Drinking Water Operator Certification Training

Module 27: Ozone

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Topical Outline

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Unit 1 – General Overview

Learning Objectives

- State the physical description of ozone.
- Describe where ozone comes from.
- Describe what ozone is used for.

Physical Description

- The chemical formula is O_3.
- The unit weight of ozone is 0.125 lbs./cu. ft. (at standard temperature and pressure). This is heavier than air (which is 0.076 lbs./cu. ft. at standard temperature and pressure).
- Ozone has a pungent smell. The smell in the air after a close lightning strike comes from ozone.
- Ozone is clear to bluish in color.
- Ozone is chemically unstable. It is a very strong oxidant and will react very quickly with many other chemicals.
- Because ozone is a strong oxidant, it can be hazardous to handle. Ozone safety and handling requirements and first aid procedures must be followed.

Natural Process

- Ozone is generated in nature.
  - Passing high voltage electric arcs through air (or oxygen) converts part of the O_2 into O_3. This is what happens (and why you smell ozone) when lightning strikes.

On-Site Generation

- Since ozone is chemically unstable, it cannot be made and stored for later use.

Therefore, ozone for water treatment is generated on-site and used as fast as it is generated.

- Ozone is generated by passing high voltage electric arcs (basically “controlled lightning”) through a stream of very clean and dry air or concentrated oxygen inside a closed vessel.

As a Strong Oxidant

Since ozone is a strong oxidant, it is useful for:

- Oxidation of organics in raw water.
- Oxidation of iron and manganese.
- Oxidation of taste and odor forming compounds.
- Breaking down complex organic chemicals into simpler compounds.
- Prevention or treatment of musty-earthy taste and odor problems resulting from algal blooms.

As a Strong Disinfectant

Ozone is also a strong disinfectant. Inactivation of many pathogens can be obtained at lower doses and with less contact time with ozone than with chlorine.

- Ozone is especially effective against Giardia and viruses.
- Ozone is somewhat less effective against Cryptosporidium.

Compared to Chlorine

Ozone will inactivate many of the same pathogens and oxidize many of the same compounds that chlorine will.

- However, when ozone reacts with these compounds, it doesn't generate the same harmful byproducts, like trihalomethanes (THMs) and haloacetic acids (HAAs) that reaction with chlorine will generate.

Therefore, ozone can be used to reduce disinfection byproducts. However, ozone disinfection of bromide containing source waters may produce bromate, a harmful byproduct.

Key Points for Unit 1 – General Overview

- The chemical formula for ozone is O_3.
- Ozone has a pungent smell and is clear to bluish in color.
- Ozone is hazardous to handle because it is a strong oxidant.
- Ozone is generated on site.
- Ozone is a strong disinfectant.
- Ozone produces few disinfection byproducts compared to chlorine.
- Ozone can be used to oxidize iron and manganese.
- Ozone can treat musty-earthy taste and odor problems resulting from algal blooms.

Unit One Exercise.

1. The chemical formula for ozone is

   ____.

2. Ozone has a _____________ smell.

3. Ozone is clear to _____________ in color.

4. Ozone is chemically unstable, and must be used as quickly as it is

   ____________________.

5. Ozone is a strong ______________ and can be __________________ to handle.

6. Ozone is generated in nature when high voltage electric arcs convert part of the

   ________________ in the atmosphere into _________________.

7. Ozone is a strong disinfectant, and does not produce harmful byproducts that

   _____________ does.

Unit 2 – Generation of Ozone

Learning Objectives

- Identify the two sources of oxygen used to generate ozone and discuss the advantages and disadvantages of each.
- Describe the main components of the power supply and generator vessel used to generate ozone.
- Describe two ways that air is dried before using it to generate ozone.
- Name the equipment used to raise the supply voltage to 3,500 volts or more.
- Describe the typical use of a programmable logic controller (PLC) in an ozone generator.

Atmospheric Oxygen (Air Prep System)

- This type of system uses ambient atmospheric oxygen for generation of ozone.
- The air used to generate ozone must be very clean and very dry.
  - Particles larger than 0.1 microns must be filtered out.
  - The air typically must be dried to a dew point of less than –80 degrees F.

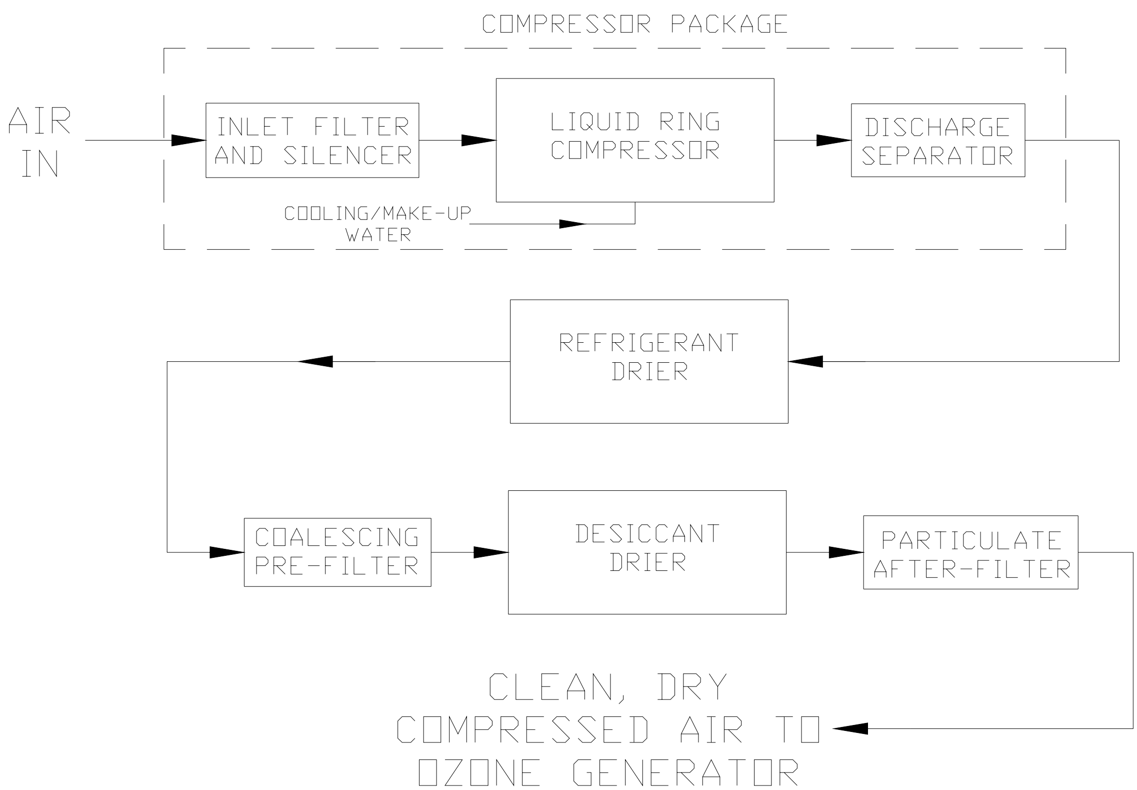

Figure 2.1 – Air Prep System Schematic

- The required air preparation equipment includes:
  - **Compressor** – The air fed to the ozone generator must be compressed to 15 to 20 pounds per square inch (psi). This application requires a high volume compressor, as the flow rate through the compressor must match the gas flow rate to the point of ozone application. Liquid ring type compressors are often used for this purpose.
  - **Filters** – The air must be free of particles larger than 0.1 micron. This includes dust, dirt, and also droplets of oil or moisture. These are removed by particulate filters, which basically strain the air, and by coalescing filters, which trap droplets of oil or moisture.
  - **Driers** – The air must be extremely dry. Two different types of driers are typically used for this application:
    - **Refrigerant Driers** work like an air-conditioner. It uses refrigeration to cool the air below the dew point and causes the moisture in the air to condense.
    - **Desiccant Driers** use an absorbent media to absorb moisture from the air. The air is forced through a closed vessel filled with granular desiccant media.

- The advantage of an air prep system:
  - Since the system uses ambient atmospheric oxygen, the raw material used to generate ozone is FREE!

- The disadvantages of an air prep system include:
  - This type of system requires more mechanical equipment than a liquid oxygen system.
  - Air prep systems can only generate ozone at concentrations up to about 3%.

Liquid Oxygen (LOX) System

- This type of system uses purchased liquid oxygen (LOX) as the source of oxygen used to generate ozone. LOX is stored on site in a bulk tank (or tanks) as a compressed liquid, the same way chlorine is stored in cylinders.
- The LOX used for ozone generation must be pure and free of hydrocarbons (<15 ppm by volume) and must be dry (dewpoint lower than –76 degrees F).
  - The ozone generator manufacturer can provide specific quality and purity requirements for LOX to be used with their equipment.
  - Make sure the LOX supplier is aware of those quality and purity requirements and will guarantee their LOX meets them.

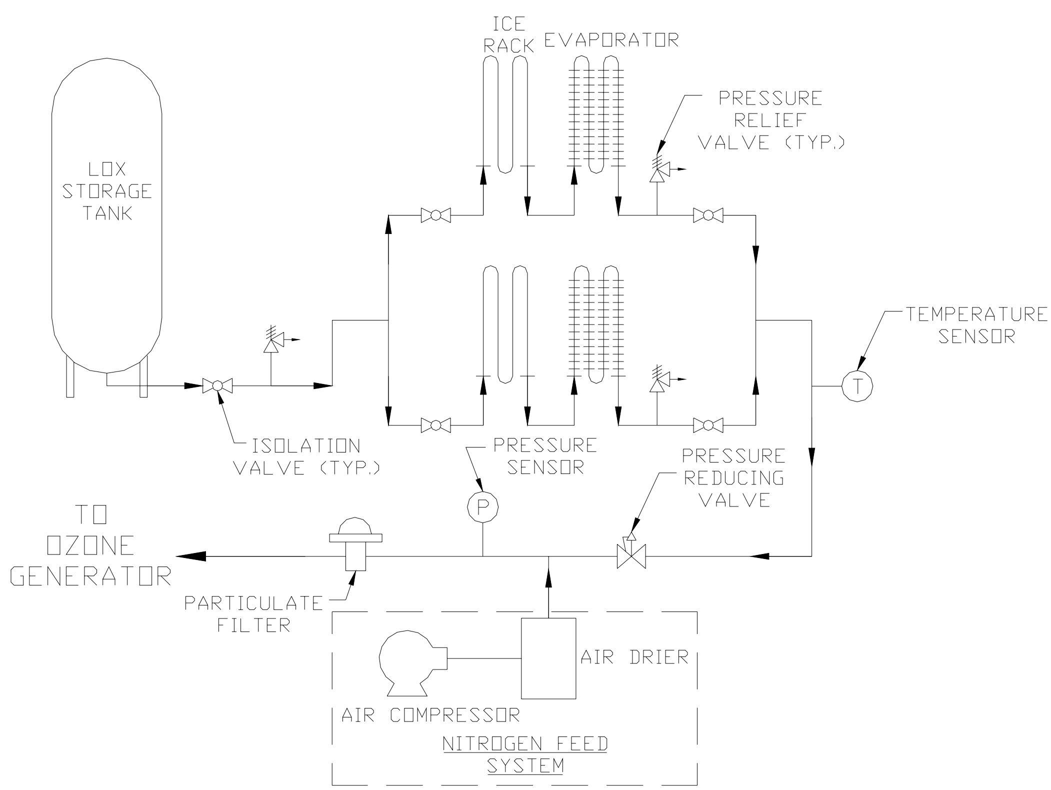

Figure 2.2 – Liquid Oxygen (LOX) Feed System Schematic

- The required equipment for a LOX feed system includes:
  - **LOX storage tank(s)** equipped with level or weight transmitters to monitor amount of LOX in storage. Tanks must also be equipped with pressure relief for safety.
  - **Ice Racks and Evaporators** in LOX systems use ambient heat to evaporate the liquid oxygen into gaseous oxygen, similar to the way liquid chlorine in cylinders is evaporated and fed as a gas.
  - **Pressure Regulators** – Pressures in LOX storage tanks can reach 200 psi. Ozone generators normally operate at pressures of 15 to 30 psi. The pressure of the oxygen being fed to the generator must be carefully controlled.
  - **Nitrogen Feed System** -- Ozone generators using a LOX feed system generally work best when there is a 3 to 5 percent concentration of nitrogen in the feed gas to the generator. This small amount of nitrogen helps to prevent build up inside the generator and reduces maintenance.
  - **Particulate Filter** – Particles larger than 10 microns must be filtered out.

