, the molar volume is 24.05 L_{STP}/mol if the standard temperature is 20°C.)

48 = gram molecular weight of ozone, g/mol

$$W_{fg} = \frac{(V_{O_2} \times GMW_{O_2}) + (V_{N_2} \times GMW_{N_2}) + (V_{AR} \times GMW_{AR})}{V_m}$$

V_{O_2} = oxygen concentration in feed-gas (98 %vol)

V_{N_2} = nitrogen concentration in feed-gas (2 %vol)

V_{AR} = argon concentration in feed-gas (0 %vol)

GMW_{O_2} = gram molecular weight of oxygen, at 32.00 g/mol

GMW_{N_2} = gram molecular weight of nitrogen, at 28.01 g/mol

GMW_{AR} = gram molecular weight of argon, at 39.95 g/mol

W_{fg} = density of feed gas from Eq. 6-11 and V_m, g/L_{NTP}

$$1.424 = \frac{(0.98 \times 32) + (2 \times 28.01) + (0 \times 39.95)}{22.412}$$

Equation 6-9 determines percent difference between the wet chemistry concentration and the UV meter displayed reading.

$$\%\ \text{Difference} = \left(\frac{\text{UV Concentration}}{\text{Wet Chemistry Concentration}} - 1\right) \times 100$$

Table 6-3 Summary of Wet-Test Results for Generator 1

Date m/dd/yyyy	Test Number	Meter Number	UV %wt	WT %wt	Vary %
3/19/2001	1	AIT-981-1	7.460	7.361	1.34
3/19/2001	2	AIT-981-1	7.551	7.469	1.10
3/20/2001	3	AIT-981-1	7.596	7.635	–0.51
3/20/2001	4	AIT-981-1	7.483	7.319	2.25
3/20/2001	5	AIT-981-1	7.474	7.351	1.67
Multiplier	1.000	Average	7.513	7.427	1.16

Table 6-4 Summary of Wet-Test Results for Generator 4

Date m/dd/yyyy	Test Number	Meter Number	UV %wt	WT %wt	Vary %
3/19/2001	1	AIT-981-4	9.079	8.894	2.08
3/19/2001	2	AIT-981-4	9.114	8.695	4.82
3/20/2001	3	AIT-981-4	9.117	8.933	2.05
3/20/2001	4	AIT-981-4	8.469	8.087	4.73
3/20/2001	5	AIT-981-4	8.008	7.636	4.87
3/20/2001	6	AIT-981-4	7.994	7.648	4.53
Multiplier	0.964	Average	8.630	8.315	3.85

$$0.37\% = \left(\frac{7.994}{7.965} - 1\right) \times 100$$

Several (minimum of five) wet chemistry test comparisons are made to fully validate the UV meter reading, as shown in Tables 6-3 and 6-4. Figures 6-7 and 6-8 display individual and average percent-difference results for tests that were conducted. The average percent difference for UV meter AIT-981-1 is 1.16% in Table 6-3 and Figure 6-7, which is within +2%. In this case the multiplier or span setting on the UV meter would stay at 1.0. The average percent difference for UV meter AIT-981-4 is 3.85% in Table 6-4 and Figure 6-8, which is beyond +2%. In this case the test procedure was re-assessed to determine if the problem was with the meter or with the wet chemistry test. Because the same wet chemistry setup was used and the persons who conducted the test for meter 1 were the same, it was judged that the difference was due to the UV meter. In this case the multiplier or span setting of the meter was adjusted down from 1.0 to 0.96, which would decrease the normal displayed reading by a factor of 0.96.

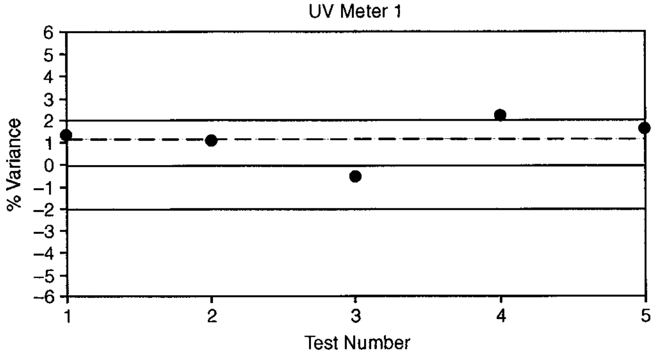

Figure 6-7 Example comparative results of the UV meter for generator 1 showing that average percent difference is within ±2%

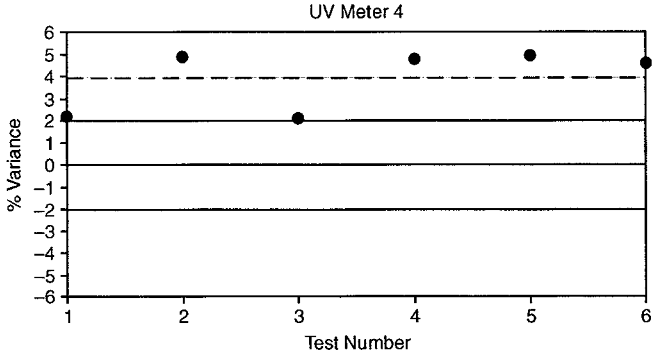

Figure 6-8 Example comparative results of the UV meter for generator 4 showing that average percent difference is beyond ±2%

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7

Ozone Residual-in-Water Measurement

Accurate measurements of ozone residual are required to properly determine disinfection credit for viruses, *Giardia*, and *Cryptosporidium*. Residual measurements can be obtained periodically by taking grab samples or by continuously sampling with on-line instruments. Accurate and reliable on-line ozone residual measurements are possible when sample piping is designed properly and instruments are installed correctly and calibrated accurately (Rakness and Hunter, 2000).

SAMPLING SYSTEM CONSIDERATIONS

The accuracy of the ozone residual measurement is affected by the sampling system layout for both grab sample tests and continuous readings from on-line meters. Successful ozone residual measurement is enhanced by sampling systems that:

1. Minimize detention time in the sample line;
2. Allow for easy collection of grab samples that can be taken without affecting the on-line instrument measurement;
3. Are properly configured such that consistent and sufficient flow is available to an on-line instrument; and
4. Provide flexibility for measuring ozone residual at a variety of sampling locations within the ozone contactor.

Sampling System Design

Sampling systems can be categorized as gravity-feed (Figure 7-1) or pumped-flow arrangements (Figure 7-2). Sample water in a gravity-feed system is drained away via a drain pipe, *not* an open channel. The gravity-flow sample is directed to a

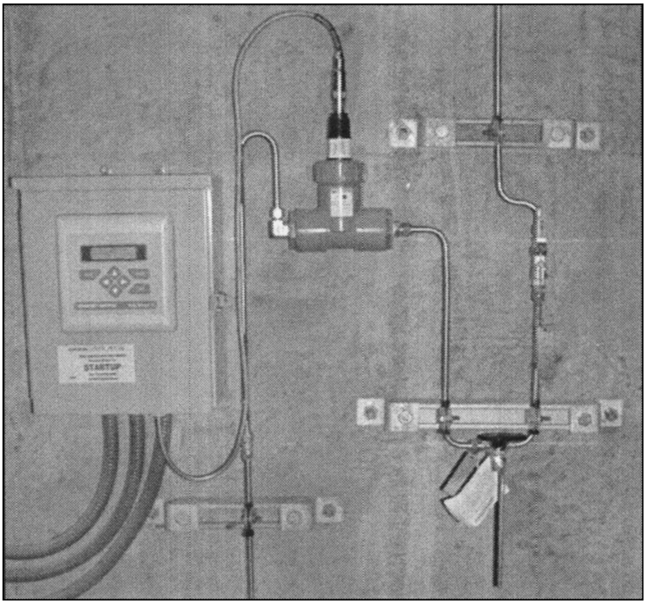


Figure 7-1 Gravity feed ozone residual sample station adjacent to ozone contactor

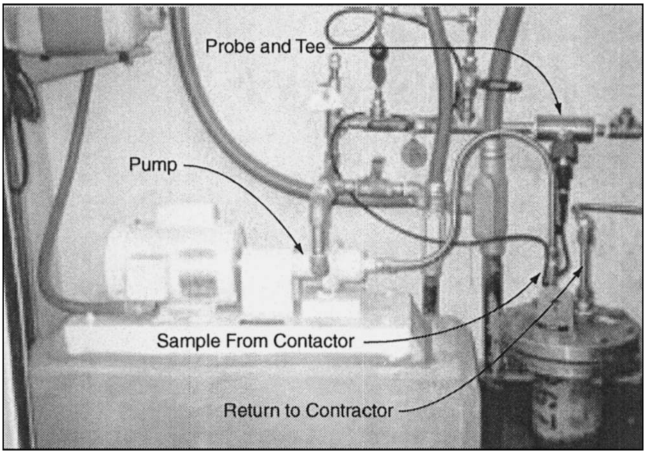


Figure 7-2 Ozone residual sample pumped through top of contactor

sump and pumped back to the front of the ozone contactor or to the front of the treatment plant. Open channel flow has the potential to develop ozone-in-air safety problems, which are caused by ozone off-gassing. Samples in a direct pump-flow arrangement (Figure 7-2) are discharged back into the contactor.

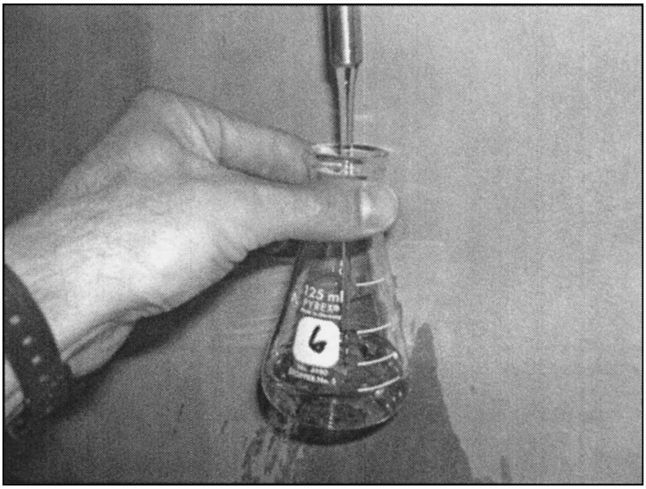
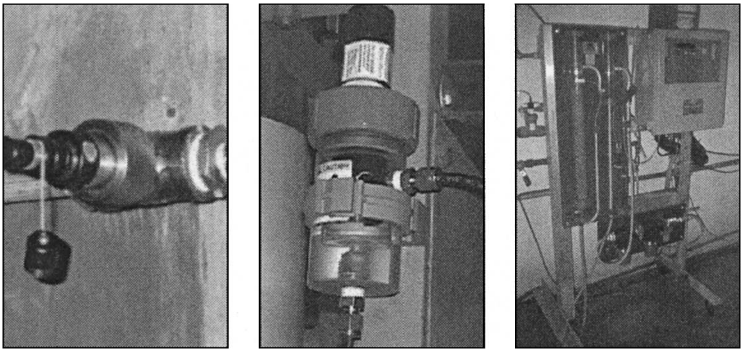


Figure 7-3 Preferred arrangement of a grab sample tap

Sample lines with ½-in. inside diameter or ¾-in. outside diameter are used successfully in both gravity- and pumped-flow sampling systems. The piping for the grab sample itself should be a small-diameter sample tube (about ⅛-in. inside diameter), as illustrated in Figure 7-3. A larger-diameter sample tube (½-in. or ¾-in.) is difficult to use because the sample flow rate is too high when the sample valve is completely or almost completely open. In addition, the sample flow is difficult to control when the sample valve is partially closed (i.e., tends to spray and lose ozone residual via off-gassing). The grab-sample tap should be located downstream of the analyzer probe location but not too far away (e.g., within 3 ft).

Types of Residual Meters

Several suppliers provide membrane probe-type residual instruments. Figure 7-4 shows a typical installation with a T-shaped probe holder located in line with the sample piping (Figure 7-4a). This setup has two important features: it minimizes sample detention time and reduces the potential for plugging of the sample line (i.e., maintains consistent sample flow past the probe). Another important consideration is to maintain sufficient (and consistent) velocity past the membrane. Velocity that is too slow will result in an inaccurate, low ozone residual value. This slow velocity has occurred at some plants because large-diameter probe holders were installed. Ozone residual was successfully measured at these plants when the large-diameter probe holders were replaced with smaller-diameter probe holders (Hunter and Rakness, 2002). Higher-than-recommended velocity past the probes will not be a problem, as long as the flow is consistent (Rakness and Hunter, 2000).



a. T-Shaped Probe b. Probe Holder c. Stripping Column

Figure 7-4 Example ozone residual on-line instruments

Suppliers of membrane probes provide specially designed probe holders that operate successfully with lower sample flow rates (Figure 7-4b). Low sample flow rate is desirable in pilot-plant applications where water flow rates are small. In the pilot plant, the grab sample must be collected so that the flow rate through the sample cell is unchanged. If flow is disrupted, the measured value from the instrument is likely to be incorrect. Probe-holder arrangements for low flows have limitations in full-scale applications for one or more of the following reasons:

1. The setup is susceptible to plugging by debris that becomes lodged inside the small-diameter pipe.
2. The sample-line detention time is increased significantly with a low sample flow rate, unless the probe-holder sample piping is configured to receive a side-stream flow from the main sample line.
3. Gas accumulation and gas binding problems have been observed within the probe holder.

