Mixing Efficiency. The sulfur dioxide solution is injected to the disinfected effluent just after the contact chamber, followed by a rapid-mix period (either in-line within a pipe or in a chamber with a mechanical mixer). An aeration diffuser or chemical-induction unit at the sulfur dioxide-injection point can also provide an adequate mix of the sulfur dioxide solution and the disinfected effluent.

Chlorine Residual. A sample of the dechlorinated effluent should be obtained and routinely tested for chlorine residual. Regulators have varying requirements for maximum chlorine residuals in dechlorinated effluent. As mentioned, the dose ratio of sulfur dioxide to chlorine residual is approximately 1:1 (each 1 mg/L of chlorine removed will require 1 mg/L of sulfur dioxide). Overdosing may cause deoxygenation of the final effluent, as well as unnecessary chemical costs. The effect on effluent oxygen level is typically low because it takes approximately 2 mg/L of SO_2 to reduce dissolved oxygen by 1 mg/L. Dissolved oxygen levels in the final effluent should be monitored to ensure that a minimum dissolved oxygen level is maintained in the final effluent.

ROUTINE OPERATIONS AND TROUBLESHOOTING. Refer to the previous section (Chlorination) because the operational checks and problems of the dechlorination components will be similar.

PREVENTIVE MAINTENANCE. Refer to the previous section (Chlorination) because similar preventive-maintenance tasks apply to the dechlorination components.

OZONATION

In wastewater applications, ozone (O_3) is used for disinfection and other purposes (e.g., pretreatment of domestic and industrial wastewater and odor control). It is also used in potable water treatment for oxidation, disinfection, and taste and odor control. Ozone forms naturally in the atmosphere via photochemical or electrical processes. The addition of energy first disassociates molecular oxygen to atomic oxygen. As more energy is added, atomic and molecular oxygen combine to form ozone (an unstable compound).

Ozone is mechanically generated via photochemical or electrical excitation methods. Photochemical methods involve UV excitation at a wavelength of less than 200 nm and can only produce ozone in limited quantities and concentration. Therefore, wastewater disinfection systems typically produce ozone via electrical corona (electrical plasma) discharge.

Electrical production of ozone requires extremely dry air or oxygen [−60 °C (−76 °F)] dewpoint at 1 atmosphere] exposed to a controlled uniform high-voltage discharge (high or low frequency). The yield of ozone is affected by the generator's geometry, the discharge gap's dimension and discharge area, the gas temperature and pressure, the applied frequency and voltage, and the physical properties of the dielectric. As heat, pressure, and the feed gas humidity increase, ozone production decreases.

Ozone is produced as a gas. It is an unstable, strongly reactive oxidant that requires onsite production. When dry air is used as a feed gas, the resulting ozone concentration (by weight) is 1 to 4%. When oxygen of sufficient purity is used as the feed gas, the ozone concentration (by weight) can vary from 3 to 10%, depending on the manufacturer. Even higher production rates are becoming both feasible and economical.

Ozone is a superior oxidant with generally rapid reaction rates and superior disinfectant capabilities. The disinfection process depends on the susceptibility of the target organism, the pH, contact time, and the concentration of the disinfectant. In general, the effectiveness of ozone as a disinfectant is not pH-dependent. Like oxygen, ozone has limited solubility. However, unlike oxygen, ozone exposure must be limited for safety reasons. Ozone will typically decompose faster in water than in air. Because of these limitations and ozone's reactivity, the ozone contactor requires special covered construction and often multiple addition points. Ozonated effluent is also subject to problems associated with disinfection byproducts, including the formation of aldehydes, acids, and brominated compounds.

The production system includes dryer, compressor or blower, ozone generator, dielectric (ground and electrode), step-up transformer (rectifier and inverter), and electrical control panel.