- The advantages of a LOX feed system include:
  - LOX systems can generate ozone at concentration up to 12% (four times that of an air prep system). A much smaller volume of gas is required to obtain the desired ozone dosage. Ozone piping and valves can be smaller. Fewer and smaller diffusers are required.
  - There are fewer mechanical components to power and maintain. There are no large electrical loads associated with the LOX evaporators and feed equipment.

- The disadvantages of a LOX system include:
  - You have to buy the LOX.
  - LOX can be hazardous to handle. Too high a concentration of oxygen in the air can be as harmful to humans as too low a concentration.

Earlier ozone systems generally used air prep systems, as LOX is fairly expensive. As newer technologies were developed and ozone generators became more efficient (i.e., could generate ozone at higher concentrations), LOX systems became more economical. Many newer ozone systems use LOX.

Figure 2.3 – Ozone Generator Power Supply Unit[1]

Inputs

- The power supply takes in normal 480 volt, 3 phase, 60 hertz power and outputs high voltage (3,500 volts to 11,500 volts, depending upon the system) medium or high frequency current to the ozone generator.

Main Components

- **Power converter/inverter module** – This device converts the incoming 60 hertz alternating current to medium or high frequency current.

- **Transformer** – The transformer converts the incoming 480 volt power supply to high voltage.

- **Cooling system** – The cooling system rejects the heat generated by the converter/inverter module and the transformer, and keeps the unit cool. If temperatures become too high in the power supply, the heat can damage the major electrical components and the electronic controls. Cooling systems can be **closed loop** or **open loop**.

- **Controls** – The power supply includes a system of electronic control devices that monitor and regulate the power output to the ozone generator. Varying the amount of power applied to the generator (frequency and voltage) is one way of controlling the amount of ozone generated. Control devices usually include:
  - The **power monitor** measures and monitors input and output voltage and frequency.
  - In addition to power monitors, the **control system** monitors cooling water temperature.
  - The power supply is generally controlled by a **programmable logic controller (PLC)**. The PLC inputs signals telling it how much ozone is required and uses that information to control the output of the converter/inverter module and transformer. It also inputs the cooling water temperature and parameters from the power monitor and shuts down the system and/or generates alarms if a problem develops.

Figure 2.4 – Ozone Generator and Power Supply[2]

Main Components

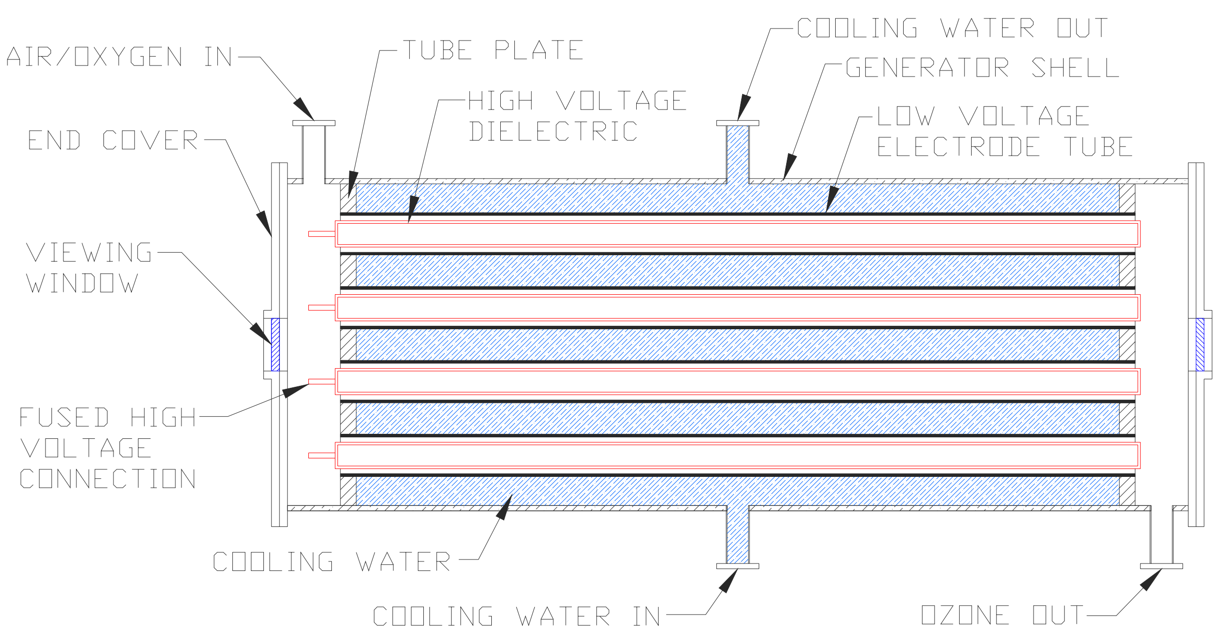

Figure 2.5 – Cross Section of Ozone Generator

Operation of Ozone Generator

- Air or oxygen is fed in at one end of the generator and flows through the gaps between the dielectrics and electrode tubes.
- The **dielectrics** provide a high voltage connection and are located inside the **electrode tubes,** which provide a grounded, low voltage connection.
  - The gap between the dielectric and the electrode tube is very uniform and precise.
- The **generator shell** encloses the electrode tubes.
- High voltage is applied to the dielectrics and discharges to the electrode tube. This electrical discharge converts a portion of the oxygen in the gas flowing through the gap to ozone.
- The air/oxygen/ozone mixture is then discharged from the other end of the generator and is sent to the point of application.
- **Cooling water** is circulated between the tubes, inside the shell, to remove the heat generated by the electric arcs.

The amount of ozone generated can be controlled by varying the amount of electrical power applied to the generator, as discussed in the Power Supply section, or it can be controlled by regulating the flow rate of air or oxygen to the generator.

Key Points for Unit 2 – Generation of Ozone.

- Liquid oxygen (LOX) or air can be used to generate ozone.
- If air is used to make ozone, it must be clean and dry.
- Air must be filtered to remove particles larger than 0.1 microns.
- Ozone generators require high voltages of 3,500 to 11,500 volts.
- Water is used to cool ozone generating equipment.
- LOX is considered dangerous because it is an extremely cold liquid.
- More equipment is needed to make ozone from air compared to using LOX.
- A programmable logic controller (PLC) is used to control the power supply in an ozone generator.

Unit Two Exercise.

1. What are the advantages of a LOX feed system?

___

___

___

2. What are the disadvantages of a LOX feed system?

___

___

___

3. What is the primary purpose of the power supply unit of an ozone generator?

___

___

___

4. What is the primary purpose of an ozone generator?

___

___

___

5. Describe two ways that an operator can control the amount of ozone that is generated.

   a. ___

   b. ___

[1] PCI Wedeco. "Ozone Generator Power Supply Unit." 2002. North American Municipal Sales Meeting, Ozone Systems Presentation. [CD ROM] (6 May, 2002).

[2] PCI Wedeco. "Ozone Generator and Power Supply." 2002. North American Municipal Sales Meeting, Ozone Systems Presentation. [CD ROM] (6 May, 2002).

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Unit 3 – Application of Ozone

Learning Objectives

- Identify the two main methods of applying ozone.
- Discuss the main components of each ozone application method.

Overview

- Since ozone is a gas, it must be dissolved into the water to react with the various compounds to be removed.
- There are two main types of systems used to dissolve ozone into water: diffuser system and side stream injection.

Special Considerations

- The facilities used to apply ozone must allow contact time after the ozone is dissolved for the chemical reaction and disinfection to take place.
- Since ozone is hazardous, there are special safety considerations.
  - Ozone must be fed in an enclosed chamber or vessel. No vapors can be allowed to escape.
  - All materials that may come into contact with ozone must be resistant to ozone.
  - All dissolved ozone must be destroyed before the water leaves the contact chamber or vessel. Dissolved ozone can be neutralized by feeding sodium bisulfite.
  - All areas in the vicinity of where ozone is being fed must be monitored for ozone leaks.

Microbiological Induced Corrosion (MIC) of 300 series stainless steels when used with fresh waters is becoming recognized as a potentially serious problem. Iron utilizing bacteria are suspected of causing damage to stainless steel pipes and containers when water containing organic matter is left stagnant or has a low flow rate through the stainless steel pathways. Pinholes may develop after a biofilm has formed as iron bacteria in the water start attacking a localized site on the inside surface of the stainless steel that is often near a weld. The biofilm becomes encrusted which then tends to shield it from the bacteria inactivation capabilities of ozone or other biocides such as chlorine. Numerous cases of encrusted biofilms have been reported after fresh untreated water was left in the stainless steel pipes and containers for several days. The pinholes will eventually break through the stainless steel material and result in a leak. The pinholes must be cleaned and welded.[1]

Periodic drying and inspection of the inside surfaces of the stainless steel material will help to detect potential MIC caused pinholes before they become leaks. Reduction in the amount of organic matter in the source water and periodic planned maintenance inspections may be needed to reduce MIC problems to an acceptable level.

Check with your engineer if MIC is suspected in your installation.

Description

- The diffuser method of application uses fine bubble diffusers to release ozone gas into the water. These fine bubbles are “transferred” (dissolved) into the water.
  - Diffusers are generally made of ceramic. They can be rod shaped or dome shaped.

- Diffusers need 18 to 20 feet of submergence for efficient transfer of gas into the water.
  - Generally about 95% of the ozone applied is transferred into the water. The rest escapes into the air above the water, which is why ozone must be applied in an enclosed chamber or vessel.

Operating Principles

- Diffusers are generally used in closed concrete basins as in Figure 3.1. A typical basin is divided into multiple chambers by baffle walls.

- There must be isolation valves or gates for the water and ozone. The isolation valves or gates for water should be submerged or “trapped” so that ozone gas from the area above the water cannot escape.

- There must be sample taps to measure dissolved ozone at several points in the basin.