One supplier provides a stripping-column instrument that typically receives a side-stream sample from the main sample line (Figure 7-4c). The column performs best when the ozone decay rate is slow (i.e., when ozone half-life is long) and the sample is free of debris that might plug the small sample lines.

Meter Installation Considerations

Figure 7-5 illustrates components of a probe-type sample station that promote successful, continuous on-line ozone residual measurement. Each station contains a T-holder for the sampling probe that is in line with the sample flow, a small-diameter pipe for grab sampling, and valves for flow control. This setup allows sample flow to be checked manually on a periodic basis. Manual flow measurement is illustrated instead of a flowmeter, because flowmeters are

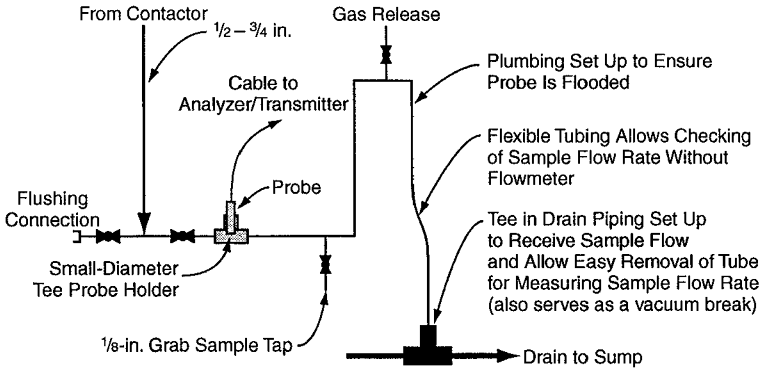


Figure 7-5 Gravity sample station for probe-type ozone residual analyzer

susceptible to plugging with debris that might exist in the sample. The setup also allows the sample flow to be discharged into a tee that is open to the atmosphere (i.e., sample piping is not hard-piped to the drain pipe). This open-air connection prevents fluctuations in sample flow that occur due to backpressure within the drain piping (i.e., backpressure due to fluctuation in the sump's water surface elevation). The water flow inside the drain piping creates a vacuum at the drain inlet that pulls in ambient air and, more important, prevents ozone off-gassing problems. Also shown in Figure 7-5 is a flushing connection that allows backflushing of the sample line with a strong chlorine solution in the event that the sample line becomes fouled (e.g., out of service for a period of time).

Disinfection treatment objectives, water quality conditions, and plant operating flow rate affect the ozone residual profile within a contactor. At certain times during the year, the residual profile might extend to the end of the contactor and at other times the residual might extend only halfway through the contactor. Flexibility should be provided for sampling ozone residual over a wide variety of operating conditions. Figures 7-6 and 7-7 illustrate the importance of flexibility by indicating that the ozone sample can be collected at any one of 10 independent sampling stations that are dedicated to the outlet of each chamber. This independent arrangement minimizes detention time in the sample piping (i.e., shortest possible distance from the sample inlet to the probe) and provides flexibility in selecting the measurement location. Measurement location can be changed if sufficient probe cable length is provided. This allows one instrument-transmitter location to service several sampling stations—instead of moving the sample to the probe location, the probe can be moved to the sample. Note that the instrument-transmitter unit is mounted at a fixed location and the cable is brought from the probe to the instrument-transmitter.

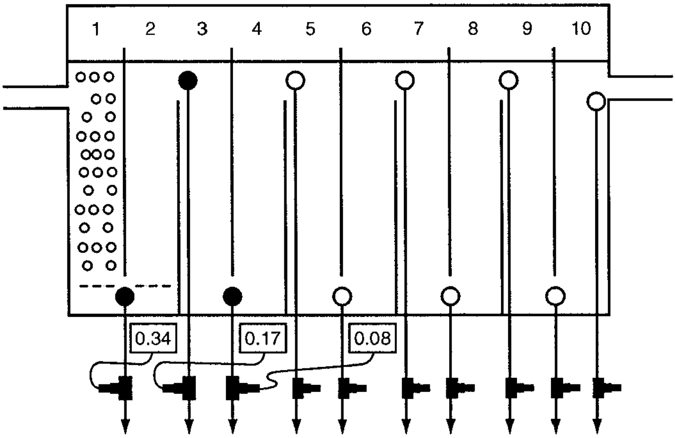


Figure 7-6 Residual sampling location selection for virus or *Giardia* disinfection

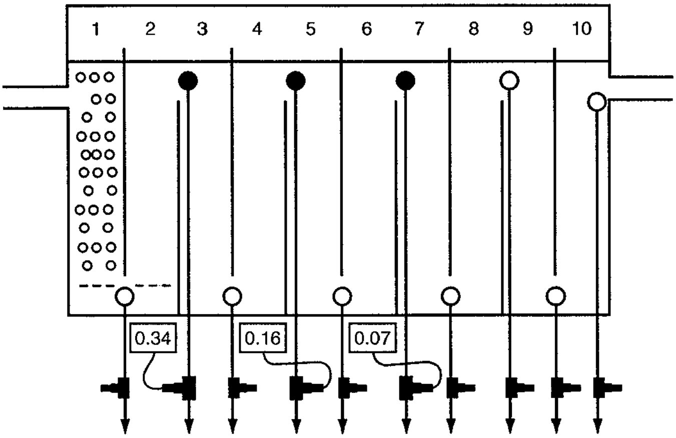


Figure 7-7 Residual sampling location selection for *Cryptosporidium* disinfection

Figure 7-6 displays results from the instruments that measure ozone residual at the outlets of chambers 1, 2, and 3, which is typical for disinfection during warm water conditions (i.e., rapid ozone decay rate). The probes can be moved to a new location to activate another sampling arrangement. For example, Figure 7-7 displays results from the instruments that measure ozone residual at the outlets of chambers 2, 4, and 6, which is typical of cold water conditions (i.e., slow ozone decay rate). The shortest possible sample-line detention time is achieved by moving the probe to the sample station. Unwanted, longer detention time occurs when the sample is piped to a fixed probe location.

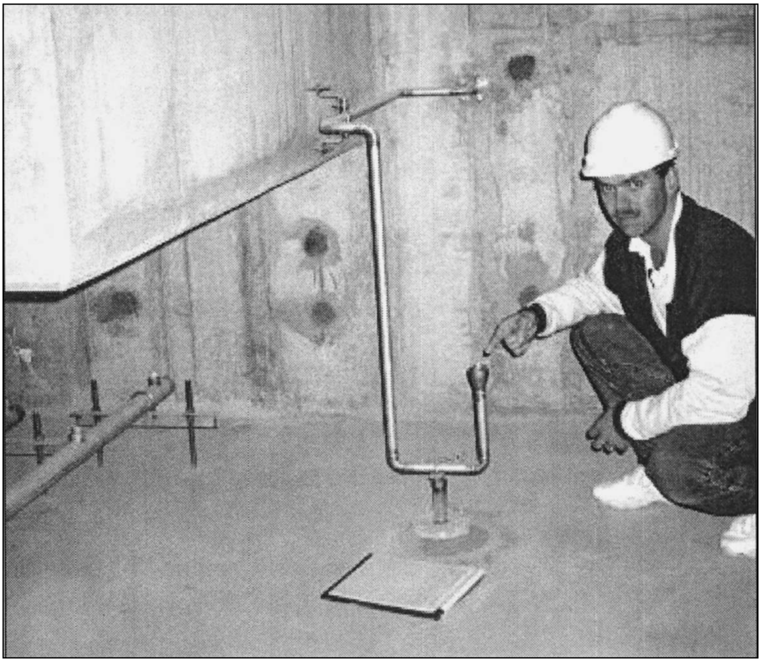


Figure 7-8 Flared sample inlet in the water flow stream at outlet of diffusion chamber

Inside the contactor, the inlet to the sample pipe should be strategically located in the main flow stream. This is shown in Figure 7-8 for the chamber outlet of an over–under baffled bubble-diffuser contactor (i.e., the sample inlet should be located away from the wall and into the flow stream). To obtain a representative sample, the inlet should extend into the contactor (about ¼ to ½ of the contactor width). A sample inlet that is turned up and flared helps reduce the entrance of gas bubbles that would negatively affect instrument and grab sample results.

Minimum sample-line detention time is achieved through proper design of sample-line length and diameter and provision of sufficient sample flow rate. A short detention time is critical when ozone decay is very rapid (i.e., ozone half-life is short). Sample detention time is considered adequate if total ozone decay within the sample line is <10% for the worst-case condition, which is the most rapid ozone decay rate (Rakness and Hunter, 2000). Figure 7-9 shows the relationship between sample-line detention time and ozone residual loss within the sample line at selected ozone decay rates (expressed as ozone half-life). The residual at the sampling station is 90% of the residual inside the contactor when the sample-line detention time is 10 sec and the ozone half-life is 1 min. The measured residual is

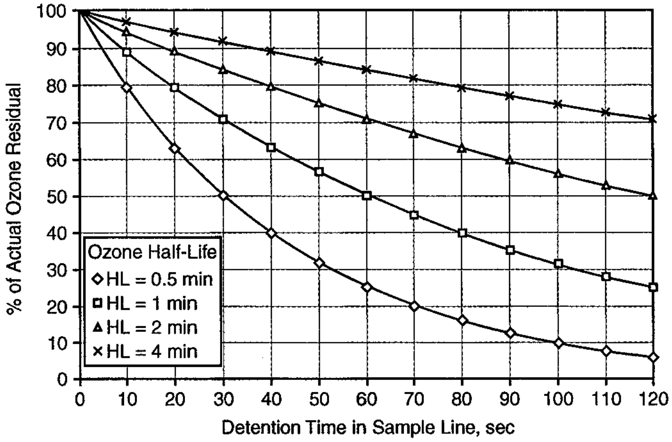


Figure 7-9 Ozone residual loss in sample line due to decay

one half of the residual inside the contactor when the sample-line detention time is 60 sec and the ozone half-life is 1 min. Sample-line detention time is a very important design consideration.

When possible, on-line ozone residual sampling systems should be installed in access corridors that are adjacent to the contactor. Figure 7-1 displays an individual-chamber sample station within an access corridor. Replicate stations exist for the other chambers along the contactor. When side access is impossible, the chamber's sample station can be located on top of the contactor in a protective housing, where the sample flow is pumped to the instrument (see Figure 7-2).

An inadequately designed sampling system that was ultimately abandoned is shown in Figure 7-10. The system, which received sample flow that was piped a long distance from the contactor to dedicated instruments for each sampling point, was abandoned due to excessive ozone decay that occurred inside the long lines of sample pipe.

The sampling system shown in Figure 7-11 includes one analyzer probe that receives flow from several sampling locations. Solenoid valves were designed to change sample points automatically. The setup was intended to use one instrument per contactor, yet obtain ozone residual measurements from multiple locations. However, the arrangement could not be operated as intended, because the valves would frequently stick open or remain closed. In addition, debris in the sample would become wedged within the valve housing, thus allowing off-line sample flow to blend with on-line sample flow. This sampling system could be used to monitor residual from one location at a time, but operators had to manually control the sample location. Solenoid valves on sample lines have generally been unsuccessful.

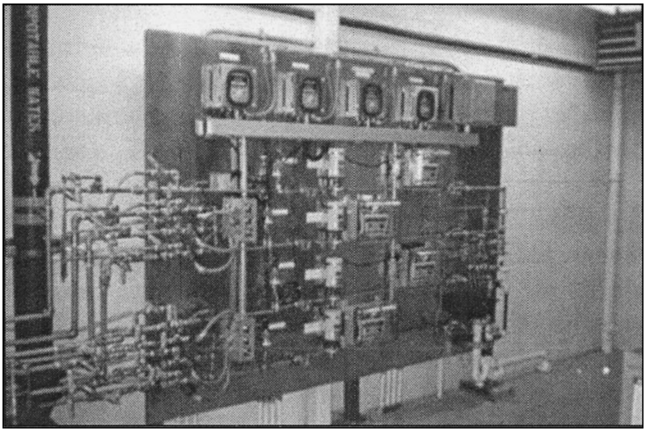


Figure 7-10 Ozone residual sample station for all contactor sampling points

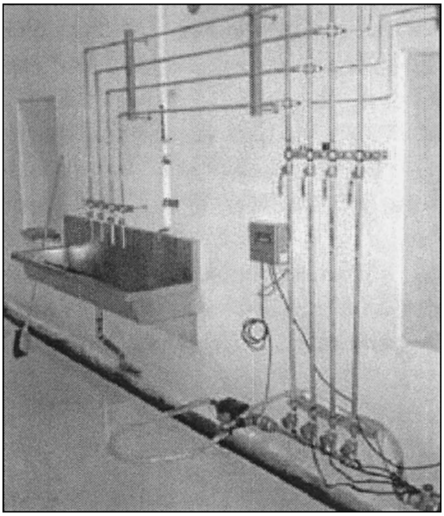


Figure 7-11 Sample station with solenoid valve on multiple sample lines

The grab sample setup in Figure 7-11 was problematic in at least two ways. First, the grab sample was subjected to a longer detention time because the sample was piped to the sink. This could be a major issue at plants where the ozone decay rate is quite fast (i.e., short ozone half-life). Second, grab sample flow decreased sample flow past the residual probe, which affected the analyzer's residual measurements. A better arrangement is to place the grab sample flow so that it does not impact the residual analyzer measurement.