Ozone is a strong oxidant and virucide. The ozone disinfection mechanisms include

- Direct oxidation/destruction of the cell wall with leakage of cellular constituents outside the cell;
- Reactions with radical byproducts of ozone decomposition; and
- Damage to the constituents of the nucleic acids (purines and pyrimidines) inside the cell, which alters their genetic material, thereby preventing cell replication.

When ozone decomposes in water, the free radicals hydrogen peroxy ($\cdot HO_2$) and hydroxyl ($\cdot OH$) are formed. They have great oxidizing capacity and play an active role in disinfection. It is generally believed that the bacteria are destroyed because of protoplasmic oxidation, which results in cell wall disintegration (cell lysis).

EQUIPMENT DESCRIPTION. A typical ozonation system includes several elements (Table 26.9 and Figure 26.14).

.9 Ozone disinfection system components and their uses.

:nts	Types	Functions
	Glass fiber, paper, or metal; low-pressure drop; minimum 6 months use	Inlet filter: 10 μm; pre-dryer filter solids 100%: 0.3 to 1 μm; moisture 100%: 1.75 μm; postdryer filter solids 100%: 0.3 μm; solids 95%: 0.1 μm; filter solids and moisture at various stages of air preparation.
ressor	Oil free—centrifugal, reciprocating, rotary	Provides continuous flow of air or oxygen.
er	Air or water, single countercurrent shell and tube	Lowers gas temperature and lowers dewpoint.
	Refrigerant dryer, direct expansion, chilled water exchangers	A pre-dryer to lower equipment for complete drying at 76 °F dewpoint.
	Dessicant, pressure swing, heat-generating	Dries gas to limit nitric oxide production and maximize ozone production.
y inverter	Low frequency (none required)	Not used: 50 to 60 Hz.
	Medium frequency	60 to 1000 Hz.
	High frequency	Operating above 1000 Hz.
	Frequency converter	Used to increase power densities at generator cell; AC is rectified to DC, filtered, or thyristor-inverted back to AC current; both frequency and voltage are controlled.
ner	Low-input, high-output step-up	Low frequency, 8 to 20 kV; medium frequency, 8 to 12 kV; to achieve required power densities; the lower the frequency, the higher the applied voltage.
neter or r, ammeter ıency meter	Powerstat or inverter; variable inverter	Low frequency, 5:1 turndown; medium frequency, 10:1 turndown; high frequency, 15:1 turndown; controls and indicates applied voltage frequency.
:	Typically in an ozone generator, the dielectric is a compound [air (oxygen) and glass (ceramic)]; it can be a plate or tube	The medium between two plates in a capacitor, the ozone generator, the generator cell.
e	High voltage or ground	High-voltage electrodes provide more than 1000 V to charge the dielectric; this is discharged to the ground electrode (corona).
· rotameter		

Table 26.9 Ozone disinfection systems components and their uses (*continued*).

Components	Types	Functions
	Graduated adjustable gas-flow tube with indicator	Adjusts air–oxygen flowrate into the ozonator.
Inlet gas-pressure gauge	Graduated	Indicates the inlet gas pressure to the gas-flow rotameter.
Pressure-relief valve	Spring-loaded or weighted air-pressure relief	Allows excess air pressure to be released from the reaction vessel shell.
Ozone destructor	Catalytical (manganese dioxide 0.25- to 018-in. extrusions) destructor to have 0.72-second residence time, a linear velocity of 2.2 ft/sec, gas stream temperature 15 °F above ambient or thermally at 300 °C for 3 to 5 seconds	Removes offgas ozone by converting it to oxygen.

Note: (°F − 32) 0.5556 = °C; in. × 25.4 = mm; ft/sec × 0.3048 = m/s.