- There must be provision to feed a neutralizing chemical, usually sodium bisulfite, to neutralize any remaining dissolve ozone before the water leaves the contact basin.

- All access hatches must be sealed.

- The chamber should operate under a slight vacuum to prevent the escape of ozone gas. This is done using an ozone destruct unit. The destruct unit has an exhaust blower that draws air from above the water in the contact basin and maintains the vacuum. The air drawn off the basin goes through a catalytic destructor that destroys any ozone before discharging the air to the atmosphere. The basin is equipped with a vacuum relief valve to prevent the vacuum from becoming high enough to damage the basin structure.

- Ozone may cause foam to form on the water surface in the basin. As a result, spray nozzles should be provided at several points at the top of the basins to knock down the foam.

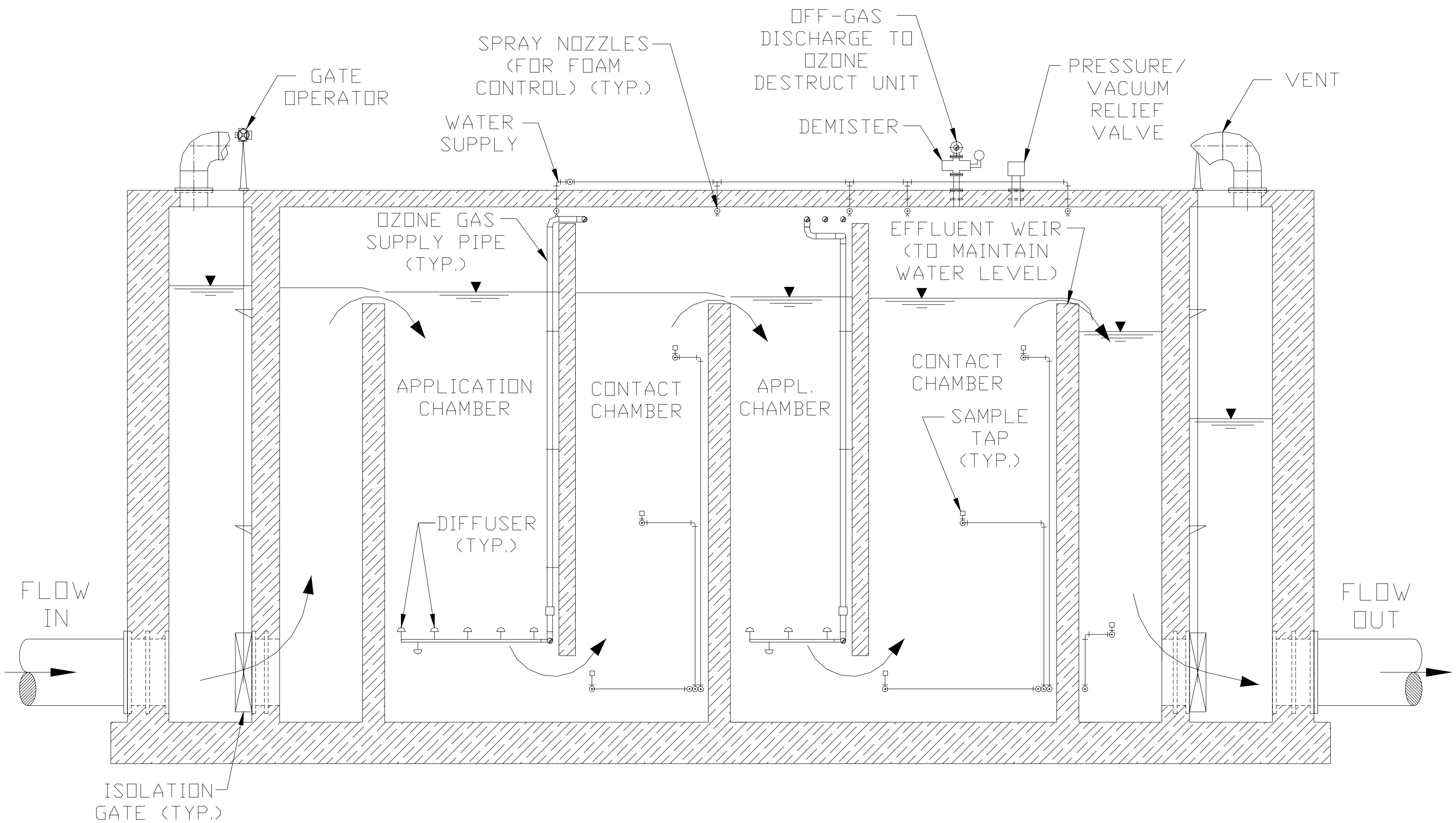

Figure 3.1 – Ozone Contact Basin

How Ozone Is Applied

- This process description pertains to the plant design shown in Fig 3.1. Other plant designs may require a different set of process steps.

- Ozone is generally applied in stages, i.e. not all of the ozone is fed at the inlet of the contact basin.
  - A portion of the ozone is applied by diffusers located in the first chamber in figure 3.1.
  - Contact time is provided in the second chamber (no diffusers).
  - Another portion of the ozone is applied again in the third chamber by additional diffusers.
  - Additional contact time is provided in the fourth chamber. This pattern is continued for each additional stage in the ozone contact basin.
  - Ozone is usually applied in either two or three stages.
  - Ozone application techniques may vary depending on the design of the tanks.

- Baffles are designed to direct water flow 1) downward (counter to upward gas flow) in areas where diffusers are located, and 2) upward through the contact chambers, so flow can be directed back downward over the next stage diffusers.

Advantages and Disadvantages of Diffuser System

- Advantages of diffuser systems include:
  - Are suitable for treatment processes using ozone for oxidation or for disinfection.
  - Are better for disinfection applications than side stream injection because the large volume of the contact basin provides much more disinfectant contact time.

- Disadvantage of diffuser systems:
  - Require more space and usually have a higher construction cost than side stream injection systems because of the large contact basin required for a diffuser system.

☑ **Exercise for Diffuser Systems.**

1. List two types of chambers in an ozone contact basin. Describe what occurs in each chamber.

a. ____

____

____

b. ____

____

____

2. List at least 3 ozone application safety controls and / or measures that must exist in a diffuser system.

a. ____

b. ____

c. ____

Description

- The side stream method of application diverts part of the main process flow and pumps it through an injector. The injector operates on the same basic principle as a chlorine gas ejector. This method is often used to provide oxidation and is used in smaller plants or bottled water plants.
  - The water flow creates a vacuum, which pulls the air/oxygen/ozone mixture into the flow stream where it is dissolved into the water.
  - The side stream, which has been dosed with ozone, is then recombined with the main process stream.

Figure 3.2 – Skid Mounted Side Stream Injection System [2]

Main Components

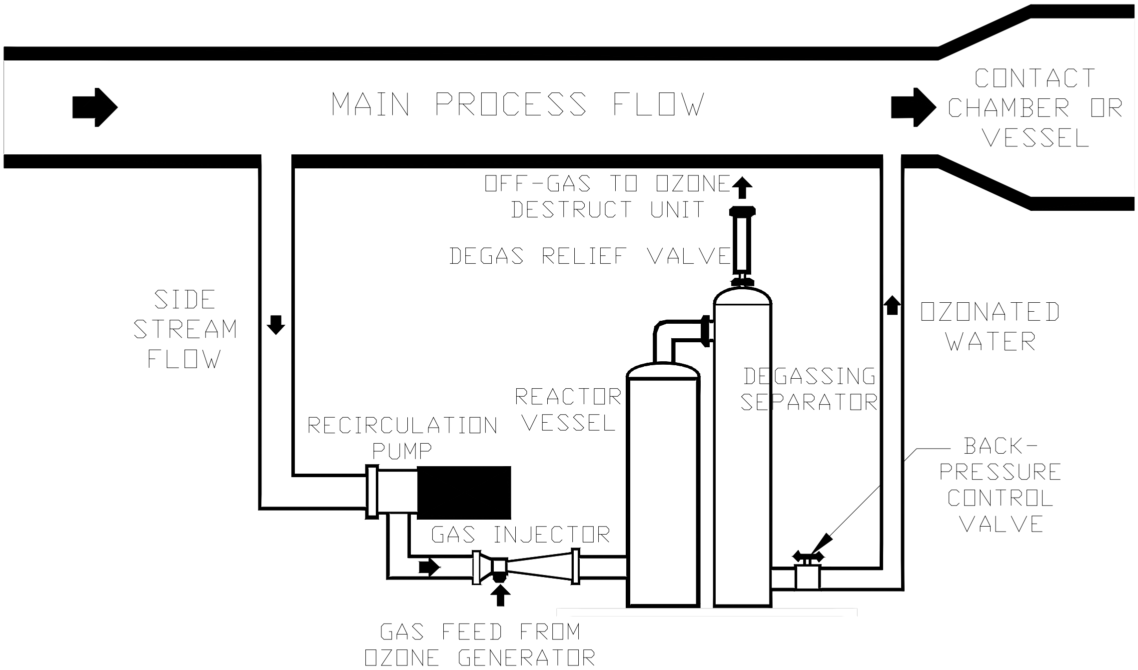

Figure 3.3 – Side Stream Injection System Schematic [3]

Operating Principles in Application of Ozone

- The **recirculation pump** draws off a portion of the process flow and provides the necessary pressure boost to push the "side stream" through the injector, reactor vessel, and degassing separator.
- The **side stream** is pumped through a nozzle in the injector creating a high velocity jet. The high velocity jet creates a vacuum, which pulls the air/oxygen/ozone mixture coming from the ozone generator into the water and provides very intense mixing.
- The **reactor vessel** provides volume and detention time for the injected air/oxygen/ozone mixture to transfer (dissolve) into the water. Transfer efficiencies for side stream injection systems can vary from 65% to 95%, depending upon the ratio of gas volume to liquid volume (V_g/V_l) flowing through the injector.
- The **degassing separator** separates any bubbles of undissolved gas from the water before it is recombined with the main process stream.
- The **degas relief valve** vents the gas removed by the degassing chamber to the **ozone destruct unit** to destroy any undissolved ozone. The destruct unit for a side stream system works the same way as the destruct unit used with a contact basin system.

- The **reactor vessel** and **degassing separator** need to be at a certain pressure (usually 30 to 40 psi) to function properly. The **backpressure control valve** maintains that pressure.
- After the desired ozone contact time is obtained, any residual ozone must be neutralized. This can be done by feeding sodium bisulfite.

Advantages and Disadvantages of Side Stream Injection

- Advantages of side stream injection:
  - Usually occupy a smaller footprint (i.e., the equipment is smaller and takes up less space) and cost less to construct than a contact basin system.
  - Can be well suited for treatment plants using ozone for oxidation only. The oxidation reactions take place very quickly, and no significant amount of contact time is needed.
- Disadvantages of side stream injection:
  - Transfer efficiencies can vary significantly (65% to 95%) with a side stream system, depending upon the V_g/V_l ratio. Transfer efficiencies for a contact basin remain fairly constant, usually between 90% and 95% for a properly designed contact basin.
  - It is difficult to obtain a significant amount of contact time for disinfection with side stream injection. In order to obtain enough contact time for disinfection, a contact basin must be provided downstream of the side stream equipment, which offsets the lower construction cost and smaller footprint of the side stream system.