Next Page

INDIGO TRISULFONATE COLORIMETRIC OZONE RESIDUAL MEASUREMENT

On-line residual analyzers are typically calibrated (or standardized) by taking several grab sample measurements. Grab sample testing is conducted based on the instructions provided in *Standard Methods* (1998) for determining ozone residual (see part 4500–Ozone). The calibration protocol is discussed in the following section.

The indigo trisulfonate colorimetric technique is the accepted method for determining ozone residual by grab sampling (*Standard Methods*, 1998). The method is easy to use and accurate when implemented correctly. The indigo method presumes use of high-quality indigo trisulfonate that has a proportionality constant of $f = 0.42\ \text{L mg}^{-1}\text{cm}^{-1}$. The f-value is based on an indigo molar absorbance value, ε, of ~20,000 $M^{-1}\text{cm}^{-1}$. Impure indigo product and outdated indigo reduce the reported ozone residual by as much as 25% or more (Gordon et al., 2000a, 2000b; Rakness et al., 2001; Gordon and Bubnis, 2002; Rakness et al., 2002). Methods to identify impure and outdated indigo are part of the residual measurement procedure.

The indigo colorimetric method is based on the delta absorbance (600 nm wavelength) between a nonreacted blank solution and an ozone-reacted sample solution. The f-value in Eq. 7-1 of 0.42 L mg^{-1} cm^{-1} was determined from ozone residual calibration curves that used high-purity indigo product with ε ~20,000 M^{-1} cm^{-1} (Gordon et al., 2000b). The source or basis ozone residual values were obtained from ultraviolet light (UV) absorbance measurements ($\varepsilon_{260\text{nm}}$ ~3,000 $M^{-1}\text{cm}^{-1}$) at 260-nm wavelength for distilled and buffered laboratory test water. Unfortunately, direct UV absorbance at 260-nm wavelength is impractical in natural waters because of measurement interference from dissolved organic molecules. Interference is much less with the indigo-trisulfonate test.

$$\text{mg/L} = \frac{100 \times \Delta\text{Abs}}{f \times SV \times b} \qquad \text{(Eq. 7-1)}$$

Where:

ΔAbs = delta absorbance between sample and blank of equal volume
b = path length of chamber, cm
SV = volume of sample, mL (normally 90 mL)
f = sensitivity coefficient of 0.42 L mg^{-1} cm^{-1}, also called proportionality constant

Equation 7-2 indicates that the necessary absorbance measurement is 0.25 cm^{-1} for a procedurally made indigo solution that has a molar concentration of 1.248×10^{-5} M and ε = 20,000 M^{-1} cm^{-1}. Figure 7-12 shows the relationship between molar absorbance and the deviation in ozone residual when using impure indigo trisulfonate reagent. The reported residual is about 10% to 25% lower when the 100-mL blank absorbance value ranges between 0.20 cm^{-1} and

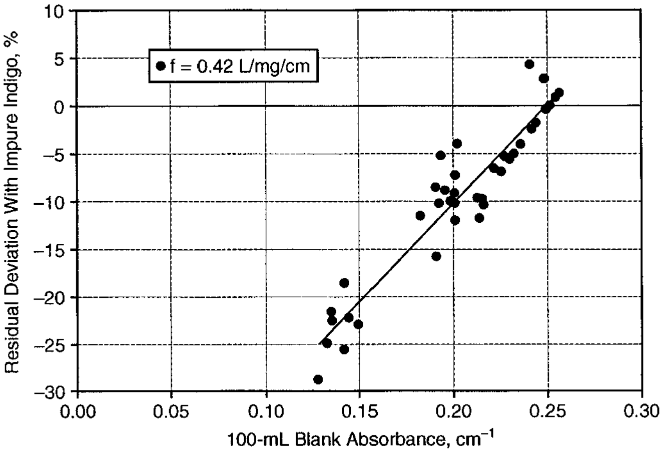


Figure 7-12 Ozone residual percent deviation with impure or outdated indigo (Rakness et al., 2001)

0.13 cm^{-1}, respectively. Less than 5% error occurs when the absorbance is 0.225 cm^{-1}. Stock solution shelf life is about 3 to 4 weeks (Rakness et al., 2002). Reagent II solution shelf life is about 1 week.

$$\text{Absorbance} = \varepsilon \times M \qquad \text{(Eq. 7-2)}$$

Where:

Absorbance = measured absorbance per 1-cm path length, cm^{-1}
ε = molar absorbance, M^{-1} cm^{-1}
M = molar concentration, M

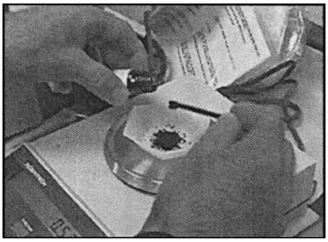
Gravimetric Standard Method Procedure

The gravimetric procedure (i.e., determining volume based on weight) for measuring ozone residual is easy to implement in the field and is highly accurate when properly performed (Yates and Stenstrom, 2000). Table 7-1 lists detailed steps for this method. Table 7-2 displays data and calculation results for an example residual test.

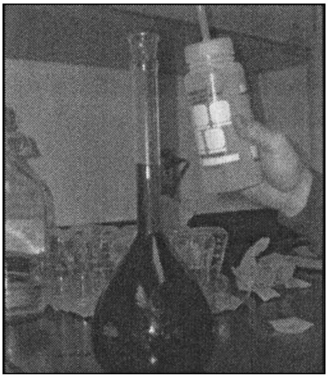
In Table 7-2, a tare weight of 83.62 g is indicated for flask 10, which is used to determine the absorbance of the blank solution. The blank solution flask's final weight, including 10.0 mL reagent II aliquot plus added distilled water, was 179.77 g. The blank solution's absorbance measurement was 0.234 cm^{-1} at wavelength = 600 nm. The total volume of the 10.0-mL reagent II aliquot, plus added distilled water, was determined by subtracting the tare weight of flask 10 from its total weight, assuming that 1 mL of liquid weighs 1 g (i.e., 96.15 mL = [179.77 g – 83.62 g] × 1 mL/1 g). Notice that the total volume of the blank

Table 7-1 Gravimetric Ozone Residual Indigo Trisulfonate Procedure

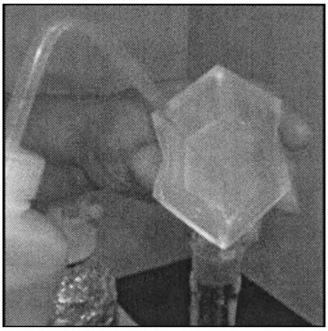
1. Prepare indigo stock solution (see also step 3).
   a. Weigh out 770 mg of potassium indigo trisulfonate ($C_{16}H_7N_2O_{11}S_3K_3$; molecular weight = 616.74 g/mol).
   b. Add about 500 mL distilled water and 1 mL concentrated phosphoric acid to a 1-L volumetric flask.
   c. Add 770 mg potassium indigo trisulfonate and mix well.
   d. Fill to 1-L mark with distilled water and mix well.
   e. The stock solution should be stored in the dark and should be good for 4 to 5 weeks.



2. Prepare indigo reagent II solution.
   a. To a 1-L volumetric flask, add 100 mL indigo stock solution.
   b. Add 10 g sodium dihydrogen phosphate (NaH_2PO_4).
   c. Add 7 mL concentrated phosphoric acid and mix well.
   d. Dilute with distilled water to 1-L mark and mix well.
   e. Store reagent II solution in the dark so it will retain adequate strength for 1 to 7 days.



3. Direct reagent II solution preparation alternative.
   a. Add ~500 mL distilled water to 1-L volumetric flask.
   b. Add 7 mL concentrated phosphoric acid.
   c. Add 10.0 g sodium dihydrogen phosphate, rinse well, and mix well.
   d. Carefully weigh out 0.077 grams potassium indigo trisulfonate, rinse all powder into the solution, mix well, fill to 1-L mark with distilled water, and mix well again.



4. Prepare flasks for sampling.
   a. Clean, dry, and label several 125-mL Erlenmeyer flasks (enough for each sample plus one blank).
   b. Obtain the tare weight of each flask.

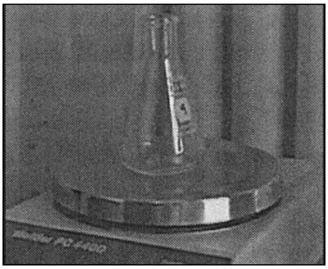


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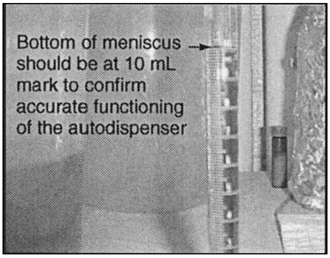
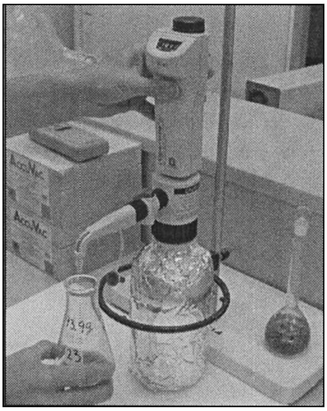
Table 7-1 Gravimetric Ozone Residual Indigo Trisulfonate Procedure (continued)

5. Verify accuracy of 10-mL automatic dispensing pipette (see step 6).

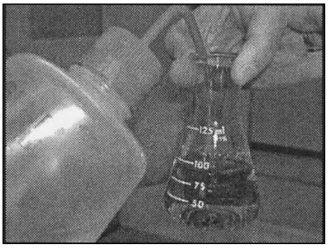


Bottom of meniscus should be at 10 mL mark to confirm accurate functioning of the autodispenser

6. Add 10 mL of reagent II solution to every flask.



7. Add approximately 90 mL distilled water to one flask and use this flask as the blank.



8. Collect ozone sample.
   a. Do not run sample down the side of the flask because this might cause ozone off-gassing.
   b. Fill until a light blue color remains.
      Do not completely bleach indigo or residual will be incorrect.

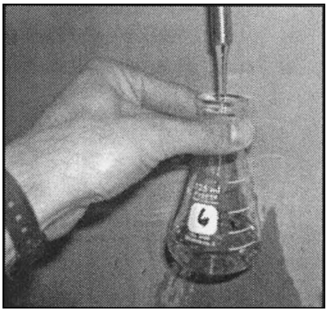


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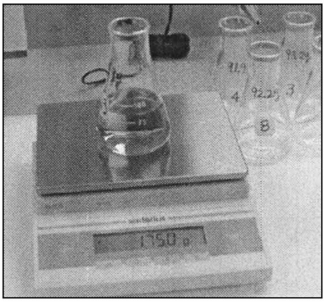
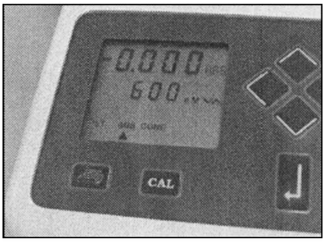
Table 7-1 Gravimetric Ozone Residual Indigo Trisulfonate Procedure (continued)

9. Dry outside of sample and blank flasks.

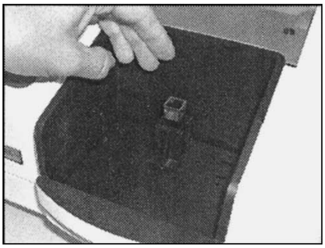
10. Weigh sample and blank flasks.
    a. Total weight for sample is tare weight of flask, plus 10 mL indigo, plus added sample.
    b. Total weight for blank is tare weight of flask, plus 10 mL indigo, plus added distilled water.



11. Prepare the spectrophotometer for measuring absorbance.
    a. Identify the chamber path length (e.g., 1 cm, 5 cm).
    b. Set the wavelength to 600 nm.



12. Measure absorbance.
    a. Follow instructions for spectrophotometer concerning zeroing the instrument.
    b. Record absorbance of each sample.
    c. Record absorbance of the blank.