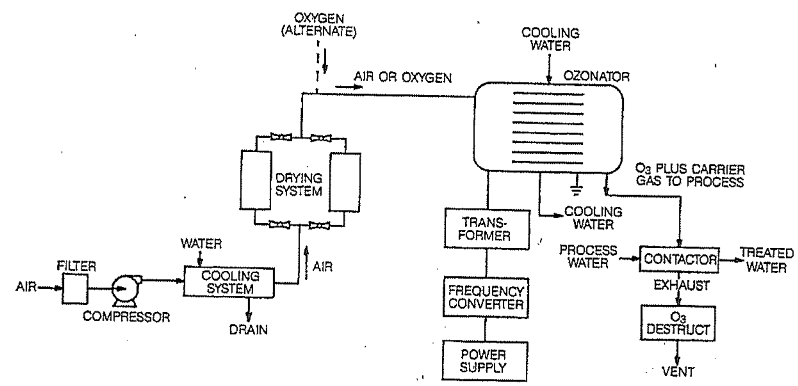

Figure 26.14 Schematic of an zone generation system.

BASIC STARTUP AND SHUTDOWN. Startup and shutdown procedures are as follows.

Startup. The following steps should be taken to start up an ozonation system:

1. Place the power-supply circuit breaker (on–off switch) in the "off" position.
2. Start the cooling water supply through the ozonator.
3. Make certain that the air path to the ozone contact chamber is open and that the ozone destruction unit is operating.
4. Start the air or oxygen supply to the ozonator.
5. Adjust the air pressure to the reaction vessel by operating the pressure-regulating valve. If air pressure exceeds the air-relief valve setting [typically approximately 90 kPa (13 psi)], the relief valve will open.
6. Purge the ozonator for at least 30 minutes with clean, dry air before applying power to the electrodes.
7. To begin producing ozone, place the circuit breaker in the "on" position.
8. Adjust the voltage with the potentiometer to the desired output, as indicated on the voltmeter.

Shutdown. The following steps should be taken to shut down an ozonation system:

1. Using the voltage potentiometer, turn off the power to the electrodes.
2. Place the power switch in the "off" position.
3. Purge with clean, dry air for 30 minutes to evacuate all ozone.
4. After purging, close all air valves to the reaction chamber.
5. Turn off the water.

PROCESS CONTROL. The principal process-control considerations are mixing and detention time. Because ozone decomposes naturally and is consumed rapidly, it must be contacted uniformly in a near plug-flow contactor. Maintenance of an ozone residual at a given concentration for a specific period (detention time) is necessary for proper disinfection. Contact time is dictated by aqueous residual.

DATA COLLECTION, SAMPLING, AND ANALYSIS. Chapter 17 describes sampling, sample handling, and analyses for indicator bacteria. *Standard Methods* (APHA et al., 2005) describes procedures for these bacterial tests and also for ozone dose and residual tests. Typically, both types of tests are needed.

For the ozone residual test, an ozonated effluent sample must be collected from the effluent end of the ozone contactor. The sample must be drawn directly into the testing vessel and the analysis performed immediately thereafter.

The ozone dose must be calculated based on the gas flow and concentration into the contactor versus the gas flow and concentration out of the contactor and the aqueous ozone residual and flow. The calculation requires consideration of gas volume and concentration versus aqueous volume and concentration.

ROUTINE OPERATIONS AND TROUBLESHOOTING. Table 26.10 lists routine operational checks for ozonation equipment and possible remedies if these checks indicate potential problems.

SAFETY. Exposure to even small quantities of ozone can cause serious health problems (Table 26.11). Ozone is extremely reactive and will corrode most metals, plastics, and elastometers; therefore, leaks can adversely affect electrical systems, seals, and metals. Properly calibrated ozone monitoring equipment is needed for both the work area and the ozone offgas destruction units. Care should also be given to releases to surrounding vegetation as a result of long-term ventilation or other release. Ambient monitors should provide for a work-area alarm at 0.1 ppm, and shutdown and area ventilation at the 0.3 ppm ambient residual level. The monitoring equipment should be tested weekly and calibrated as required by the equipment manufacturer.