Key Points for Unit 3 – Application of Ozone.

- Ozone is applied to water by diffusers or side stream injection.
- Ozone must be applied to water in a closed chamber since only 95% of the ozone dissolves in the water.
- Diffusers are generally used in closed concrete basins.
- Stainless steel basins are sometimes used.
- Microbiological induced corrosion (MIC) of stainless steel piping and basins may be caused by a form of iron bacteria.
- Side stream injection of ozone is often used in bottled water production.
- Diffuser systems generally provide more contact time than side stream injection.
- Diffuser systems are larger and more expensive than side stream injection systems.
- Residual ozone can be neutralized with sodium bisulfite.

Exercise for Side Stream Injection.

1. A treatment plant is looking to construct an ozone application method for oxidation use (and not disinfection). You have been asked to recommend whether the plant should construct a diffuser system or a side stream injection system. What would you recommend and why?

____
____
____
____

2. What cautions would you give the plant about your recommendations?

____
____
____
____

1 Kobrin, G., "Microbiological Influenced Corrosion of Stainless Steels by Water Used for Cooling and Hydrostatic Testing", The Nickel Development Institute publication #10085 (1998)

2 PCI Wedeco. "Ozone Injection Skid." 2002. North American Municipal Sales Meeting, Ozone Systems Presentation. [CD ROM] (6 May, 2002).

3 Side Stream Injection System -- www.gdt-h2o.com/ (30 May 2003).

Unit 4 – Ozone System Operation

Learning Objectives

- Calculate ozone generation rate using the ozone dosage and plant flow.
- Calculate CT (Concentration x Time) when using ozone for disinfection.
- Describe the parameters that need to be monitored by the operator for each main piece of equipment.

Required Ozone Generation Rate

The required ozone generation rate is calculated as follows:

$O_3 = (Q \times D \times 8.34) \div E$

Where: O_3 = Ozone generation rate (lbs/day)

Q = Plant flow rate (MGD)

D = Desired ozone dose (mg/L)

E = Transfer efficiency (expressed as a decimal)

- The first part of the equation is the same formula used for any chemical to convert a flow rate in MGD and a dosage in mg/L to a feed rate in lbs/day.
- The transfer efficiency accounts for the fact that not all the ozone applied is “transferred” into the water. Some is not dissolved and is vented to waste.

Exercise

What is the required ozone generation rate if a plant is treating 14 MGD with a dosage of 2.5 mg/L of ozone? The plant uses a **LOX system** that generates ozone at a concentration of 12% and contact basins with a transfer efficiency of 92%.

Actual Ozone Generation Rate

Actual ozone generation rate – Once the required ozone generation rate is determined, an Operator must be able to verify that the required amount is actually being generated. Five (5) steps and calculations, illustrated in the following *Sample Exercise*, must be performed to verify that the required amount of ozone is being generated.

Sample Exercise to Verify Ozone Generation Rate

❶ Use the required ozone generation rate (lbs/day) and measured ozone concentration (percent by weight to calculate the **A) ozone gas flow rate in standard cubic feet per minute (scfm)**, and **B**) **total feed gas weight (lbs/day).**

❶ A **Ozone volumetric gas flow rate (scfm)** -- Determine the volumetric flow rate of ozone being fed. Ozone weighs approximately 0.125 lbs per standard ft^3.

Volume O_3 = O_3 lbs/day ÷ O_3 weight (lbs/ft3) ÷ 1440 min/day

Therefore, the volumetric flow rate of ozone is:

Volume O_3= 317 lbs/day ÷ 0.125 lbs/ft^3 ÷ 1440 min/day = ________ scfm

❶ B **Total feed gas weight (lbs/day)** -- Determine the total weight of feed gas by using the weight of ozone generated and ozone concentration in the feed gas. The concentration of ozone in the feed gas is measured by an ozone residual analyzer on the ozone generator discharge. The ozone concentration is given in percent by weight (12% for this example).

Feed Gas (lbs/day) = O_3 lbs/day ÷ 0.12

Therefore, the total weight of feed gas is:

Feed Gas (lbs/day) = 317 lbs/day ÷ 0.12 = ___________ lbs/day

❷ For a LOX system as in our example, calculate the amount of **nitrogen** in the feed gas by **A**) **weight in lbs/day**, and **B**) **volume in scfm**.

❷ A **Nitrogen weight (lbs/day)** -- LOX systems typically have approximately 3% nitrogen (by weight) added to the feed gas to help reduce build-up of deposits in the generators (caused by small amounts of contaminants in the LOX supply).

N_2 (lbs/day) = total weight of feed gas (lbs/day) x 0.03

Therefore, the weight of nitrogen is:

N_2 (lbs/day) = 2,642 lbs/day x 0.03 = ________ lbs/day

❷ B **Nitrogen volumetric flow rate (scfm)** -- Nitrogen weighs about 0.072 lbs per standard ft^3.

Volume N_2 = N_2 lbs/day ÷ 0.072 lbs/ft^3 ÷ 1440 min/day

Therefore the volumetric flow rate of nitrogen would be:

Volume N_2 = 79 lbs/day ÷ 0.072 lbs/ft^3 ÷ 1440 min/day = ________ scfm

❸ For a LOX system, determine the volumetric flow rate of **oxygen** in the feed gas stream by calculating the A) **weight (lbs/day)** and B) **volumetric flow rate (scfm)**.

Hint: Since the ozone and nitrogen amounts are already known, the oxygen amount is the amount needed to equal the existing total weight.

❸ A Oxygen weight (lbs/day)

O_2 (lbs/day) = total weight of feed gas x [1 – (Ozone concentration + Nitrogen concentration)]

Therefore, for this example the oxygen weight in lbs/day is:

O_2(lbs/day) = 2,642 lbs/day x [1 – (0.12 + 0.03)] = __________ lbs/day

❸ B Oxygen volumetric flow rate (scfm)

Volume O_2 = weight in lbs/day ÷ weight in lbs per standard ft^3 ÷1440 min/day

Oxygen weighs approximately 0.082 lbs per standard ft^3.

Therefore, the volumetric flow rate of oxygen would be:

Volume O_2= 2,246 lbs/day ÷ 0.082 lbs/ft^3 ÷ 1440 min/day = ________ scfm

Steps ❷ and ❸ were used to determine the volumetric flow rate of the two components of the gas flow that are <u>not</u> ozone. For an air prep system, there is only one component other than ozone: air at 0.076 lbs per standard ft^3. Therefore, for air prep systems:

– Step ❷ is not required.

The formula in Step ❸ **A** would only have ozone concentration, instead of ozone concentration + nitrogen concentration. Therefore, the formula would be:

O_2 (lbs/day) = total weight of feed gas x (1 – Ozone concentration)

– The formula in Step ❸ **B** would use the unit weight of air (0.076 lbs/ft^3), instead of the unit weight of oxygen (0.082 lbs/ft^3).

❹ Calculate **total volumetric gas flow rate (scfm).**

Total volumetric flow rate = O_3 scfm + N_2 scfm + O_2 scfm

Therefore, for this example, the total volumetric gas flow rate would be:

❺ Compare calculated flow rate to actual measured flow rate.

If the ozone generation system is measuring 21.6 scfm of feed gas at a 12% concentration of ozone, it should be generating the required amount of ozone.

Ozone Generation Rate Calculation Considerations

Air prep system calculations are basically completed the same as LOX system calculations. The only difference is that the portion of feed gas that is not ozone would be air (and not nitrogen and oxygen as in a LOX system), at a unit weight of 0.076 pounds per standard ft^3.

Gas flow meters typically provide a reading in standard cubic feet per minute. If the gas flow meter in your system does not read in scfm, the flow reading must be converted to scfm before doing these calculations. Consult the flow meter O&M manual or manufacturer to verify whether or not a particular meter reads in scfm, and to identify the calculations required for scfm conversion if needed.

More information about **side stream injection systems** is available in Appendix 3 and your instructor will discuss it with you if time permits.

Use of Ozone for Disinfection

Ozone is a powerful disinfectant. The level of disinfection achieved with ozone is measured by using CT (Concentration x Time).

- Since ozone decays rapidly, it cannot maintain significant residual concentration for extended time. The residual concentration can vary significantly over a short contact time.
- Because of this, CT for ozone disinfection is calculated using the beginning ozone residual, ending ozone residual, detention time, and a decay constant. The decay constant must be calculated first.

Decay constant is a measure of how fast the ozone residual dissipates.

The decay constant is calculated as follows:

$K = \ln (C_2 \div C_1) \div DT$

Where: K = Decay constant

C_2 = Ozone residual concentration at the end of the contact time (mg/L)

C_1 = Ozone residual concentration at the beginning of the contact time (mg/L)

DT = <u>Effective</u> detention time

"ln" signifies to take the natural logarithm (Base e) of $(C_2 \div C_1)$

- C1 should be measured a few seconds after the ozone is applied because ozone will react with many contaminants in the water very quickly, using up part of the applied ozone. The short delay between ozone application and initial residual measurement allows time for those chemical reactions to take place, and results in a more accurate measurement of the actual residual left for disinfection.

Ozone demand is the amount of ozone consumed by the initial chemical reactions.

Ozone demand can be calculated as follows:

O_3 demand = Dosage of ozone applied – Initial ozone residual (C1)

Calculating the CT

Once the decay constant is calculated, CT can be calculated as follows:

$CT = C_1 \times [e^{(K \times DT)} - 1] \div K$

Where: CT = Measure of disinfection achieved (Concentration x Time)

C_1 = Initial ozone residual concentration (mg/L)

e = Base of natural logarithms

K = Decay constant

DT = Effective detention time (minutes)

Estimating the Ozone Residual Concentration

Using the decay constant, you can estimate the ozone residual concentration at any time after the initial measurement is taken. The formula to do this is:

$C_i = C_1 \times e^{(KxDT)}$

Where: C_i = Calculated ozone residual at any time, “i” (mg/l)

C_1 = Initial ozone residual concentration (mg/L)

e = Base of natural logarithms

K = Decay constant

DT = Effective detention time at time “i”

- If you calculate ozone residuals for several points in time during the detention period and plot them on a graph, you will see a curve. CT achieved is represented by the area under that curve.

For example: Given an ozone contact basin with an initial ozone residual of 2.2 mg/l, a total detention time of 4 minutes, and a decay constant of –0.22.

- The ozone residual concentration formula can be used to calculate ozone residual at several points in time. For this example, it will be every 30 seconds (0.5 minutes). At 0.5 minutes, ozone residual is:

$C_i = 2.2 \times e^{(-0.22 \times 0.5)} = 1.97$ mg/l

- Results of same calculation at 0.5 minute intervals for remaining detention period:

Detention Time (minutes)	Ozone Residual (mg/L)
1.0	1.77
1.5	
	1.42
2.5	1.27
3.0	
3.5	1.02
4.0	0.91

☑ Fill in the missing numbers in the above table by using the graph in Figure 4.1 on the next page.

- Plotting the results on a graph will give the curve shown in Figure 4.1.