13. Complete calculations.

Table 7-2 Summary of Data Required and Results for Example Ozone Residual Test

Date	*2/16/2004*	
Probe #	*2*	
Test #	*1*	
Chamber #	*5*	(1–12)
Time	*1255*	24-hr

Determination of Absorbance of Blank and Molar Absorbance of the Indigo

Flask #	Final wt. g	Absorbance/ cm	Tare Weight g	Total Volume mL	ABS @ 100mL /cm
10	*179.77*	*0.234*	83.62	96.15	0.225

Determination of Ozone Residual—Gravimetric Indigo Method

Reading #	Monitor Reading mg/L	Flask #	Final wt. g	Absorbance/ cm	Tare Weight g	Total Volume mL	Sample Volume mL	Ozone Residual mg/L
1	*0.42*	*1*	*167.39*	*0.159*	94.10	73.29	63.29	0.41
2								
3				(space for additional standardization tests)				
4								
5								
Average	0.42			f = 0.420				0.41

solution was 96.15 mL and the measured absorbance was 0.234 cm^{-1}. By proportion calculation, the absorbance is 0.225 cm^{-1} if the blank solution volume was 100 mL.

$$\text{by proportion: } \frac{0.234\ \text{cm}^{-1}}{100\ \text{mL}} \times 96.15\ \text{mL} = 0.225\ \text{cm}^{-1}$$

The 100-mL value for blank solution absorbance is determined because it is used as a quality control check. If the 100-mL blank absorbance value is too low, new stock solution, new reagent II solution, or new indigo product should be obtained. The lower limit is set by the utility and might be 0.225 cm^{-1} or 0.200 cm^{-1}. The reported ozone residual value is reduced by 5% or 10%, respectively, of the true ozone residual (Figure 7-12). When establishing the lower limit value, the following items should be considered:

1. A low blank absorbance value yields a lower value for reported ozone residual. This means that disinfection action is underreported (i.e., more conservative) due to lower reported CT value.

2. The blank absorbance value should be as high as possible in order to more accurately report disinfection action.
3. It is sometimes difficult to maintain a high absorbance value because:
   a. Aging of the indigo solution results in frequent preparation of reagent I and reagent II solutions. Given this situation, utilities make up reagent II solution directly (see step 3 in Table 7-1) to reduce loss of indigo product.
   b. Indigo product received from the chemical supplier might be impure (i.e., freshly prepared reagent II solution does not reach desired absorbance value). If this occurs, the utility should send back the product and search for a supplier that delivers high-quality indigo.

In Table 7-2, a tare weight of 94.10 g is indicated for flask 1, which was used for one of the grab samples. A 10.0-mL aliquot of reagent II was added to flask 1 and sample water was directed into the solution until a light blue color remained. Flask 1's total weight was 167.39 g, including 10.0 mL reagent II aliquot plus added sample. The reacted-sample solution's absorbance was 0.159 cm^{-1} at wavelength = 600 nm. The total volume of the 10.0-mL reagent II aliquot and reacted sample was 73.29 mL (73.29 mL = [167.39 g – 94.10 g] × 1 mL/1 g). The reacted-sample volume was 63.29 mL, which is 10.0 mL less due to the volume of reagent II that was first added to the flask.

Equation 7-3, which is a modification of Eq. 7-1, is used to calculate the ozone residual of the reacted sample. The numerator in Eq. 7-3 properly accounts for the absorbance strength of the reagent II solution that is added to both the blank and sample flasks. Ten milliliters of reagent II solution is added to the sample flask for most tests. However, reagent II volume might be increased to assess elevated ozone residual value or decreased to minimize reagent II and reacted sample volume (e.g., bench-scale ozone stock solution residual test and reacted-sample residual test, as discussed in chapter 3). In all cases, 10 mL of reagent II is used in the blank. The calculated value for ozone residual in the example is 0.41 mg/L.

$$\text{mg/L} = \frac{\left[(\text{ABS}_{\text{blank}} \times \text{TV}_{\text{blank}}) - \left(\frac{\text{IV}_{\text{sample}}}{10}\right)\right] - (\text{ABS}_{\text{sample}} \times \text{TV}_{\text{sample}})}{\text{f} \times \text{SV} \times \text{b}} \qquad \text{(Eq. 7-3)}$$

$$\text{solution} = \frac{\left[(0.234 \times 96.15) \times \left(\frac{10}{10}\right)\right] - (0.159 \times 73.29)}{0.42 \times 63.29 \times 1} = 0.41 \text{ mg/L}$$

Where:

$\text{ABS}_{\text{blank}}$ = measured absorbance of the blank, at 0.234 cm^{-1}

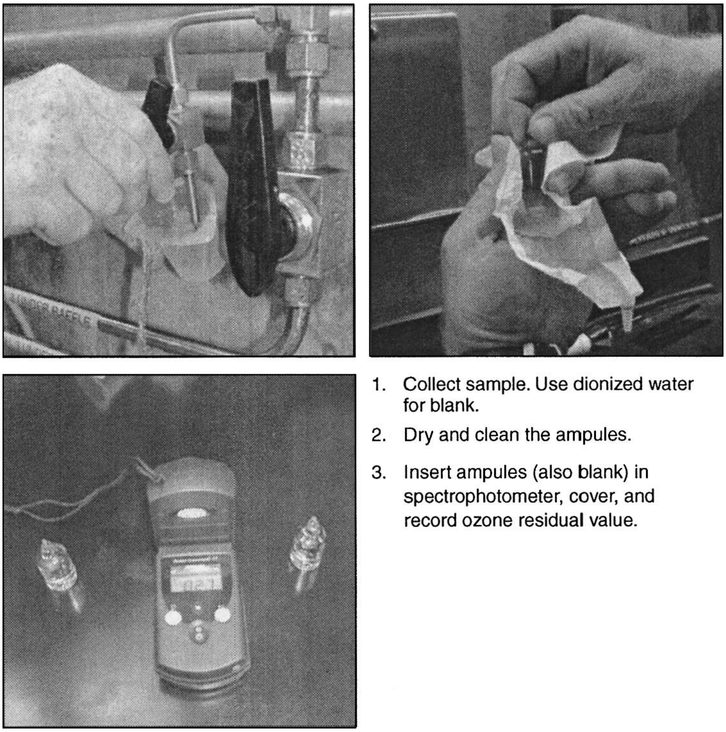
TV_{blank} = total volume of blank solution, at 96.15 mL

IV_{sample} = volume of reagent II solution that is added (Indigo Volume) to *sample* flask, mL. Normally, 10 mL of reagent II solution is added to the sample.
NOTE: Always add 10.0 mL of reagent II solution to the blank flask.
ABS_{sample} = measured absorbance of the reacted sample, at 0.159 cm^{-1}
TV_{sample} = total volume of reacted sample, at 73.29 mL
f = sensitivity coefficient of 0.42 L mg^{-1} cm^{-1}, also called proportionality constant
SV = volume of reacted sample, at 63.29 mL
b = path length of spectrophotometer's chamber, at 1 cm

Hach Ampule Procedure

A commercially available modification of the indigo colorimetric method is available (Hach Chemical Company, Loveland, Colorado) (Hunter and Rakness, 2002). Powdered indigo reagent is enclosed in a small glass ampule under vacuum. When the tip of the ampule is broken under the water surface, a specific volume of the sample water is drawn into the ampule and mixed with a specific amount of indigo powder (i.e., low-, medium-, and high-range measurement). Low-range ampules are used when the ozone residual is less than 0.25 mg/L. Medium-range ampules are used to measure ozone residual between zero and 0.75 mg/L, and high-range ampules are used to measure ozone residual between zero and 1.50 mg/L.

When using this method, a small beaker is held under the sample flow and allowed to overflow continuously (Figure 7-13). The sample flow and beaker size should be selected to minimize detention time in the beaker, thus minimizing ozone decay during sample collection. The ampule is submerged in the beaker and the tip of the ampule is broken against the side of the beaker close to the point where the sample enters the beaker (see Figure 7-13). The ampule is then held in the overflowing beaker until it is completely full. If there are too many bubbles in the sample flow, the ampule may not fill with water completely. In some instances, the vacuum is insufficient or the ampule is only partially full. In these cases, the ampule should be discarded. The sample flow and beaker position should be adjusted to minimize bubbles formed by turbulence. Once the ampule is full, it is removed from the beaker and inverted several times to mix the sample completely. Colder water requires several inversions for complete mixing. The exterior of the ampule should be wiped dry and clean before it is inserted into the spectrophotometer (see Figure 7-13). The spectrophotometers measure absorbance and display the ozone residual value. Several types of spectrophotometers are available from the supplier for use with the ampules, including a dedicated ozone instrument like the one shown in Figure 7-13. The portable ozone-specific spectrophotometer shown in Figure 7-13 is simple to use because the blank does



1. Collect sample. Use dionized water for blank.
2. Dry and clean the ampules.
3. Insert ampules (also blank) in spectrophotometer, cover, and record ozone residual value.

Figure 7-13 Summary of ampule procedure (Hach, Loveland, Colorado)

not need to be re-inserted for every sample measurement. Ampule results can be verified prior to use with the procedure discussed earlier in this chapter (*Standard Methods* [1998; see part 4500–Ozone]).

CALIBRATING ON-LINE OZONE RESIDUAL INSTRUMENTS

Because natural variability of ozone residual has been observed in the contactor (Figure 7-14), several ozone residual grab samples are needed to properly verify the accuracy of on-line ozone residual instruments. Variability is greatest at the outlet of bubble-diffuser ozone dissolution chambers. Figure 7-14 shows grab and on-line residual data collected during manual operation when ozone gas flow, ozone generator power, and contactor inlet water flow all were constant.

Three to five simultaneous grab sample and instrument measurements should be collected during each calibration check. Fewer grab samples are appropriate at downstream sample locations where residual has stabilized. Figure 7-15 outlines a calibration protocol that is used by several water utilities. The protocol involves determining if the average value for the on-line analyzer measurements is within

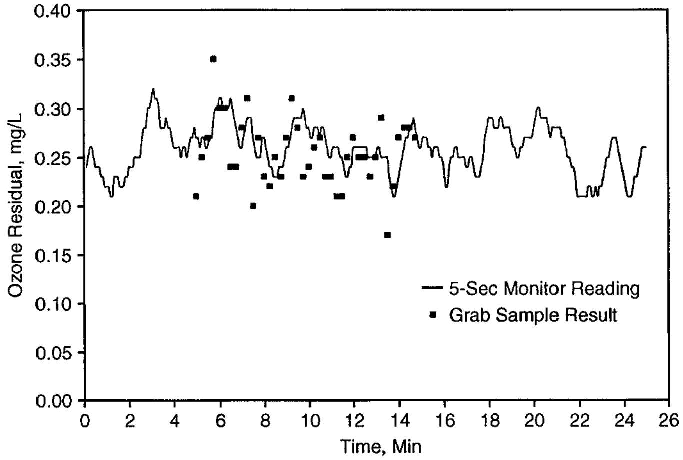


Figure 7-14 Ozone residual variability at outlet of diffusion chamber

1. Collect at least three to five ozone residual grab samples using the modified gravimetric indigo method, as outlined in Table 7-1. (Alternatively, use Hach ampule readings instead of the *Standard Methods* gravimetric tests.)
2. Record analyzer reading *at the same time* each grab sample is collected. Wait about 15 to 30 sec between each grab sample/analyzer reading.
3. Calculate the grab sample ozone residual value.
4. Calculate the average grab sample and average analyzer residual values.
5. Select the target range for the analyzer. The high end of the range is the grab sample average plus the selected deviation value of the grab samples (e.g., 10%). The low end of the range is the grab sample average minus the deviation value of the grab samples (e.g., 10%).
6. Determine if the average analyzer reading is within the target range.
7. The analyzer is considered calibrated if the average reading is within the target range.
8. Repeat the test if the average analyzer value is outside the target range.
9. A calibration adjustment to the analyzer reading is unnecessary if the average reading is within the target range for the second test.
10. A calibration adjustment to the analyzer reading is recommended if the average reading is outside the target range for both the first and second tests.
11. The suggested calibration adjustment is one half of the difference between the analyzer average and the grab sample average. Adjust the current reading on the analyzer at the time of the adjustment.

Figure 7-15 Ozone residual analyzer calibration-check protocol

Table 7-3 Summary Table for On-Line Analyzer Calibration Results

Date	2/5/2004	ID	Contactor	Cell
Probe #	1	127	1	1
Test #	1			
Time	1230			

Blank Absorbance Information	Flask #	Final wt. g	Absorbance	Abs @ 100 mL	Tare, g	T vol, mL	Path Length	
	10	188.10	0.248	0.240	91.50	96.60	1	cm

	Meter	Gravimetric Indigo			Grab	Tare	Total	Sample	Ozone
Test #	Rdg. mg/L	Flask #	Final wt.	Absorbance	Residual mg/L	Weight g	Volume mL	Volume mL	Residual mg/L
1	0.40	1	167.39	0.128	0.51	90.91	76.48	66.48	0.51
2	0.41	2	165.16	0.150	0.50	92.83	72.33	62.33	0.50
3	0.38	3	170.57	0.130	0.49	93.46	77.11	67.11	0.49
4	0.39	4	168.23	0.148	0.46	92.12	76.11	66.11	0.46
5	0.37	5	174.34	0.136	0.42	92.11	82.23	72.23	0.42
Average	0.39				0.48				0.48

The suggested adjustment amount is 0.04 mg/L

Grab Average	0.48	mg/L		
Avg+Deviation	0.53	mg/L		
Meter Average	0.39	is outside the allowable range	Acceptable Range is	10%
Avg–Deviation	0.43	mg/L		

an allowable deviation range. The deviation range is a percentage of the grab sample average value. A value of 10% was used in Table 7-3.

The example calibration check in Table 7-3 indicates that the average of five grab samples was 0.48 mg/L, which is a 10% deviation range of 0.43 to 0.53 mg/L. The analyzer reading average was 0.39 mg/L, which was outside the deviation range. The suggested adjustment to the analyzer measurement is 0.04 mg/L, which is 50% of the difference between the analyzer average and grab-sample average values (i.e., 0.50 × [0.48 mg/L – 0.39 mg/L]). This 50% adjustment approach helps to avoid overcorrecting of the analyzer.