Ozone can exist in gaseous form for a significant period of time. Extreme caution should be taken when dealing with ozone gas-handling systems. Therefore, the ozone generator, distribution, contacting, off-gas, and ozone destructor inlet piping should be purged prior to opening the various systems or subsystems. A minimum of two SCBAs must remain in the immediate vicinity of the ozonation system.

Entry into the ozone contactor should follow accepted confined-space-entry protocols. Personnel must recognize the possibility of oxygen deficiencies or trapped ozone gas despite their best efforts to purge the system. Steps to be followed include

1. Halt ozone flow to the contactor train. Valve off or, preferably, blank off the ozonized gas pipe to the contactor if possible.
2. Purge the contactor with oxygen or prepared air.
3. Valve off or, preferably, blank off all possible cross-connections with other ozonation trains.
4. Open all access hatches and begin ventilation as the contactor is dewatered.
5. Dewater the contactor.
6. Continue the ventilation procedure.
7. Have the contactor interior tested for ozone, oxygen, and gaseous contaminants (e.g., hydrogen sulfide) by personnel wearing protective clothing and SCBAs.

.10 Routine operational checklist and troubleshooting guide for ozonation.

	What to check	Potential problems	Corrective actions
	Proper air flow	Dirt or dust clogging filter	Replace filter.
pressor r	Proper air volume and pressure	Low air volume or pressure	Open valves and verify that air filter is clean.
ler	Compressor	Improper cooling	Recharge with refrigerant.
		Not running	Replacement probable.
	Fan	Not running	Replacement probable.
ng filter	Proper air flow	Dirt or oil clogging filter	Clean or replace filter and drain trap.
	Desiccant cartridge	Spent cartridge	Replace.
	Dryer system and refrigerant	Improper drying	Recharge with refrigerant.
		Compressor not running	Replacement probable.
	Frequency output	Final thyristor or inverter	Replace unit or thyristor.
mer	Output voltage	Low output	Verify proper input voltage.
			Increase potentiometer setting.
		No output	Verify proper input voltage; replacement probable.
meter	Dial setting corresponds to voltmeter	No voltage control	Verify proper volunteer operation; potentiometer replacement probable.
er	Verify readout with potentiometer setting	Meter rating too low	Verify proper potentiometer setting.
			Verify proper transformer output.
			Calibrate voltmeter.
			Replacement probable.
enerator	Inlet gas-flow rate	Insufficient volume or pressure; leak	Start and increase gas flow from compressor or blower; repair leak.
		Moisture content too high	Verify proper operation of gas cooler or dryer systems.
	Inlet cooling-water flow	Insufficient flowrate	Provide proper water supply for unit size.
			Check for kinked, broken, or otherwise restricted water-supply tubing.

TABLE 26.10 Routine operational checklist and troubleshooting guide for ozonation (*continued*).

Items	What to check	Potential problems	Corrective actions
	Dielectric electrodes	Breaker tripped	Examine dielectric tube or plate closely for a defect that may result in grounding grounding arc; defect could be pinhole, crack, or break in glass.
		Excessive buildup of deposits on the exterior	Clean dielectric tube and troubleshoot the exterior air supply for failure of the gas-drying system.
Gas-flow rotameter	Gas flow to ozone reaction vessel	Gas flow too low or too high	Increase or decrease gas flow by operating needle valve.
		Gas-flow indicator not functioning	Remove ozonator from service and clean rotameter.
Pressure-regulating valve	Compare pressure-relief and gauge settings.	Pressure setting too high or too low.	Adjust to recommended setting.
Ozone destructor	Excessive ozone in ozone-destructor effluent	Leak	Repair leak.
		Catalyst black	If water on catalyst is black, heat to 212 °F*.
		Catalyst not black	Replace or consult manufacturer.
		Catalyst crushed	Replace—make certain bed is not fluidizing.

*(°F − 32) 0.5556 = °C.