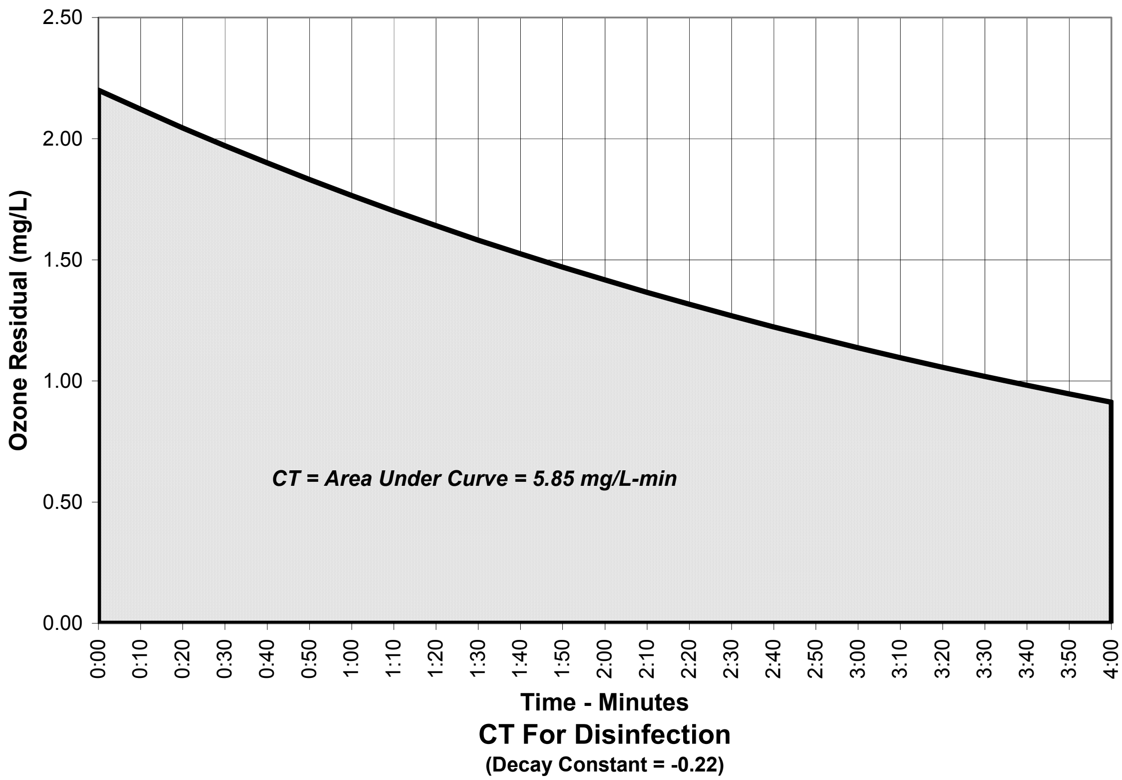

Figure 4.1 CT for Disinfection

- The CT, 5.85 mg/L-min in this case, is represented by the area under the curve in Figure 4.1.

Required Ozone CTs

The following tables present required CTs to achieve various log inactivations for viruses, *Giardia*, and *Cryptosporidium*, at various temperatures, when using ozone for disinfection. The units for concentration are mg/L and the unit for time is minutes, thus CT has units of mg/L x min.

Table 4.1 – Inactivation of Viruses with Ozone

% Inactivation	Log Inactivation	T=0.5°C CT	T=5°C CT	T=10°C CT	T=15°C CT	T=20°C CT	T=25°C CT
99	2	0.9	0.6	0.5	0.3	0.25	0.15
99.9	3	1.4	0.9	0.8	0.5	0.4	0.25
99.99	4	1.8	1.2	1.0	0.6	0.5	0.3

Table 4.2 – Inactivation of *Giardia* with Ozone

% Inactivation	Log Inactivation	T=0.5°C CT	T=5°C CT	T=10°C CT	T=15°C CT	T=20°C CT	T=25°C CT
68	0.5	0.48	0.32	0.23	0.16	0.12	0.08
90	1.0	0.97	0.63	0.48	0.32	0.24	0.16
96.8	1.5	1.5	0.95	0.72	0.48	0.36	0.24
99	2.0	1.9	1.3	0.95	0.63	0.48	0.32
99.7	2.5	2.4	1.6	1.2	0.79	0.60	0.40
99.9	3.0	2.9	1.9	1.4	0.95	0.72	0.48

Table 4.3 – Inactivation of *Cryptosporidium* with Ozone

% Inactivation	Log Inactivation	T=1°C CT (mg/L x min)	T=13°C CT (mg/L x min)	T22°C CT (mg/L x min)
	0.5	6	2	0.6
90	1.0	12	4	1.5
96.8	1.5	24	8	3.0
99	2.0	40	11	4.4
99.7	2.5	45	15	6.0
99.9	3.0	62	22	8.0

- Even under “worst case” conditions (cold water temperature and high log inactivation), ozone is extremely effective against viruses and Giardia, as indicated by the low CT values (1.8 mg/L-min for 4 log inactivation of viruses at 0.5º C and 2.9 for 3 log inactivation of Giardia at 0.5º C).
- Ozone is not as effective against Cryptosporidium, as indicated by the higher required CTs.
- High particle counts may require longer contact times.

Exercise

Given the following parameters:

a. Plant flow = 22 MGD

b. Ozone dosage = 3.0 mg/L

c. Initial ozone residual = 1.9 mg/L

d. Effective detention time = 3.5 minutes

e. Final ozone residual concentration = 0.7 mg/l

f. Air Prep system – generates ozone at a concentration of 3%

g. Diffuser/contact basin system with 95% transfer efficiency

Calculate the following:

1. Required ozone generation rate (lbs/day)
2. Total volumetric gas flow rate (scfm)
3. Ozone demand
4. CT achieved

1. Required ozone generation rate (lbs/day).

2. Total volumetric gas flow rate (scfm)

3. Ozone demand

4. CT achieved

4. A) Decay Constant:

4. B) CT Achieved:

General

In order to effectively operate an ozone system, operators must be aware of the operational information that is available to them through the instrumentation and controls. They also must know parameters associated with normal operations, and what actions to take if parameters differ from normal operations.

- All components associated with ozone systems are usually controlled by a programmable logic controller (PLC), which is furnished and programmed by the equipment manufacturer.
- Operators must become familiar with the operating procedures for their particular system.

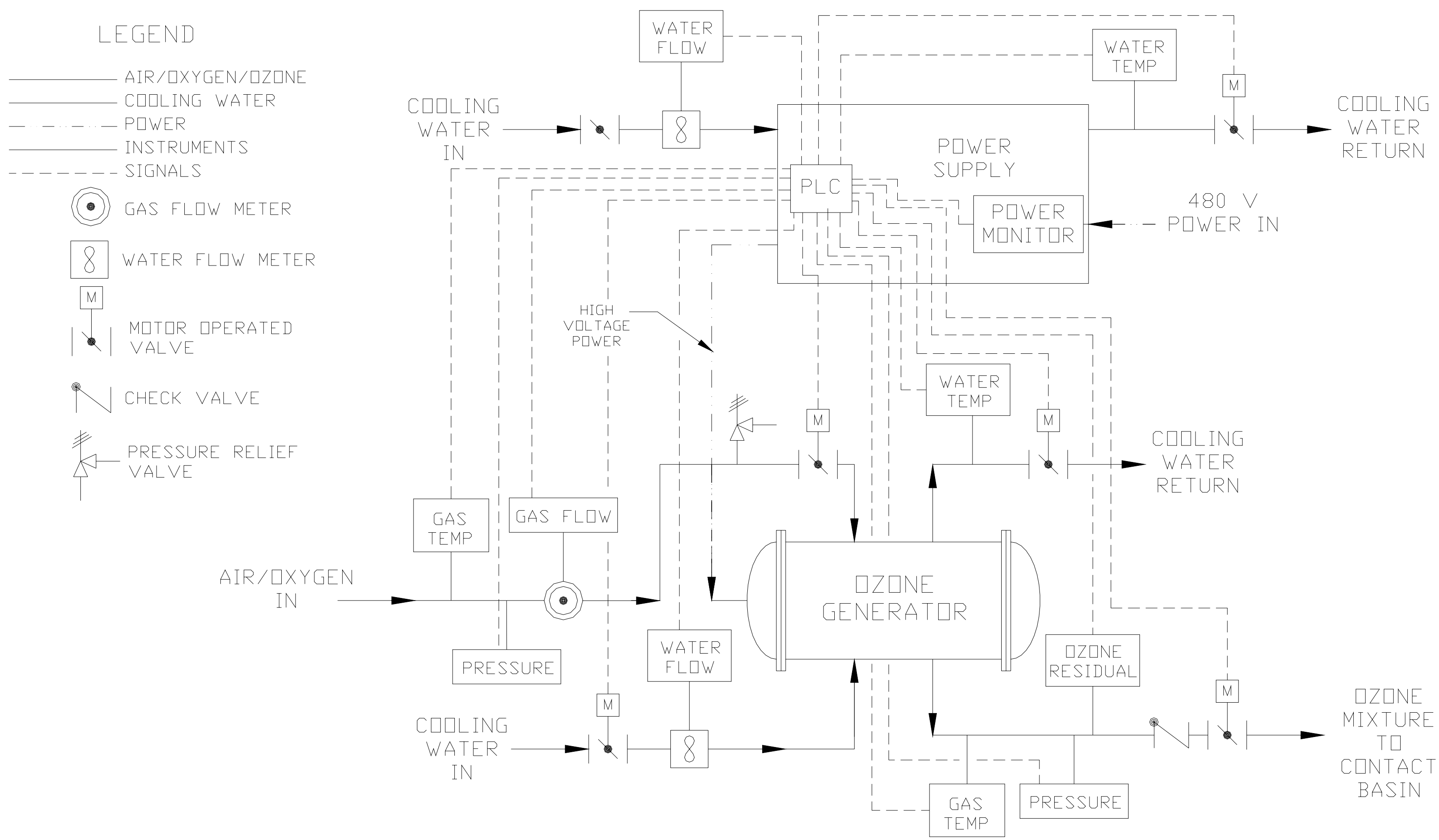

Figure 4.2 – Ozone Generator and Power Supply Control Diagram

Power Supply Operating Parameters

The following feedback should be available to the operator from the power supply. (Please refer to Figure 4.2.) The operator should be aware of the normal ranges of these parameters.

- Power consumption, which relates to ozone generation rate and generator efficiency. The operator should have an idea of the amount of power consumption that corresponds to various ozone generation rates.
- Cooling water temperature.
- Cooling water flow.

Ozone Generator Operating Parameters

The following feedback should be available to the operator from the ozone generator. (Please refer to Figure 4.2.) The operator should be aware of the normal ranges of these parameters.

- Open/close status of isolation and flow control valves.
- Air/oxygen supply gas flow rate, which is used to calculate/verify ozone generation rate.
- Ozone concentration in generator discharge (used along with air/oxygen flow rate to calculate/verify ozone generation rate).
- Gas temperature in generator inlet and discharge.
- Gas pressure in generator inlet and discharge.
- Cooling water temperature.
- Cooling water flow.