The suggested percentage adjustment value of 10% is not meant to be a fixed number. Individual plant operating experience should be used to determine the best value. Also, minimum and maximum adjustments should be considered. For example, it might be impractical to make adjustments below 0.03 mg/L. At the same time, adjustments might always be implemented above 0.08 mg/L.

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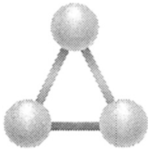

8

Measuring and Calculating Ozone System Gas Flow and Moisture Content

Two aspects of successful ozone system operation include accuracy of the gas flow measurement and understanding of the factors that affect moisture content of the feed-gas and moisture content inside the ozone generator, which is represented by dew point temperature. Gas flow measurement accuracy is important for process monitoring and control and for verifying performance capability of the installed ozone generator. Different types of gas flow meters are used in ozone systems. Methods to ensure accuracy of measurement in field installations are discussed in this chapter. Moisture content calculations are explained to indicate how small disruptions in system operation can have significant impact on generator performance and maintenance, particularly considering that the desired moisture content inside the generator is 1 ppm_{wt} and moisture content outside the generator (i.e., ambient air) might be 10,000 to 30,000 ppm_{wt}.

GAS FLOW MEASUREMENT—TYPE AND VERIFICATION

Accurate gas flow measurement is important in at least one or preferably two locations in an ozone system. First, the ozone product-gas flow rate to each ozone contactor is measured to control disinfection or other process performance. Second, the feed-gas flow rate into each ozone generator is measured to document the ozone production rate in each generator. Thermal mass flowmeters and orifice plates are commonly used in these locations.

Thermal mass flowmeters provide accurate readings even when gas flow is 10% of the maximum flow, i.e., a 10:1 turndown. However, flowmeters are factory calibrated and might become inaccurate during transport and installation. The accuracy of the thermal mass flowmeter should be field checked using an orifice

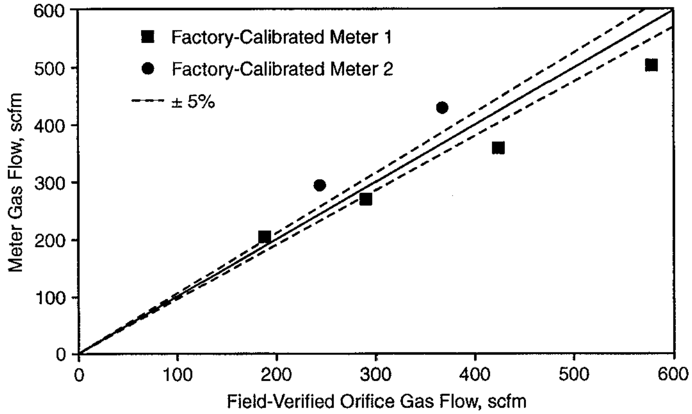

Figure 8-1 Inaccurate thermal mass flowmeter readings compared to field-verified orifice-plate gas flow rates

plate, which is also used to field-check the accuracy of other types of flowmeters (e.g., Coriolis). Orifice plate flow calculations are discussed in more detail later in this chapter. Orifice plates have a limited turndown capability of about 3:1, which limits their capability for controlling ozone (i.e., controlling gas flow to each ozone contactor) under low-flow operating conditions.

Inexpensive rotameters are often installed to measure the flow rate of ozone process gas in flow-splitting applications, such as to each bank of ozone diffusers. Also, some installations have variations of the above-described gas-flow metering approaches, e.g., use of a different flow measurement device (e.g., Coriolis meter, vortex meter, flow-tube, and venturi meter).

Importance of Field Verification

Utilities can have confidence in the accuracy of their gas flow measurements when the flow rate is field verified. Figure 8-1 shows comparative data for a field-verified orifice plate flow rate versus thermal mass flowmeter reading. The thermal mass flowmeters were installed in the field after being calibrated at the factory. As shown, both thermal mass meters at this ozone installation showed flow rates that were outside a desired comparative difference of ±5%. On the other hand, Figure 8-2 shows that three thermal mass flowmeters in another ozone installation were accurate to within ±5% of the field-verified orifice plate flow rate. Correctly installed, factory-calibrated meters can provide accurate flow readings. However, field verification for accuracy is highly desirable. Orifice plate meters located on the ozone generator inlet piping can be used to field verify thermal mass flowmeters located on the ozone piping to the contactors. If thermal mass flowmeters are used

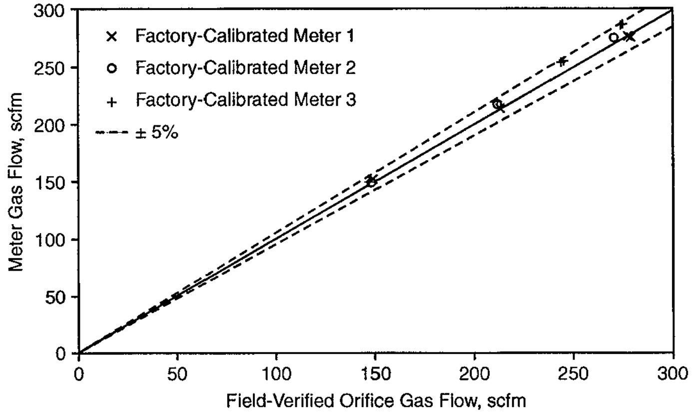

Figure 8-2 Accurate thermal mass flowmeter readings compared to field-verified orifice-plate gas flow rates

to measure gas flow rate to each ozone generator, an orifice plate flowmeter should be installed upstream so that it can be used to confirm field accuracy of the thermal mass flowmeter. *NOTE: The upstream orifice plate should be located downstream of the pressure-regulating valve to minimize operating pressure, which will improve accuracy of the orifice plate readings.*

Orifice Plate Gas Flow Calculations

An orifice plate is a flat stainless steel plate that has a bore of diameter smaller than the pipe into which it is installed (Figure 8-3). The gas flow calculation uses Bernoulli's principle concerning velocity increase and corresponding pressure differential as the gas squeezes through the bore. The orifice-plate mass flow rate equation, Eq. 8-1, can be solved using field measurements and orifice-plate specifications supplied by the orifice-plate supplier (Cusick, 1977; Rakness et al., 1998; Rakness and Hunter, 2000). Equation 8-1 yields mass flow in pounds per second or kilograms per second, depending on units of measurement. Mass flow is converted to standard volumetric flow, as discussed in appendix A.

$$W = K \times A_2 \times Y \times F_a \times \sqrt{2 \times g \times \rho_w \times h \times \rho_1} \qquad \text{(Eq. 8-1)}$$

Where:

W = mass flow, lb/sec or kg/sec

$K = \dfrac{C}{\sqrt{1-\beta^4}}$, with coefficient of discharge C specified by the orifice-plate supplier and β the ratio of orifice plate diameter divided by inside pipe diameter

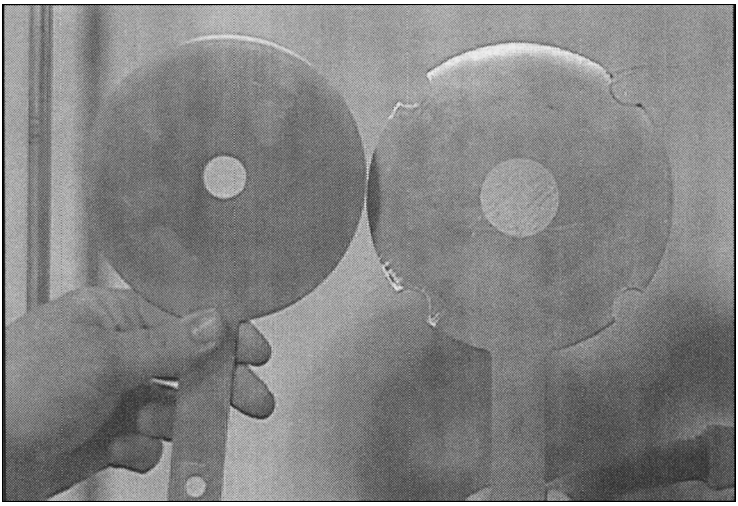

Figure 8-3 Orifice plates with different bore sizes for accurate measurement of lower (left) and higher (right) gas flow rates

Some orifice-plate suppliers provide a value for special orifice factor (S_o) instead of coefficient of discharge, C. Given S_o, C may be found using Eq. 8-2:

$$C = S_o \times \sqrt{\frac{1-\beta^4}{\beta^2}} \qquad \text{(Eq. 8-2)}$$

A_2 = area of meter's throat, ft^2 or m^2

Y = gas expansion factor supplied by the orifice-plate supplier or calculated using Eq. 8-3 (Cusick, 1977):

$$Y = 1 - \{[0.41 + (0.35 \times \beta^4)] \times x/k\} \qquad \text{(Eq. 8-3)}$$

where x = DP/P_1 and k = 1.4 (ratio specific heat)

F_a = orifice-area correction factor supplied by the orifice-plate supplier

g = gravitational constant, 32.174 ft/sec^2 or 9.807 m/sec^2

ρ_w = density of water, 62.4 lb/ft^3 or 1,000 kg/m^3

h or DP = differential pressure across orifice, ft or m of water

ρ_1 = density of the gas upstream of the orifice plate, lb/ft^3 or kg/m^3

$$\rho_1 = \frac{MW_a}{V_{NTP}} \times \frac{P_a}{P_{NTP}} \times \frac{T_{NTP}}{T_a} \qquad \text{(Eq. 8-4)}$$

Where:

MW_a = actual molecular weight of the flowing gas, g/mol

(*NOTE: The flowing gas molecular weight usually is a constant number for the ozone generator feed-gas because the gas flow is either air or high-purity oxygen.*)

P_a = actual pressure of the flowing gas upstream of the orifice plate, psia or m of water, also called P_1

(*NOTE: Measured gauge pressure is added to measured uncorrected barometric pressure, i.e., not corrected to sea level, to obtain actual, absolute pressure.*)

P_{NTP} = normal pressure, 14.696 psia or 10.34 m of water

T_{NTP} = normal temperature of 273.15 K

T_a = actual absolute temperature of the flowing gas, K

(*NOTE: Add measured temperature in °C to 273.15 K to obtain absolute temperature of the flowing gas.*)

V_{NTP} = 22.411 L/mol

Information needed to complete Eq. 8-1 is obtained from the orifice plate supplier, including bore diameter, upstream pipe diameter, coefficient of discharge, and orifice area correction factor. Other information is measured in the field, including differential pressure, upstream pressure, temperature, and, if needed, gas composition. An example calculation is shown here.

Flowmeter specification criteria for the example calculation is as follows:

C = coefficient of discharge—0.6042

D_1 = pipe diameter (inside)—52.5 mm (2.067 in)

D_2 = orifice throat diameter—23.5 mm (0.9254 in)

Y = gas expansion factor, 0.9783 from orifice plate supplier, or calculated value using Eq. 8-3 is:

$$0.9557 = 1 - \{0.41 + [0.35 \times 0.4477^4] \times [(8.33 \div 57.0) \div 1.4]\}$$

F_a = orifice area correction factor—0.9999

MW_a = molecular weight—29 g/mol (air)

P_a or P_1 = actual pressure—7.04 m (23.1 ft) of water gauge pressure or 17.38 m (57.0 ft) of water absolute pressure (10 psig or 24.7 psia, assuming location is at sea level and barometric pressure is 14.7 psi)

T_a = specified reference temperature for the flowing gas—26.7°C or 299.85 K (80°F or 539.67 R) h or DP = specified maximum differential pressure—2.54 m of water (100 in. of water or 8.33 ft of water)

Calculation steps are as follows:

1. Find beta ratio (D_2/D_1)—0.4477 dimensionless.
2. Find meter factor, K—0.6167,

$$\text{dimensionless } K = \frac{0.6042}{\sqrt{1 - 0.4477^4}} = 0.6167$$

3. Find throat area of the orifice, A_2—0.0004337 m^2 (0.004671 ft^2).
4. Find density of the flowing gas using Eq. 8-4, ρ_1.

$$\rho_1 = \frac{29}{22.411} \times \frac{24.7}{14.7} \times \frac{491.67}{539.67} \times \frac{1 \text{ lb}}{453.6 \text{ g}} \times \frac{28.32 \text{ L}}{\text{ft}^3} = 0.1236 \text{ lb/ft}^3$$

or,

$$\rho_1 = \frac{29}{22.411} \times \frac{17.38}{10.34} \times \frac{273.15}{299.85} = 1.981 \text{ g/L or kg/m}^3$$

5. Calculate differential pressure ($h \times \rho_w$) in the required units of kg/m^2 (lb/ft^2). The density of water is 1 kg/L (62.43/lb/ft^3).

$$8.33 \text{ ft} \times 62.43 \text{ lb/ft}^3 = 520.2 \text{ lb/ft}^2$$

or,

$$2.54 \text{ m} \times 1 \text{ kg/L} \times 1{,}000 \text{ L/m}^3 = 2{,}540 \text{ kg/m}^2$$

6. Solve for mass flow using Eq. 8-1.
   English units:

$$W = 0.6167 \times 0.004671 \times 0.9783 \times 0.9999 \times \sqrt{2 \times 32.174 \times 0.1236 \times 520.2}$$

$$W = 0.1812 \text{ lb/sec}$$

Metric units:

$$W = 0.6167 \times 0.0004337 \times 0.9783 \times 0.9999 \times \sqrt{2 \times 9.807 \times 1.981 \times 2540}$$

$$W = 0.08219 \text{ kg/sec}$$

The orifice plate is designed for a maximum gas flow rate that meets process needs, such as feed-gas flow rate to the ozone generator. Design criteria provided to the orifice plate supplier (also called reference conditions) include type and size of pipe; maximum flow rate (lb/day or $scfm_{stp}$); flowing-gas temperature (°C or °F); flowing-gas pressure (kPa_{gauge} or psig); and either molecular weight of the gas, type of gas (air or oxygen), or gas concentration (e.g., oxygen at 98 %vol and nitrogen at 2 %vol). Design criteria also include maximum differential pressure, such as 25-in. water column. The orifice plate supplier will provide an orifice plate with a bore size that meets these criteria.