8. Once working conditions are safe, allow personnel equipped with safety harness and rope to enter the contactors, using the buddy system. With this system, a second person on the deck of the contactor watches and assists the worker in the contactor. Self-contained breathing apparatuses must be kept immediately adjacent to the work area.

Because of the hazardous nature of ozone gas, security measures must be in place to ensure that only authorized personnel have access to the ozone gas-generation and -handling systems.

TABLE 26.11 Health effects of ozone.

Zone	Concentration (ppm)	Duration of exposure	Effect
Acceptable zone	0.01– 0.04	—	Odor threshold
	0.1	—	Minor eye, nose, and throat irritation.
	0.1	8-hour average exposure limit	
	>0.1	Few minutes	Continuous headache, shortness of breath.
	0.25	2 to 5 hours	Reduced lung function and ability to do physical work (for persons with a history of heart and lung disease).
	0.3	15-minute exposure limit	
	0.4	2 hours	Reduced lung function during moderate work for all persons.
Hazardous zone	>0.6	2 hours	Chest pain, dry cough.
	1	1 to 2 hours	Lung irritation (coughing), severe fatigue.
	>1.5	2 hours	Reduced ability to think clearly. Continuing cough and extreme tiredness, maybe lasting for 2 weeks; severe lung irritation with fluid buildup.
	9	Intermittent	Severe pneumonia (arc welders).
Critical zone	10	Immediately dangerous to life and health	
	11	15 minutes	Rapid unconsciousness.
	50	30 minutes	Expected to be fatal

PREVENTIVE MAINTENANCE. Preventive maintenance, performed routinely, increases the life expectancy and efficiency of equipment. There must be no leaking connections or other leaks in or around the ozonator because this is an electrical shock hazard.

Extreme caution must be exercised when working near the dielectric tube, transformer, or other electrical-system components, because electricity in excess of 20 000 V may be encountered.

The following considerations apply to a preventive maintenance program for ozonation:

- Inspect and clean the ozonator, air supply, and dielectric assemblies on a scheduled basis, as recommended by the manufacturer.
- Collect samples of ozone gas from the sample tap and determine the percent ozone generated via an iodometric or UV monitor. If a reduction in ozone production is observed, check the air supply for proper moisture content. Also check to ensure that coolant flow (cooling water) and applied voltage are proper.
- Lubricate the compressor or blower consistent with the schedule and instructions recommended by the manufacturer. Ensure that all compressor sealing gaskets are in good condition, and replace them as necessary.
- Monitor the ozone generator operating temperature and clean the cooling-system components as necessary.
- Check the supply air (gas) for moisture content (dewpoint). If the supply gas is moist, the ozone will react with the moisture to form a highly corrosive condensate on the internal components of the ozonator.
- Clean the ozone-generation cells periodically to maintain maximum efficiency.

OTHER DISINFECTION METHODS

BROMINE CHLORIDE. Bromine chloride (BrCl), which is occasionally used for wastewater disinfection, is a mixture of bromine and chlorine. Twelve times more bromine chloride than chlorine will dissolve in water. Products of bromine chloride mixed with water are stronger oxidants and disinfectants than chlorine. Also, in the presence of amines, bromine chloride forms bromamines, which are better disinfectants than chloramines. The bromamines have a short half-life, resulting in less toxic effects in receiving water than chloramines. So, debromination to remove bromine residuals is seldom needed.

Bromine chloride mixes with water to form hypobromous acid and hydrochloric acid:

$$BrCl + H_2O \rightarrow HOBr + HCl \qquad (26.17)$$

Bromine chloride mixes with amines to form monobromamine and hydrochloric acid:

$$BrCl + NH_3 \rightarrow NH_2Br + HCl \qquad (26.18)$$

Process Description. A pressurized system using either air or nitrogen gas feeds the bromine chloride solution. The pressure forces the bromine chloride liquid from the