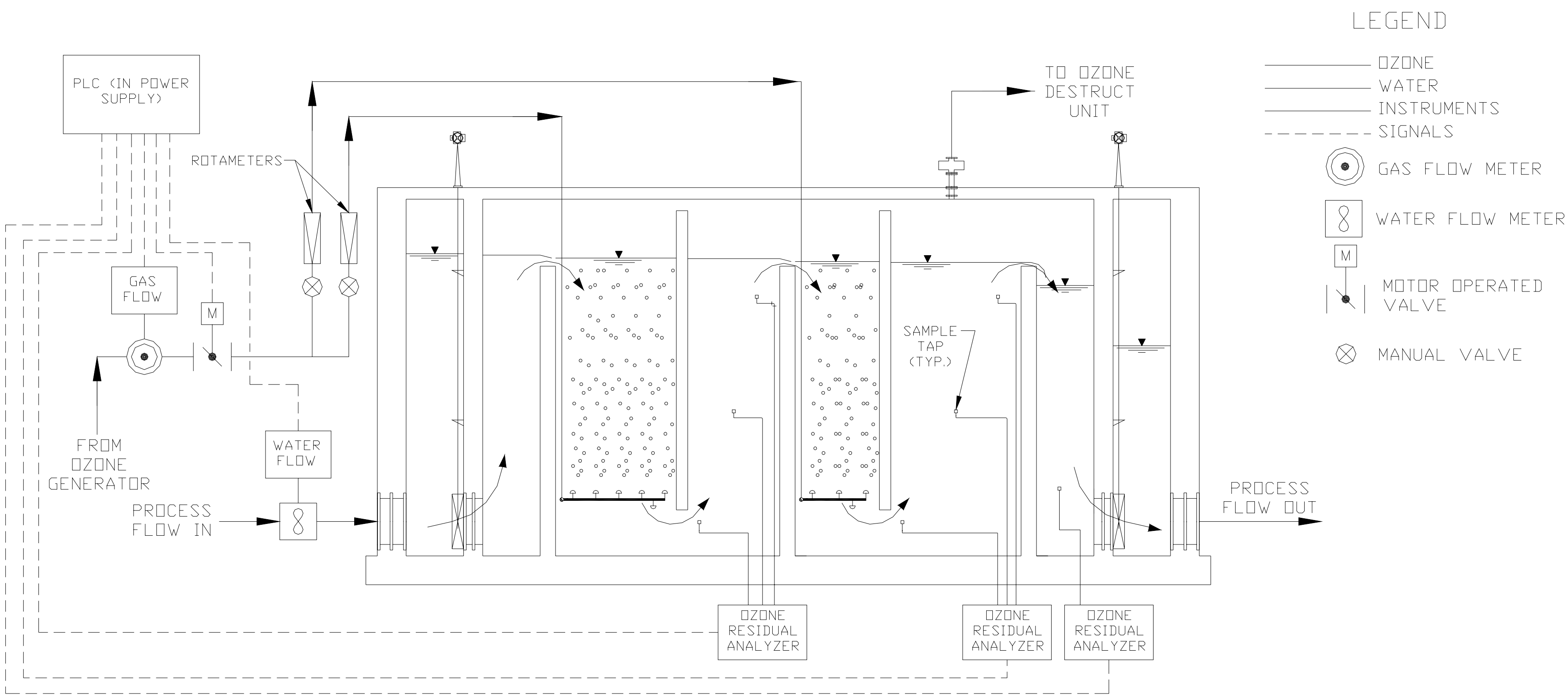

Figure 4.3 – Ozone Contact Basin Control Diagram

Contact Basin (Diffuser System) Operating Parameters

The following information should be available to the operator from various meters and instruments associated with the contact basin. (Please refer to Figure 4.3.)

- Open/close status of isolation and flow control valves.
- Gas flow split between parallel basins and first and second stages of individual basins.
- Dissolved ozone residual at several locations in the basin. (These are needed to calculate CT. See individual manufacturer's instructions for installation, operation, and maintenance of ozone residual analyzers.)
- Process water flow rate. (This is needed to calculate CT.)

Dissolved ozone residual in process water leaving contact basin should be measured. (This must measure as zero, however the operating parameters in some large plants may have a goal of a small residual of approximately 0.2 mg/l for water leaving the contact basin. Check with your engineer.)

Ozone Destruct System Operating Parameters

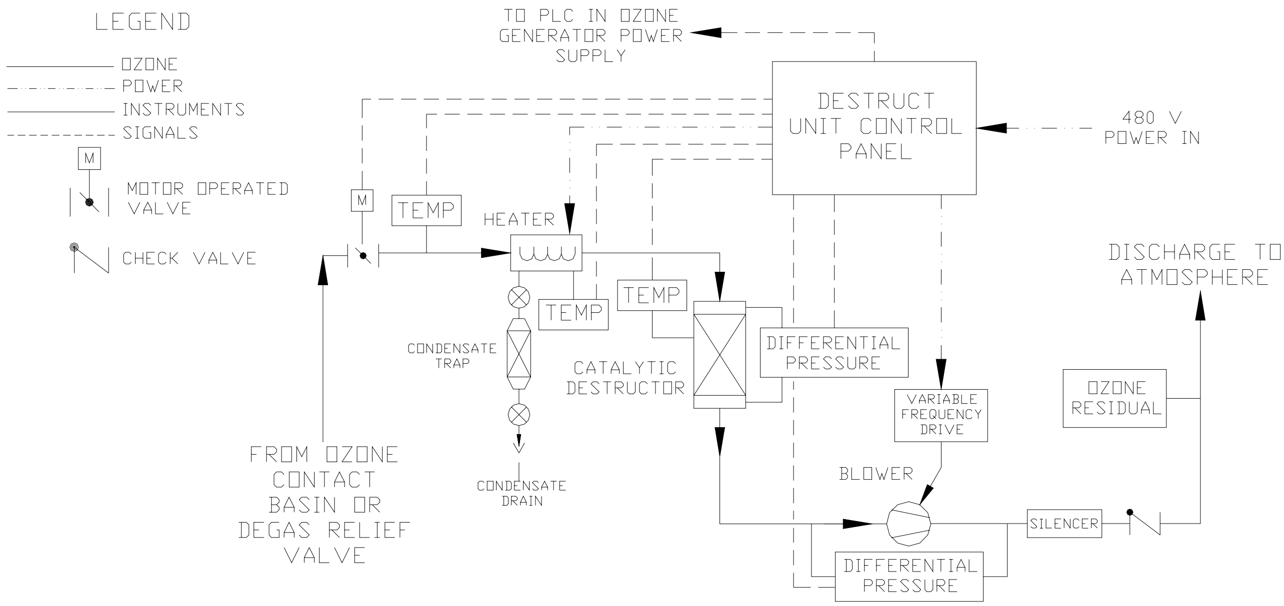

Figure 4.4 Ozone Destruct System Control Diagram

The following information should be available to the operator from various meters and instruments associated with the ozone destruct units. (Please refer to Figure 4.4.) The operator should be aware of the normal ranges of these parameters.

- Open/close status of isolation valves.
- Differential pressure across exhaust blower, which will give an indication that the blower is operating properly.
- Inlet gas temperature.
- Temperature in gas pre-heater.
- Pressure drop across catalyst chamber.
- Catalyst temperature.
- Ozone concentration in blower discharge. (The concentration should be below 0.1 parts per million (ppm), by volume.)

Ozone/Oxygen Leak Monitoring

Since ozone is a hazardous gas, ambient atmospheric ozone levels must be monitored at several different locations in the ozone facility. OSHA limits for contaminants and confined space requirements should be closely followed.

- Ambient atmospheric ozone levels should be below 0.1 ppm, by volume. Ozone levels above that should activate an alarm.
- If the ambient ozone level reaches 0.3 ppm by volume, the ozone system must be shut down. The operator must be familiar with emergency shutdown procedures.

Oxygen levels must also be monitored in facilities using LOX. Excessively high oxygen levels are also hazardous to human health.

Air Prep Systems

- Compressors and refrigerant driers – Inspect, lubricate, and adjust per manufacturer's instructions.
- Desiccant driers – Periodically replace or regenerate desiccant media.

Power Supplies

- Follow manufacturer's recommendations.

Generators

- Electrodes – Periodically clean and/or replace.
- Inside of generator – Inspect for evidence of corrosion and/or cooling water leaks.
- Ozone generator – Measure efficiency.

Generator efficiency is defined as the amount of power it takes to generate a pound of ozone.

The ozone generator manufacturer can provide you with normal expected generator efficiencies. If the measured kwh/lb is higher than expected, the generator likely needs repair or maintenance. Manufacturers will often guarantee certain generator efficiencies.

Appendix 4 has an example of how to calculate ozone generator efficiency.

Contact Basin

- Contact basin – Periodically drain for cleaning and inspection.
- Diffusers – Examine for cracks, damage, or defective seals.
- Ozone piping and supports – Examine for corrosion or evidence of leaks.

Some ozone systems use stainless steel contact tanks and piping. Figure 4.5 shows the bottom of two large stainless steel contact tanks and the water inlet pipes coming into the side of the tanks near the bottom. An occasional problem in using stainless steel material is pinhole formation in the metal due to the activity of gallionella bacterium in the water. These bacteria occur naturally and can cause Microbiologically Influenced Corrosion (MIC). The stains on the vertical stainless steel pipe in the foreground of figure 4.5 are thought to be indicators of pinhole formation in the pipe. After getting rid of the gallionella bacterium, pinholes in the stainless steel pipes and contact tanks must be repaired by welding.

This type of bacteria can be treated by chlorine dosing or by thoroughly drying the moisture out of the tank. A large facility may be able to shut down, clean, and repair half of their tanks while the remaining tanks are supplying water for the distribution system.

Figure 4.5 Stainless Steel Piping Showing Evidence of MIB Pinholes

Destruct Units

- Exhaust blower – Inspect, lubricate, and adjust per manufacturer's recommendations.
- Catalyst – Inspect and replace if necessary.

Instrumentation and Analyzers

- Clean and calibrate per manufacturer's instructions.

Microbiologically Influenced Corrosion (MIC) Checks

- Periodically dry and inspect the inside surfaces of stainless steel pipes and containers for evidence of MIC pinholes or evidence of encrusted biofilms that may result in pinholes.
- Weld pinholes as required.

Key Points for Unit 4 – Ozone System Operation

- Transfer efficiency means that a small amount of ozone is not dissolved in water and must be vented to waste.
- The CT or (concentration x time) must be known when using ozone for disinfection.
- Ozone demand = ozone dosage – initial ozone residual.
- Ozone decays rapidly making it difficult to maintain an ozone residual.
- A 2-log inactivation means that 99% of pathogens are inactivated.
- An ozone destruct system is used to destroy excess ozone.
- Ozone is a hazardous gas, and ambient atmospheric ozone levels must be monitored.
- Generator efficiency is the amount of electrical power needed to produce one pound of ozone.
- Contact basins must be periodically drained for cleaning and inspection.

Exercise for Unit 4.

1. A 2-log inactivation results in a ______________% inactivation of pathogens.
2. A contact basin should be periodically _______________ for cleaning and inspection.
3. Ozone piping and supports must be examined periodically for evidence of____.
4. CT is an abbreviation for ___________________________________
5. A PLC is often used to control equipment in a ozone system. What does PLC stand for? ____.
6. The _________________________ injection process is often used in bottled water plants.
7. MIC stands for ___________________________________ ____________________________ _______________________________.