The differential pressure transmitter is installed such that the 20-mA (i.e., maximum) signal from the transmitter displays the maximum flow rate for the design differential pressure. The transmitted flow signal will be correct, provided flowing-gas temperature and pressure meet design conditions. However, flowing-gas temperature and pressure are likely to be variable. Also, gas molecular weight might be different. Equation 8-5 is used to correct for nonreference conditions. This equation can be programmed into the plant supervisory control and data acquisition (SCADA) computer so that the corrected gas-flow rate is displayed. Notice that signals are also required from flowing-gas temperature and pressure transmitters.

$$CF = \sqrt{\frac{T_{ref}}{T_a}} \times \sqrt{\frac{P_a}{P_{ref}}} \times \sqrt{\frac{MW_{ref}}{MW_a}} \qquad \text{(Eq. 8-5)}$$

Where:

CF = correction factor when actual gas composition, temperature, and pressure are different from reference conditions

T_{ref} = specified reference temperature for the flowing gas, K (R)

T_a = actual temperature of the flowing gas, K (R)

P_a = actual absolute pressure of the flowing gas upstream of the orifice plate, $kPa_{absolute}$ or psia (includes plant uncorrected barometric pressure, which is usually a fixed average value based on plant elevation)

P_{ref} = specified reference absolute pressure for the flowing gas, $kPa_{absolute}$ or psia

MW_{ref} = specified reference molecular weight for the flowing gas, g/mol

MW_a = actual molecular weight for the flowing gas, g/mol

NOTE: Molecular weight correction is implemented only when significant change is expected, such as operating with air or oxygen as the feed gas.

MOISTURE CONTENT CALCULATIONS

Ozone is generated using an electric discharge process that is subject to short-circuiting and inevitable failure unless the feed-gas is extremely clean and dry. Comprehensive air-drying and filtering systems are required when air is the feed-gas. With oxygen feed-gas systems, the oxygen that is generated on-site and the liquid oxygen (LOX) supply itself typically deliver dry gas to the ozone generator. However, oxygen-fed ozone systems include moisture dew point probes in case moisture enters the feed-gas pipeline from an unexpected source or from the nitrogen supply system (i.e., air supply) of a LOX-fed ozone system.

Moisture content in feed-gas is typically expressed as dew point temperature. The relationship between dew point temperature and moisture content is a function of operating pressure and relative humidity. A good understanding of moisture source and removal is helpful in both designing and troubleshooting ozone generation systems.

Moisture content in the product gas from the ozone generator is a function of the hydrocarbon concentration of the feed-gas and the moisture content of the generator inlet feed-gas. The rate of decrease of ozone generator energy efficiency and extent of maintenance problems caused by elevated concentration of hydrocarbon in the feed-gas is not well understood. However, it is generally felt that hydrocarbon concentration should be minimized; specifications for LOX supply contracts usually limit hydrocarbon concentration to 15 or 20 ppm_{vol}.

Moisture content and dew point temperature calculations are explained in the following paragraphs. Table 8-1 is the reference moisture content look-up table.

Moisture Content and Dew Point Temperature in Ambient Air

Moisture content in ambient air is a function of ambient-air temperature, relative humidity, and elevation (i.e., atmospheric pressure). Example calculations are given here for the following conditions:

Ambient temperature = 100°F
Relative humidity = 80%
Plant elevation = 1,200 ft mean sea level (MSL)

1. Through interpolation, find the moisture content for the listed temperature using Table 8-1. At 100°F, interpolated moisture content at standard pressure and 100% relative humidity is 43,608 ppm_{wt}.
2. Adjust moisture content for stated relative humidity of 80%. Moisture content at standard pressure and 80% relative humidity is 34,886 ppm_{wt} ($34{,}886\ \text{ppm}_{\text{wt}} = 43{,}608 \times 0.80$).
3. Adjust moisture content for stated elevation of 1,200 ft MSL in two substeps.
    a. Find the approximate barometric pressure using Eq. 8-6 (American Fisheries Society, 1984). The solution for 1,200 ft elevation is 728 mm Hg.
    b. Calculate moisture content in proportion to pressure values. The solution is 36,420 ppm_{wt} (i.e., $36{,}420\ \text{ppm}_{\text{wt}} = 34{,}886 \times 760/728$), where 760 mm Hg is the standard pressure value from Table A-3 in appendix A.

$$BP = 10^{\left(a - \frac{h}{b}\right)} \qquad \text{(Eq. 8-6)}$$

Where:

BP = barometric pressure, mm Hg

Table 8-1 Moisture Content of Air at Standard Pressure and 100% Relative Humidity

°C	°F	ppm by wt
–100	–148	0.00904
–95	–139	0.02400
–90	–130	0.06000
–85	–121	0.11120
–80	–112	0.31680
–75	–103	0.77130
–70	–94	1.64000
–65	–85	3.34200
–60	–76	6.74300
–55	–67	13.11000
–50	–58	24.64000
–45	–49	44.55000
–40	–40	79.25000
–35	–31	138.10000
–30	–22	234.40000
–25	–13	390.30000
–20	–4	673.10000
–15	5	1,020.00000
–10	14	1,606.00000
–5	23	2,485.00000
0	32	3,788.00000
5	41	5,421.00000
10	50	7,658.00000
15	59	10,690.00000
20	68	14,750.00000
25	77	20,160.00000
30	86	27,310.00000
35	95	36,730.00000
40	104	49,110.00000

Source: ASHRA reference

a = 2.880814
b = 64,790.7
h = plant elevation, ft MSL

Dew point temperature of ambient air at standard pressure (importance of pressure is discussed later) is obtained from Table 8-1 by knowing moisture content. Dew point temperature is the temperature when the gas is 100% saturated for the stated pressure condition. Through interpolation, if necessary, find the dew point temperature at standard pressure in Table 8-1 that is associated with moisture content of 34,886 ppm_{wt}. The dew point temperature is 94.7°F.

Moisture Content and Dew Point Temperature of the Feed-Gas

Moisture content of the ozone system feed-gas is a function of flowing-gas temperature, flowing-gas pressure, and barometric pressure. Example calculations are given for the following conditions:

Flowing-gas temperature = 89°F
Flowing-gas pressure = 19 psig
Barometric pressure = 728 mm Hg (determined previously for elevation 1,200 ft_{MSL}), or 14.08 psia
(14.08 psia = 728 mm_{Hg} ÷ 760 mm_{Hg} × 14.696 psia)

1. Through interpolation, find the moisture content at flowing-gas temperature listed in Table 8-1. At flowing-gas temperature of 89°F, the interpolated moisture content is 30,450 ppm_{wt} at standard pressure.
2. Adjust moisture content for operating pressure of 19 psig. First, determine absolute pressure of 33.08 psia for this example, which is gauge pressure of 19 psig plus barometric pressure of 14.08 psia. Moisture content at operating pressure is 13,528 ppm_{wt} (i.e., 13,528 ppm_{wt} = 30,450 ppm_{wt} × 14.696 psia ÷ 33.08 psia).

Dew point temperature of the feed-gas must be defined further as dew point temperature at operating pressure or dew point temperature at standard pressure. Differentiation is most important when interpreting dew point temperature values that are obtained from on-line instrumentation, especially the monitor that measures dew point temperature prior to the ozone generator. The operating-pressure dew point temperature is the same as the flowing-gas temperature when the gas is 100% saturated. A saturated condition typically exists in the discharge gas from a compressor after cooler or from a refrigerant dryer. Conversely, the dew point temperature at operating pressure is not the same as the flowing-gas temperature when the process gas is unsaturated, such as after the desiccant dryer of an air-fed system, which is before the ozone generator.

Dew point temperature at standard pressure is obtained from Table 8-1 for the indicated moisture content. For example, dew point temperature at standard pressure is 65.3°F at a moisture content of 13,528 ppm_{wt}.

Dew point temperature monitoring of the feed-gas to the ozone generator is required for ozone systems. Ozone systems are shut down at standard-pressure dew-point temperatures of –76°F or higher (–60°C or higher), which is a moisture content of 6.7 ppm_{wt} from Table 8-1. However, successful ozone installations generally operate at standard-pressure dew-point temperatures of –100°F or lower, which is moisture content of 1.1 ppm_{wt} from Table 8-1.

The dew point probe senses moisture content and digitally displays the dew point temperature value on the analyzer. Probe location (e.g., pressure condition) influences displayed dew point value, because moisture content is affected by pressure. Consider a probe that is operating at 16 psig pressure and barometric pressure is 14.08 psia (i.e., absolute pressure is 30.08 psia). Assume that the displayed dew point temperature reading is –100°F. This means that the pressure-condition (30.08 psia) moisture content is 1.1 ppm_{wt}. However, the standard-pressure moisture content is less, at 0.52 ppm_{wt} (i.e., 0.52 ppm_{wt} = 1.1 ppm_{wt} × 14.696 psia ÷ 30.08 psia). From Table 8-1, the standard pressure dew point temperature is –108°F when moisture content is 0.52 ppm_{wt}. From this example, it is important to note that the most conservative value for dew point temperature is displayed when the dew point probe is installed at operating pressure conditions.

Moisture Content and Dew Point Temperature of the Contactor Off Gas

Moisture content of the contactor off-gas is a function of flowing-gas temperature and barometric pressure. (NOTE: A slight vacuum of –4 in. water is ignored.) Example calculations are given below for the following conditions:

Flowing-gas temperature = 79°F

Barometric pressure = 728 mm Hg (determined previously for elevation 1,200 ft_{MSL}), or 14.08 psia (14.08 psia = 728 mm_{Hg} ÷ 760 mm_{Hg} × 14.696 psia)

1. Through interpolation, find the moisture content at flowing-gas temperature from Table 8-1. At flowing-gas temperature of 79°F, the interpolated moisture content is 21,749 ppm_{wt} at standard pressure.
2. Adjust moisture content for operating pressure of 14.08 psia. Moisture content at operating pressure is 22,700 ppm_{wt} (i.e., 22,700 ppm_{wt} = 21,749 ppm_{wt} × 14.696 psia ÷ 14.08 psia).

Off-gas that travels from the outlet of the contactor to the ozone destruct-unit is subjected to ambient temperature conditions, because off-gas piping is typically not insulated. Sometimes, the ambient temperature is colder than the water temperature (i.e., lower than off-gas temperature), especially during the fall or on cool summer nights. Under these conditions the off-gas temperature is reduced. The result is a lowering of the moisture content holding capacity of the off-gas, which will result in water condensation that could lead to potential damage to the ozone destruct heater and/or catalyst.

Moisture content capacity of the contactor off-gas at reduced temperature is a function of flowing-gas temperature and barometric pressure. (NOTE: Slight vacuum of –4 in. water is ignored.) Example calculations are given for the following case when the off-gas temperature decreases from 79°F to 60°F.

Flowing-gas temperature = 60°F
Barometric pressure = 728 mm Hg (determined previously for elevation 1,200 ft_{MSL}), or 14.08 psia
(14.08 psia = 728 $\text{mm}_{\text{Hg}} \div 760\ \text{mm}_{\text{Hg}} \times$ 14.696 psia)

1. Through interpolation, find the moisture content at flowing-gas temperature from Table 8-1. At flowing-gas temperature of 60°F, the interpolated moisture content is 11,141 ppm_{wt} at standard pressure.
2. Adjust moisture content for operating pressure of 14.08 psia. Moisture content at operating pressure is 11,629 ppm_{wt} (i.e., 11,629 ppm_{wt} = 11,141 $\text{ppm}_{\text{wt}} \times$ 14.696 psia ÷ 14.08 psia).

This example indicates significant reduction in moisture content capacity at 60°F (11,629 ppm_{wt}) versus 79°F (22,700 ppm_{wt}). Consequently, moisture drain lines must be provided on the off-gas piping or condensed water might damage the ozone destruct heater or catalyst (see Chapter 4).