Unit 5 – Safety and Handling

Learning Objectives

- State the materials suitable for contact with ozone.
- Describe the health hazards related to ozone and the first aid steps in dealing with them.
- Describe required safety equipment and procedures when dealing with ozone.

A Strong Oxidant

- Ozone should contact suitable materials only, including 316 stainless steel for piping and PTFE (Teflon) for gaskets. Silicon gaskets are sometimes used for contact with ozonated water, for instance, on ceramic diffusers.

- Ozone can cause an explosion if it comes in contact with oil or grease. For this reason, all piping and equipment must be specially cleaned to remove all traces of oil or grease before being used for ozone service. This is often done at the factory and components are shipped in sealed packages. ("Cleaned for oxygen/ozone service" must be specified when you order/purchase components.) Extra care must be taken to avoid contamination after components are removed from the packaging and while they are being installed.

A Material Safety Data Sheet (MSDS) for ozone is included as Appendix 1[1].

Health Hazards

- Exposure to high concentrations of ozone are associated with the following health hazards:
  - Concentrations above 0.5 ppm, by volume, will irritate eyes and respiratory organs.
  - Concentrations reaching 5 ppm, by volume, can cause serious illness and death.
  - Long-term exposure can cause chronic bronchial ailments. The longer the length of exposure, the lower the concentration required to cause chronic health problems.

First Aid

- Plant operators in a plant using ozone must be familiar with the appropriate first aid procedures in the event of an accident or leak. Proper procedures include:
  - Move the victim to fresh air.
  - Adjust the victim to sitting position if person is experiencing breathing difficulty.
  - Give the victim oxygen, if possible.
  - Start artificial respiration if the victim stops breathing.

- Plants using ozone should have an eye wash and self-contained breathing apparatus available.

Safety Rules and Procedures

- Fires in and around ozone equipment and facilities must be extinguished using carbon dioxide or dry powder fire extinguishers.
- Make sure electrical power is disconnected and locked out before working on any piece of equipment.
- Make sure ozone generators and/or contact basins are purged of ozone before opening. The manufacturer's Operations & Maintenance (O&M) manual should include procedures for purging.
- Provide properly functioning ambient ozone detectors in all parts of the ozone facility where personnel may be present. These ozone leak detectors must be regularly inspected and calibrated, in accordance with the manufacturer's instructions.
- Regularly inspect all seals and equipment to make sure they are sound and working properly.
- Follow confined space entry procedures to enter any enclosed contact basin.

LOX Hazards

Some of the hazards specific to liquid oxygen include:

- Equipment in contact with oxygen must also be completely free of oil and grease. Cleaning requirements are the same as for ozone.
- Health effects associated with contact with liquid oxygen include:
  - LOX is a cryogenic liquid. Exposure to liquid form will cause frostbite.
  - Respiratory difficulties result from breathing air with oxygen concentrations greater than 23.5 % for extended periods. (Oxygen levels in the atmosphere are normally about 21%.)
- Ambient oxygen leak detectors should be provided in areas where LOX or oxygen gas is handled.

A Material Safety Data Sheet (MSDS) for liquid oxygen is included as Appendix 2.[2]

Key Points for Unit 5 – Safety and Handling.

- Ozone is a strong oxidant and will react with many materials.
- Ozone in contact with oil or grease can cause an explosion.
- Small concentrations of ozone can irritate eyes and respiratory organs.
- Operators in plants using ozone should be familiar with first aid and safety rules.
- Ozone detectors should be regularly inspected and calibrated.
- Liquid oxygen (LOX) is very cold and can cause frostbite.
- Excessive oxygen can cause breathing problems.
- MSDS sheets for both ozone and LOX should be kept in the working areas.
- Appropriate OSHA rules should be followed whenever ozone or LOX are used.

Unit Five Exercise.

1. The acronym OSHA stands for: ____________________________ ___________________________

____________________________________ ______________________________.

2. The acronym MSDS stands for: _____________________________ __________________________

____________________________________ _____________________________________.

3. Manufacturers are required to supply an MSDS for every chemical that they sell.

   a. True __________ b. False __________

4. Confined space requirements should be followed whenever ozone or other hazardous gases are being used.

   a. True __________ b. False __________

5. LOX is the liquid form of oxygen and is considered to be a _______________ liquid.

[1] Osmonics Material Safety Data Sheet for Ozone.
http://www.gewater.com/library/msds/index.jsp (02 July 2004).

[2] BOC Gases Material Safety Data Sheet for Oxygen, Refrigerated Liquid.
http://www.mwsc.com/MSDS/22.PDF (30 May 2003).

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Appendix 1
Sample Ozone Material Safety Data Sheet (MSDS)

OSMONICS

5951 Clearwater Drive • Minnetonka, Minnesota 55343-8995 USA • Phone (952) 933-2277 • Fax (952) 933-0141

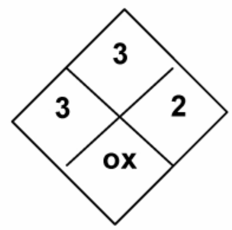
MATERIAL SAFETY DATA SHEET

Product Name: Ozone (Ambient Air or Oxygen Feed Gas) **Date Prepared:** 16 Jan 01

PRODUCT AND COMPANY IDENTIFICATION

Manufacturer/Supplier:
Osmonics
5951 Clearwater Drive
Minnetonka, MN 55343-8995
Emergency Telephone:
(952) 933-2277
(800) 424-9300 CHEMTREC
Common Name: Ozone
Chemical Name: Triatomic Oxygen

NFPA Codes:



Health: 3
Fire: 3
Reactivity: 2
Special: Oxidizer

MATERIAL COMPOSITION

Hazardous Components (1% or greater for hazardous components, 0.1% or greater for carcinogens)	**CAS#**	**%**	**OSHA PEL**	**ACGIH TLV**	**Other Limits Recommended**
Ozone (O_3)	10028-15-6	100*	0.1 ppm ($0.2\ mg/m^3$)	0.1 ppm (c) ($0.2\ mg/m^3$)	0.3 ppm STEL, 5 ppm IDLH

*Equipment emits ozone at 1-4% concentration by weight for ambient air feed gas and 5-15% for oxygen feed gas.

PHYSICAL/CHEMICAL CHARACTERISTICS

Boiling point: -170°F (-112°C)

Vapor pressure: >1 atm
[1 mm Hg & -292.7°F (-180.4°C)]

Vapor density: 1.65
(Air = 1)

Solubility in water: Almost insoluble
[0.0003 g/100 mL at 68°F (20°C)]

Appearance and odor: Colorless/blueish gas with pungent odor detectable at 0.01 to 0.04 ppm, sharp disagreeable odor at 1 ppm

Specific gravity: 1.614

Melting point: -313°F (-192°C)

Evaporation rate: Not applicable
(H_2O= 1)

Water reactive: Not applicable

pH: Not applicable

FIRE AND EXPLOSION HAZARD DATA

Flash point: Not applicable **Auto-ignition temp:** Not applicable

Flammability limits in air % by volume:
Lower explosive limit (LEL): Not applicable
Upper explosive limit (UEL): Not applicable

Special fire fighting procedures: Ozone is an oxidizer and will accelerate combustion; use media appropriate for extinguishing surrounding materials.

Unusual fire and explosion hazards: Can react explosively with readily oxidizable substances and reducing agents. It may present dangerous fire hazards when exposed to aniline, diethyl ether, hydrogen iodide, nitrogen oxides, organic liquids, lithium aluminum hydride, metal hydrides, nitroglycerin, hydrazine, stilbene, ammonia, arsine, nitrogen, and phosphine. Ozone is also incompatible with acetylene, alkyl metals, citronellic acid, fluoroethylene, hydrogen, and tetramethyl ammonium chloride. Ozone reacts with alkenes to form peroxides that are often explosive. Gelatinous explosive ozonides are formed with benzene and other aromatic compounds. Ozone may also react with bromine and hydrogen bromide. Combustion is also possible if high concentrations of ozone off-gas are exposed to carbon-containing ozone destruct devices.

STABILITY AND REACTIVITY DATA

Stability: Unstable. Ozone gas rapidly decomposes to oxygen (O_2).

Reactivity: Reacts with any oxidizable organic or inorganic material. Ozone reacts with alkenes and other unsaturated organic compounds to form ozonides, many of which are highly unstable and explosive.

Conditions to avoid: Avoid contact with oxidizable materials, powerful reducing agents, and heat or flame.

Hazardous decomposition: None.

HEALTH HAZARD DATA

Emergency overview: Ensure adequate ventilation has been engineered in the area where the ozone generation equipment is located. Exposure to ozone may cause headaches, irritation of the eyes, throat and mucous membranes, coughing, dizziness and tightness in the chest.

Potential health effects:

Eyes: Irritating to eyes.

Skin: Not an expected route of entry.

Ingestion: Not an expected route of entry.

Inhalation: Irritating to respiratory system. May cause respiratory complications, coughing, difficulty breathing, chest pain, headache, pulmonary edema, and bronchial pneumonia.

Chronic/carcinogenicity:
NTP: Not listed
OSHA: Not listed
IARC: Not listed

Medical restrictions: Persons with asthma, allergies, respiratory disorders, or emphysema may be further aggravated by exposure to ozone.

FIRST AID MEASURES

Eyes: In the event of irritating eye contact, promptly wash eyes with copious amounts of water for 15 minutes (lifting upper and lower lids occasionally) and obtain medical attention.

Skin: Not applicable

Ingestion: Not applicable

Inhalation: Respiratory protection may be necessary in the event of an accidental release of ozone. An ozone leak can easily be detected by its characteristic pungent odor. If a large amount of ozone is inhaled, move the person to fresh air and seek medical attention immediately.

EXPOSURE CONTROL/PERSONAL PROTECTION

Engineering controls: Ozone generation equipment should never be operated without the parallel use of an efficient destruct unit to destroy any off-gassing ozone. Provide general or local exhaust ventilation systems to maintain airborne concentrations as low as possible.

Personal protection:

Eyes/face: None required

Skin: None required

Respiratory: For concentrations greater than 0.1 ppm, use a NIOSH-approved supplied air respirator or self-contained breathing apparatus (SCBA).

Handling: Not applicable

Storage: Ozone cannot be stored. Use ambient room ozone monitor for detection.

DISPOSAL INFORMATION

RCRA hazardous waste: Not applicable (gas)

Waste disposal: Ozone rapidly decomposes to form oxygen (O_2). Small to moderate amounts of excess ozone can be vented to a fume hood or other exhaust system. A 1% off gas at 10 cfm or more is considered to be a large amount of ozone. When large amounts of excess ozone are anticipated, the excess gas should be passed through a series of traps containing a 1 to 2% solution of potassium iodide (or other reducing agent), or a catalytic destruct module before venting to atmosphere.

OTHER

Prepared by: Osmonics Regulatory Affairs Department (952) 933-2277

The above information and recommendations are believed accurate and reliable. Because it is not possible to anticipate all conditions of use, additional safety precautions may be required.

User responsibility: Each user should read and understand this information and incorporate it into individual site safety programs in accordance with applicable hazard communication standards and regulations.