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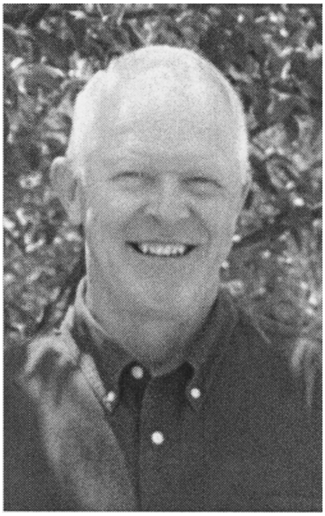
About the Author

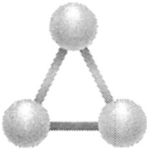


Kerwin Rakness has more than 28 years experience in ozone treatment of water and wastewater. He was the primary author for the ozone section of the *USEPA Disinfection Design Manual* for wastewater treatment and was contributing author of the AwwaRF book titled *Ozone in Water Treatment: Application and Engineering*. He was project manager for the Ozone Energy Optimization project that was co-sponsored by the Awwa Research Foundation and the Electric Power Research Institute Community Environmental Center.

Mr. Rakness is co-owner of Process Applications, Inc., a consulting firm that specializes in optimization assistance at water and wastewater treatment plants. He has provided start-up and optimization training at more than 50 ozone systems for drinking water treatment. He has presented and published many technical papers and was presented with the International Ozone Association's Best Paper Award for his paper on ozone transfer efficiency. He is a member of the *Ozone: Science and Engineering* editorial review board and IOA International Board and chair of Task Group 4300-Ozone, Standard Methods for the Examination of Water and Wastewater. He has bachelor of science and master of science degrees in civil and environmental engineering from South Dakota State University.

Figures

Tables



Appendix A

Ozone Calculations and Conversion Factors

A simplified schematic of an ozone system is shown in Figure A-1. Key locations for process measurement are gas flow (G), ozone concentration (Y), water flow (L), and generator power (P_W). These measurements are used for process monitoring and control calculations, excluding disinfection performance. Disinfection measurements and calculations are discussed in chapter 2.

Ozone process parameters that are used for design, monitoring, control, and optimization of ozone systems are listed in Table A-1 (page 284). Formulas for calculations are described in Table A-2 (page 285). The use and usefulness of each parameter are discussed briefly in the following paragraphs.

FEED-GAS FLOW AND DENSITY

Water treatment professionals use water conversion factors every day but typically have limited experience with gas conversion factors. Water is an incompressible fluid with a nearly constant density of 1 g/mL, or 8.344 lb/gal. Working with gas is more complicated because gas is a compressible fluid. Gas density changes occur due to variations in pressure, temperature, and composition (i.e., gas oxygen, nitrogen, argon, and ozone concentration).

Gas flow is sometimes reported as mass flow (kg/hr or lb/dy) but usually it is reported as volumetric flow (m^3/hr, ft^3/min [cfm]). Gas density usually is reported as g/L or lb/ft^3. Reported values for volumetric flow and gas density must be referenced to a pressure and temperature condition, which is usually standard temperature and pressure (STP) in English units and normal temperature and pressure (NTP) in metric units. The standard and normal pressure is 1 atm. Table A-3 (page 286) lists other units used to express standard and normal pressure, such as 14.696 psi and

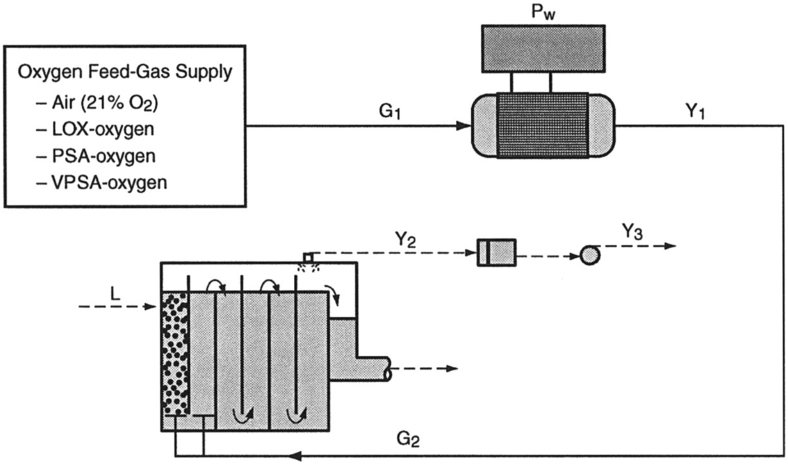


Figure A-1 Simplified schematic of an ozone system showing key process measurements

101.3 kPa. Normal temperature is usually 0°C. Standard temperature is not consistent and might be 60°F, 68°F, or 70°F. The term *NTP* is used almost exclusively outside of the United States; *STP* is a commonly used term in the United States. In all instances the standard temperature value should be stated to avoid confusion. Gas density, mass flow, and volumetric flow relationships should be well understood for proper design and operation of an ozone facility.

Gas composition and molecular weight are key parameters for determining density of the feed-gas to the ozone generator. Table A-4 (page 286) displays the molecular weight of individual gasses that make up different types of ozone generator feed-gas, as well as density information at NTP_{0C}. Table A-5 (page 287) displays similar information for STP_{68F}.

Equation A-1 calculates feed-gas density for a gas with a known gram molecular weight (GMW) at given molar volume. The term *GMW* is the weight, in grams, of one molar volume of the gas, which is the volume that is occupied by 6.023×10^{23} molecules of the gas (Avogadro's number). One molar volume (V_M) is 22.411 L at NTP_{0C}.

$$D = \frac{GMW}{V_M} \qquad \text{(Eq. A-1)}$$

Where:

D = density of the gas, g/L
GMW = gram molecular weight of the gas, g/mol
V_M = molar volume at selected standard temperature, L/mol

NTP_{0C} solution for air:

$$1.292\ \text{g/L} = \frac{28.96\ \text{g/mol}}{22.411\ \text{L/mol}}$$

or

$$0.0807\ \text{lb/ft}^3 = \frac{1.292\ \text{g}}{\text{L}} \times \frac{\text{lb}}{453.592\ \text{g}} \times \frac{28.317\ \text{L}}{\text{ft}^3}$$

Equation A-2 determines overall feed-gas GMW, by proportion, using the individual gases percent-by-volume concentration and GMW. Equations A-3 and A-4 determine molar volume at temperatures other than 32°F or 0°C, in °F or °C, respectively.

$$GMW_{\text{feed-gas}} = \frac{(\%vol_{O_2} \times GMW_{O_2}) + (\%vol_{N_2} \times GMW_{N_2}) + (\%vol_{Ar} \times GMW_{Ar})}{100} \qquad \text{(Eq. A-2)}$$

Where:

$GMW_{\text{feed-gas}}$ = gram molecular weight of feed-gas, g/mol
$\%vol_{O_2}$ = percent-by-volume concentration of oxygen in air, %vol
GMW_{O_2} = gram molecular weight of oxygen, g/mol
$\%vol_{N_2}$ = percent-by-volume concentration of nitrogen in air, %vol
GMW_{N_2} = gram molecular weight of nitrogen, g/mol
$\%vol_{Ar}$ = percent-by-volume concentration of argon in air, %vol
GMW_{Ar} = gram molecular weight of argon, g/mol
100 = converts the %vol (e.g., 20.941 %vol is 0.20941 vol/vol)

Air feed-gas solution:

$$28.96\ \text{g/mol} = \frac{(20.941 \times 31.9988) + (78.122 \times 28.0134) + (0.937 \times 39.948)}{100}$$

$$V_M = 22.411\ \text{L/Mol} \times \frac{(ST + 459.7\ R)}{(32 + 459.7\ R)} \qquad \text{(Eq. A-3)}$$

Where:

V_M = molar volume at selected standard temperature, L/mol
22.411 = molar volume at 32°F
ST = selected standard temperature, such as 68°F
32 = temperature corresponding to molar volume of 22.411 L/mol
459.7 = absolute temperature, Rankin

STP_{68F} solution:

$$24.052\ \text{L/Mol} = 22.411\ \text{L/Mol} \times \frac{(68 + 459.7\ R)}{(30 + 459.7\ R)}$$

$$V_M = 22.411 \text{ L/Mol} \times \frac{(\text{ST} + 273.15 \text{ K})}{(30 + 273.13 \text{ K})} \qquad \text{(Eq. A-4)}$$

Where:

V_M = molar volume at selected standard temperature, L/mol

22.411 = molar volume at 0°C

ST = selected standard temperature, such as 20°C

0 = temperature corresponding to molar volume of 22.411 L/mol

273.15 = absolute temperature, Kelvin

STP_{20C} solution:

$$24.052 \text{ L/Mol} = 22.411 \text{ L/Mol} \times \frac{(20 + 273.15 \text{ K})}{(30 + 273.15 \text{ K})}$$

OZONE CONCENTRATION IN GAS

The most common units for expressing ozone concentration are percent by weight (%wt), parts per million by volume (ppm_v), and milligrams per liter (mg/L, same as g/m^3). Other units used infrequently are percent by volume (%vol) and parts per million by weight (ppm_W). Ozone concentration is measured continuously in the field using the principle of ozone adsorption by ultraviolet (UV) light. Wet chemistry validation of UV meter accuracy is described in chapter 6.

Table A-6 (page 288) shows relationships among the ozone concentration parameters for both air and oxygen feed-gas ozone systems at NTP_{0C}. Table A-7 (page 289) shows relationships at STP_{68F}. Type of feed-gas (e.g., air or oxygen), operating ozone concentration, and selected standard (e.g., NTP or STP) are factors that affect the concentration relationship. For example, notice in Tables A-6 and A-7 that the mg/L-to-%wt conversion factor is different in every case.

Equation A-5 is used to convert from mg/L to %wt. The NTP_{0C} example calculation is for an air-fed ozone system operating at an ozone concentration of 6.47 mg/L.

$$Y_1' = \frac{100\, Y_1}{W_{fg}\left(1{,}000 + \dfrac{0.5\, Y_1 V_m}{GMW_{O_3}}\right)} \qquad \text{(Eq. A-5)}$$

Where:

Y_1' = ozone concentration, percent by weight (NOTE: 1 %wt means 1 lb ozone per 100 lb gas, or 0.01 lb/lb.)

Y_1 = ozone concentration, mg/L

100 = conversion of mass ratio to percent expression

V_m = molar volume (22.411 L/mol)

GMW_{O_3} = gram molecular weight of ozone, g/mol

W_{fg} = density of feed-gas, g/L_{NTP}

NTP_{0C} solution is 0.5 %wt assuming air is the feed-gas that has an ozone concentration of 6.47 mg/L.

$$0.5 = \frac{100 \times 6.47}{1.2922 \times \left(1{,}000 + \frac{0.5 \times 6.47 \times 22.411}{48}\right)}$$

Equation A-6 is used to convert from %wt to mg/L. The NTP_{0C} example calculation is for an air-fed ozone system operating at an ozone concentration of 1.0 %wt.

$$Y_1 = \frac{1{,}000\ W_{fg}Y_1'}{100 - \frac{0.5\ W_{fg}Y_1'V_m}{GMW_{O_3}}} \qquad \text{(Eq. A-6)}$$

NTP_{0C} solution assuming air is the feed-gas that has an ozone concentration of 1.0 %wt.

$$12.96 = \frac{1{,}000 \times 1.2922 \times 1.0}{100 - \frac{0.5 \times 1.2922 \times 1.0 \times 22.411}{48}}$$

Concentration units of ppm_V and ppm_W are obtained from the volumetric and weight concentrations, respectively. For example, 0.61 %vol is 6,100 ppm_V and 1 %wt is 10,000 ppm_W. Equation A-7 converts from mg/L to %vol. The maximum concentration, in mg/L, is determined assuming that the ozone concentration is 100 %vol.

$$Y_1'' = \frac{Y_1}{Y_{1-max}} \times 100 \qquad \text{(Eq. A-7)}$$

Where:

Y_1'' = ozone concentration, percent by volume (NOTE: 1 %vol means 1 ft^3 ozone per 100 ft^3 gas, or 0.01 ft^3/ft^3.)

Y_1 = ozone concentration, mg/L_{NTP} or mg/L_{STP}

$Y_{1\text{-}max}$ = maximum ozone concentration (density), mg/L, at 100 %vol ozone is 2,141.8 mg/L at NTP_{0C} and 1,995.7 at STP_{68F}

Table A-1 Summary of Important Measured Ozone Parameters

Parameter	Symbol	Units	Equation	Comment
Feed-gas flow	G_1	scfm (ft^3/min) or Nm^3/hr	Measured	Flow of feed-gas into the ozone generator. This measurement is used to calculate ozone production, parameters that are based on ozone production, and size of ozone destruct facilities.
Product-gas flow	G_2	scfm (ft^3/min) or Nm^3/hr	Measured	Flow of ozone product gas from the ozone generators. This measurement is used to monitor and control the gas flow rate to individual ozone contactors in order to obtain balanced disinfection performance from parallel contactor units.
Product-gas ozone concentration	Y_1	%wt or g/Nm^3	Measured	Ozone concentration in the product-gas from the ozone generator. This measurement is used to calculate ozone production, plus other parameters that are based on ozone production.
Off-gas ozone concentration	Y_2	%wt or g/Nm^3	Measured	Ozone concentration in the off-gas from the ozone contactor. This measurement is used to calculate ozone transfer efficiency, which is an assessment of the capability of the diffusion system (e.g., diffusers) to transfer ozone into the water.
Vent-gas ozone concentration	Y_3	ppm_v	Measured	Ozone concentration in the vent-gas from the ozone destruct unit. This measurement is used to monitor the discharge of ozone into the atmosphere, which might be a regulatory requirement. The reading is also used to assess the efficiency of the ozone destruction process.
Power demand	P_w	kW	Measured	Power demand of the ozone generator. This measurement is used to assess the efficiency of the ozone generator, which is measured as specific energy (kWh/lb or kWh/kg).
Water flow	L	mgd or ML/d	Measured	Water flow rate through the ozone contactor. This measurement is used to determine the applied ozone dosage and other parameters that are based on applied ozone dosage.

scfm = standard cubic feet per minute
Nm^3/hr = normal cubic meters per hour
%wt = percent ozone concentration by weight
g/Nm^3 = grams ozone per Normal cubic meter
ppm_v = part per million by volume
kW = kilowatt
mgd = million gallons per day
ML/d = million liters per day, or mega liters per day

Table A-2 Summary of Important Calculated Ozone Parameters

Parameter	Symbol	Units	Equation	Comment
Ozone production	P	lb/day or kg/day	a. $P = G_1 \times Y_1'$ b. $P = G_2 \times Y_1$	Ozone production is the mass flow of ozone from the generators. a. Gas flow, G_1, is converted to mass flow (lb/day or kg/day) and is multiplied by ozone concentration (%wt). b. Gas flow, G_2, is expressed as volumetric flow (Nm^3/hr) and is multiplied by ozone concentration (g/Nm^3).
Applied ozone dose	D	mg/L	$D = \frac{P}{L}$	Applied ozone dose is the ozone feed rate per unit volume of water, similar to dosage of other chemicals in the water treatment plant, such as chlorine.
Transfer efficiency	TE	%	Concentration-based $TE = \frac{Y_1 - Y_2}{Y_1} \times 100$ Mass-based $TE = \frac{(G_2 \times Y_1 - G_3 \times Y_2)}{G_2 \times Y_1} \times 100$ Where G_3 is the off-gas flow rate, which is typically not measured.	Concentration-based transfer efficiency is an easily determined estimation of the percentage of ozone that is transferred to the water. A more involved but accurate determination of transfer efficiency includes gas flow, because gas flow might be lost (or gained) through the contactor. NOTE: In full-scale ozone applications it is difficult, impractical, and unnecessary to measure off-gas flow and accurately calculate ozone TE. The concentration-based TE can be used to effectively monitor changes in dissolution performance due to equipment malfunction, such as failure of diffuser gaskets.
Transferred ozone dose	T	mg/L	$T = D \times TE$	Transferred ozone dose is the quantity of applied ozone dose that has not escaped in the off-gas.
Specific energy	SE	kWh/lb or kWh/kg	$SE = \frac{P_w}{P} \times 24\ hr/day$	Specific energy is a measure of the performance or efficiency of the ozone generator. Generator design features, operating pressure, ozone concentration, and cooling water temperature influence specific energy.

lb/day = pounds of ozone per day
kg/day = kilograms of ozone per day
mg/L = milligrams per liter
kWh/lb = kilowatt-hours per pound
kWh/kg = kilowatt-hours per kilogram

Table A-3 Standard/Normal Pressure and Absolute Temperature

Standard/Normal Pressure	1.0 atm
	14.696 psi
	760 mm Hg
	101,325 Pa
	101.325 kPa
	2,116.2 lb/ft^2
	33.90 ft water
	10.332 m water
	1,033.2 cm water
Absolute Temperature	459.7 R
	273.15 K

Table A-4 Parameters for Determining Gas Density at NTP0C

Density of Various Feed-Gas Systems, NTP at 0°C

Parameter	Units	Air*	Oxygen†	PSA‡	VSA or VPSA§
Oxygen	%vol	20.941	98	95	92
Nitrogen	%vol	78.122	2	1	4
Argon	%vol	0.937	0	4	4
Molecular weight	g/mol	28.9598	31.9203	32.2781	32.1585
Density	g/LNTP	1.2922	1.4243	1.4403	1.4349
Density	lb/ft^3 NTP	0.08067	0.08892	0.08992	0.08958

Density of 100% Pure Gas, NTP at 0°C

Parameter	Units	Oxygen	Nitrogen	Argon	Ozone
Gram molecular weight	g/mol	32	28.013	39.95	48
Density	g/LNTP	1.428	1.25	1.783	2.142
	lb/ft^3 NTP	0.0891	0.078	0.1113	0.1337

Constants and Conversion Factors

Volume at NTP	22.411	L/mol at 0°C
Constant	453.592	g/lb
Constant	28.317	L/ft^3

* Air feed-gas

† Oxygen feed-gas with supplemental nitrogen addition

‡ Pressure swing adsorption (PSA) on-site oxygen concentration system

§ Vacuum swing adsorption (VSA) on-site oxygen concentration system (vacuum-pressure swing adsorption [VPSA])

Table A-5 Parameters for Determining Gas Density at STP_{68F}

Density of Various Feed-Gas Systems, STP at 68°F					
Parameter	Units	Air*	Oxygen†	PSA‡	VSA or VPSA§
Oxygen	%vol	20.941	98	95	92
Nitrogen	%vol	78.122	2	1	4
Argon	%vol	0.937		4	4
Molecular weight	g/mol	28.9598	31.9203	32.2781	32.1585
Density	g/LSTP	1.204	1.3271	1.342	1.337
Density	lb/ft^3 STP	0.07516	0.08285	0.08378	0.08347

Density of 100% Pure Gas, STP at 68°F					
Parameter	Units	Oxygen	Nitrogen	Argon	Ozone
Molecular weight	g/mol	32	28.013	39.95	48
Density	g/LSTP	1.33	1.165	1.661	1.996
Density	lb/ft^3 STP	0.083	0.0727	0.1037	0.1246

Constants and Conversion Factors		
Volume at STP	24.052	L/mol at 68°F
Constant	453.592	g/lb
Constant	28.317	L/ft^3

* Air feed-gas

† Oxygen feed-gas with supplemental nitrogen addition

‡ Pressure swing adsorption (PSA) on-site oxygen concentration system

§ Vacuum swing adsorption (VSA) on-site oxygen concentration system (vacuum-pressure swing adsorption [VPSA])

Table A-6 Ozone Concentration Conversion Factors at NTPoC

Air Feed-Gas at Normal Temperature and Pressure (NTP = 0°C and 1 atm)

Parameter	Units	Concentration, 0.5 %wt	Concentration, 1.0 %wt	Concentration, 2.0 %wt	Concentration, 2.5 %wt
Air feed-gas density	g/LNTP	1.2922	1.2922	1.2922	1.2922
Molar volume	LNTP	22.411	22.411	22.411	22.411
Ozone GMW	g/mol	48	48	48	48
Ozone density at 100 %vol	mg/LNTP	2,141.8	2,141.8	2,141.8	2,141.8
Ozone concentration	%wt	0.5	1.0	2.0	2.5
Ozone concentration	mg/LNTP	6.47	12.96	26.00	32.55
Ozone concentration	%vol	0.30	0.61	1.21	1.52
Ozone concentration	ppm$_v$	3,021	6,051	12,140	15,198
Ozone concentration	ppm$_w$	5,000	10,000	20,000	25,000
Ozone concentration	mg/LNTP/%wt	12.94	12.96	13.00	13.02

Oxygen Feed-Gas at Normal Temperature and Pressure (NTP = 0°C and 1 atm)

Parameter	Units	Concentration, 6.0 %wt	Concentration, 8.0 %wt	Concentration, 10.0 %wt	Concentration, 12.0 %wt
Oxygen feed-gas density	g/LNTP	1.4243	1.4243	1.4243	1.4243
Molar volume	LNTP	22.411	22.411	22.411	22.411
Ozone GMW	g/mol	48	48	48	48
Ozone density at 100 %vol	mg/LNTP	2141.8	2141.8	2141.8	2141.8
Ozone concentration	%wt	6	8	10	12
Ozone concentration	mg/LNTP	87.20	117.06	147.33	178.02
Ozone concentration	%vol	4.07	5.47	6.88	8.31
Ozone concentration	ppm$_v$	40,712	54,654	68,787	83,116
Ozone concentration	ppm$_w$	60,000	80,000	100,000	120,000
Ozone concentration	mg/LNTP / %wt	14.53	14.63	14.73	14.83

Table A-7 Ozone Concentration Conversion Factors at $STP_{68F\ or\ 20C}$

Air Feed-Gas at Standard Temperature and Pressure (STP = 20°C and 1 atm)

Parameter	Units	Concentration, 0.5 %wt	Concentration 1.0 %wt	Concentration, 2.0 %wt	Concentration, 2.5 %wt
Air feed-gas density	g/L_{STP}	1.204	1.204	1.204	1.204
Molar volume	L_{STP}	24.052	24.052	24.052	24.052
Ozone GMW	g/mol	48	48	48	48
Ozone density at 100 %vol	mg/L_{STP}	1995.7	1995.7	1995.7	1995.7
Ozone concentration	%wt	0.5	1	2	2.5
Ozone concentration	mg/L_{STP}	6.03	12.08	24.23	30.33
Ozone concentration	%vol	0.30	0.61	1.21	1.52
Ozone concentration	ppm_v	3,021	6,051	12,139	15,197
Ozone concentration	ppm_w	5,000	10,000	20,000	25,000
Ozone concentration	mg/L_{STP}/%wt	12.06	12.08	12.11	12.13

Oxygen Feed-Gas at Standard Temperature and Pressure (STP = 20°C and 1 atm)

Parameter	Units	Concentration, 6.0 %wt	Concentration, 8.0 %wt	Concentration, 10.0 %wt	Concentration, 12.0 %wt
Oxygen feed-gas density	g/L_{STP}	1.3271	1.3271	1.3271	1.3271
Molar volume	L_{STP}	24.052	24.052	24.052	24.052
Ozone GMW	g/mol	48	48	48	48
Ozone density at 100 %vol	mg/L_{STP}	1995.7	1995.7	1995.7	1995.7
Ozone concentration	%wt	6	8	10	12
Ozone concentration	mg/L_{STP}	81.25	109.07	137.27	165.87
Ozone concentration	%vol	4.07	5.47	6.88	8.31
Ozone concentration	ppm_v	40,711	54,653	68,786	83,115
Ozone concentration	ppm_w	60,000	80,000	100,000	120,000
Ozone concentration	mg/L_{STP}/%wt	13.54	13.63	13.73	13.82

Appendix B

Conversion Factors

1	psia	=	6.895	kPa
1	psi	=	27.68	in water
1	psi	=	703.07	mm water
1	in. water	=	25.4	mm water
1	lb	=	0.45359	kg
1	kWh/lb	=	2.205	kWh/kg
1	gal	=	3.785	L
1	ft^3	=	0.02832	m^3
1	gal/lb	=	8.345	L/kg
1	mgd	=	3.785	ML/d
1	Btu	=	1.055	kJ
1	Btu	=	1055	Joule
1	Btu/lb/°F	=	4.187	kJ/kg/°C
1	ft	=	0.3048	m
	ft^2	=	m^2	
	°F	=	°C	
	mil gal	=	mil L	

Units of Measure

°C	degrees Celsius
°F	degrees Fahrenheit
Btu	British thermal unit
Btu/lb	British thermal units per pound
cm	centimeter
ft	foot
ft/sec^2	feet per second squared
ft^2	square feet
ft^3	cubic feet
ft^3/min	cubic feet per minute
g	gram
g/g	grams per gram
g/L	grams per liter
g/mL	grams per milliliter
g/mol	grams per mol
g/Nm^3	grams per Normal cubic meter
g/m^3	grams per cubic meter
gal	gallon (US)
gal/hr	gallons per hour
gpd	gallons per day
gpm	gallons per minute
gpm/kW	gallons per minute per kilowatt
in.	inch
kg/L	kilograms per liter
kg/m^3	kilograms per cubic meter
kJ/kg	kilojoules per kilogram
kPa	kilopascal
$kPa_{(abs)}$	kilopascal absolute
$kPa_{(gauge)}$	kilopascal gauge
kW/hp	kilowatts per horsepower
kW/mgd	kilowatts per million gallons per day
kWd/ton	kilowatt days per ton, or kilowatts per ton per day
kWh/lb	kilowatt hours per pound
L	liter
L/mol	liters per mol
lb/d	pounds per day

Table continued next page

Units of Measure (continued)

lb/ft^3	pounds per cubic foot
lb/gal	pounds per gallon
lb/min	pounds per minute
m	meter
mL/L	milliliters per liter
m/sec	meters per second
m/sec^2	meters per second squared
m^3/hr	cubic meters per hour
mg	milligram
mg/L	milligrams per liter
mg/meq	milligrams per milliequivalent
meq/L	milliequivalents per liter
mgd	million gallons per day
mg-min/L	milligrams times minutes per liter
mL	milliliter
ML/d	million liters per day, or megaliters per day
mm	millimeter
ng/L	nanograms per liter
Nm^3/hr	Normal cubic meters per hour
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gauge
scfm	Standard cubic feet per minute
ton	ton (US)
tons/day	tons (US) per day
µg/L	micrograms per liter
Whp/mgd	water horsepower per million gallons per day

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Note: f. indicates figure; t. indicates table.