Appendix 2
Sample Liquid Oxygen Material Safety Data Sheet (MSDS)

Distributed by:	**MSDS:000022**
Machine & Welding Supply Co.	
P.O. Box 1708	**Phone: (910) 892-4016**
Hwy 301 South	**Fax: (910) 892-3575**
Dunn, NC 28335	**Internet: www.mwsc.com**

BOC GASES

MATERIAL SAFETY DATA SHEET

PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID

1. Chemical Product and Company Identification

BOC Gases,
Division of
The BOC Group, Inc.
575 Mountain Avenue
Murray Hill, NJ 07974

TELEPHONE NUMBER: (908) 464-8100
24-HOUR EMERGENCY TELEPHONE NUMBER:
CHEMTREC (800) 424-9300

BOC Gases
Division of
BOC Canada Limited
5975 Falbourne Street, Unit 2
Mississauga, Ontario L5R 3W6

TELEPHONE NUMBER: (905) 501-1700
24-HOUR EMERGENCY TELEPHONE NUMBER:
(905) 501-0802
EMERGENCY RESPONSE PLAN NO: 20101

PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID
CHEMICAL NAME: Oxygen
COMMON NAMES/SYNONYMS: Liquid Oxygen, LOX
TDG (Canada) CLASSIFICATION: 2.2 (5.1)
WHMIS CLASSIFICATION: A, C

PREPARED BY: Loss Control (908)464-8100/(905)501-1700
PREPARATION DATE: 6/1/95
REVIEW DATES: 6/7/96

2. Composition, Information on Ingredients

INGREDIENT	% VOLUME	PEL-OSHA[1]	TLV-ACGIH[2]	LD_{50} or LC_{50} Route/Species
Oxygen FORMULA: O_2 CAS: 7782-44-7 RTECS #: RS2060000	99.6 to 99.997	Not Available	Not Available	Not Available

[1] As stated in 29 CFR 1910, Subpart Z (revised July 1, 1993)
[2] As stated in the ACGIH 1994-95 Threshold Limit Values for Chemical Substances and Physical Agents

3. Hazards Identification

EMERGENCY OVERVIEW

Elevated oxygen levels may result in cough and other pulmonary changes. High concentrations of oxygen (greater than 75%) causes symptoms of hyperoxia which included cramps, nausea, dizziness, hypothermia, ambylopia, respiration difficulties, bradycardia, fainting spells and convulsions capable of leading to death. Nonflammable. Oxidizer, will accelerate combustion. Contact with liquid form may cause frostbite or freeze burns in exposed tissues.

ROUTE OF ENTRY:

Skin Contact	Skin Absorption	Eye Contact	Inhalation	Ingestion
Yes	No	Yes	Yes	Yes

MSDS: G-102
Revised: 6/7/96
Page 1 of 6

PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID

HEALTH EFFECTS:

Exposure Limits No	Irritant No	Sensitization No
Teratogen No	Reproductive Hazard No	Mutagen No
Synergistic Effects None known		

Carcinogenicity: -- NTP: No IARC: No OSHA: No

EYE EFFECTS:
Contact with liquid product may cause tissue freezing.

SKIN EFFECTS:
Contact with liquid product may cause tissue freezing.

INGESTION EFFECTS:
Contact with liquid product may cause tissue freezing.

INHALATION EFFECTS:
High concentrations of oxygen (greater than 75%) causes symptoms of hyperoxia which included cramps, nausea, dizziness, hypothermia, ambylopia, respiration difficulties, bradycardia, fainting spells and convulsions capable of leading to death. The property is that of hyperoxia which leads to pneumonia. Concentrations between 25 and 75 % present a risk of inflammation of organic matter in the body.

NFPA HAZARD CODES	HMIS HAZARD CODES	RATINGS SYSTEM
Health: 3	Health: 3	0 = No Hazard
Flammability: 0	Flammability: 0	1 = Slight Hazard
Reactivity: 0	Reactivity: 0	2 = Moderate Hazard
		3 = Serious Hazard
		4 = Severe Hazard

4. First Aid Measures

EYE:
Never introduce ointment or oil into the eyes without medical advice! In case of freezing or cryogenic "burns" caused by rapidly evaporating liquid, DO NOT WASH THE EYES WITH HOT OR EVEN TEPID WATER! Remove victim from the source of contamination. Open eyelids wide to allow liquid to evaporate. If pain is present, refer the victim to an ophthalmologist for treatment and follow up. If the victim cannot tolerate light, protect the eyes with a light bandage.

SKIN:
For dermal contact or frostbite: Remove contaminated clothing and flush affected areas with lukewarm water. DO NOT USE HOT WATER. A physician should see the patient promptly if the cryogenic "burn" has resulted in blistering of the dermal surface or deep tissue freezing.

INGESTION:
A physician should see the patient promptly if the cryogenic "burn" has resulted in blistering of the dermal surface or deep tissue freezing.

INHALATION:

PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID

PROMPT MEDICAL ATTENTION IS MANDATORY IN ALL CASES OF OVEREXPOSURE TO OXYGEN. RESCUE PERSONNEL SHOULD BE EQUIPPED WITH SELF-CONTAINED BREATHING APPARATUS. Conscious persons should be assisted to an uncontaminated area and inhale fresh air. Quick removal from the contaminated area is most important. Further treatment should be symptomatic and supportive. Inform the treating physician that the patient could be experiencing hyperoxia.

5. Fire Fighting Measures

Conditions of Flammability: Not flammable, Oxidizer		
Flash point: None	Method: Not Applicable	Autoignition Temperature: None
LEL(%): None	UEL(%): None	
Hazardous combustion products: None		
Sensitivity to mechanical shock: None		
Sensitivity to static discharge: None		

FIRE AND EXPLOSION HAZARDS:
High oxygen concentrations vigorously accelerate combustion.

EXTINGUISHING MEDIA:
Water spray to keep cylinders cool. Extinguishing agent appropriate for the combustible material.

FIRE FIGHTING INSTRUCTIONS:
If possible, stop the flow of oxygen which is supporting the fire.

6. Accidental Release Measures

Evacuate all personnel from affected area. Use appropriate protective equipment. If leak is in user's equipment, be certain to purge piping with inert gas prior to attempting repairs. If leak is in container or container valve, contact the appropriate emergency telephone number listed in Section 1 or call your closest BOC location.

7. Handling and Storage

Electrical classification:
Nonhazardous.

Liquid oxygen cannot be handled in carbon or low alloy steel. 18-8 and 18-10 stainless steel are acceptable as are copper and its alloys, nickel and its alloys, brass bronze, silicon alloys, Monel®, Inconel® and beryllium. Teflon®, Teflon® composites, or Kel-F® are preferred non-metalic gasket materials.

Check with supplier to verify oxygen compatability for the service conditions.

Stationary customer site vessels should operate in accordance with the manufacturer's and BOC's instruction. Do not attempt to repair, adjust or in any other way modify the operation of these vessels. If there is a malfunction or other type of operations problem with the vessel, contact the closest BOC location immediately.

Oxygen, refrigerated liquid is delivered to a customer into stationary, vacuum-jacketed vessels at the customer's location or in portable vacuum-jacketed "liquid" cylinders.

No smoking or open flames should be allowed near these vessels.

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PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID

Liquid oxygen vessels should be used only in well ventilated areas in accordance with manufacture and BOC's instructions. Cylinders must always be kept upright. Specialized trucks are needed for their movement. Full and empty cylinders should be stored away from flammable products.

For additional recommendations, consult Compressed Gas Association Pamphlets G-4, P-12, P-4.

Never carry a compressed gas cylinder or a container of a gas in cryogenic liquid form in an enclosed space such as a car trunk, van or station wagon. A leak can result in a fire, explosion, asphyxiation or a toxic exposure.

8. Exposure Controls, Personal Protection

EXPOSURE LIMITS[1]:

INGREDIENT	% VOLUME	PEL-OSHA[2]	TLV-ACGIH[3]	LD_{50} or LC_{50} Route/Species
Oxygen FORMULA: O_2 CAS: 7782-44-7 RTECS #: RS2060000	99.6 to 99.997	Not Available	Not Available	Not Available

[1] Refer to individual state of provincial regulations, as applicable, for limits which may be more stringent than those listed here.
[2] As stated in 29 CFR 1910, Subpart Z (revised July 1, 1993)
[3] As stated in the ACGIH 1994-1995 Threshold Limit Values for Chemical Substances and Physical Agents.

ENGINEERING CONTROLS:
Use local exhaust to prevent accumulation of high concentrations that increase the oxygen level in air to more than 25%.

EYE/FACE PROTECTION:
Safety goggles or glasses as appropriate forr the job. Faceshield is recommended for cryogenic liquids.

SKIN PROTECTION:
Protective gloves made of any suitable material appropriate for the job. Insulated gloves recommended for cryogenic liquids.

OTHER/GENERAL PROTECTION:
Safety shoes, safety shower.

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PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID

9. Physical and Chemical Properties

PARAMETER	VALUE	UNITS
Physical state (gas, liquid, solid)	: Cryogenic liquid	
Vapor pressure	: Above critical temp.	
Vapor density (Air = 1)	: 1.11	
Evaporation point	: Not Available	
Boiling point	: -297.3	°F
	: -182.9	°C
Freezing point	: -361.8	°F
	: -218.8	°C
pH	: Not Applicable	
Specific gravity	: 1.105	
Oil/water partition coefficient	: Not Available	
Solubility (H20)	: Slightly soluble	
Odor threshold	: Not Applicable	
Odor and appearance	: Clear, odorless, pale blue liquid.	

10. Stability and Reactivity

STABILITY:
Stable

INCOMPATIBLE MATERIALS:
All flammable materials.

HAZARDOUS DECOMPOSITION PRODUCTS:
None

HAZARDOUS POLYMERIZATION:
Will not occur.

11. Toxicological Information

MUTAGENIC:

Oxygen concentrations between 20 to 95% have produced genetic changes in mammalian cell assay test systems.

12. Ecological Information

No data given.

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PRODUCT NAME: OXYGEN, REFRIGERATED LIQUID

13. Disposal Considerations

Do not attempt to dispose of residual waste or unused quantities. Return in the shipping container PROPERLY LABELED, WITH ANY VALVE OUTLET PLUGS OR CAPS SECURED AND VALVE PROTECTION CAP IN PLACE to BOC Gases or authorized distributor for proper disposal.

14. Transport Information

PARAMETER	United States DOT	Canada TDG
PROPER SHIPPING NAME:	Oxygen, refrigerated liquid	Oxygen, refrigerated liquid
HAZARD CLASS:	2.2	2.2, 5.1
IDENTIFICATION NUMBER:	UN 1073	UN 1073
SHIPPING LABEL:	NONFLAMMABLE GAS, OXIDIZER	NONFLAMMABLE GAS, OXIDIZER

15. Regulatory Information

SARA TITLE III NOTIFICATIONS AND INFORMATION

SARA TITLE III - HAZARD CLASSES:
Fire Hazard
Sudden Release of Pressure Hazard

16. Other Information

Compressed gas cylinders shall not be refilled without the express written permission of the owner. Shipment of a compressed gas cylinder which has not been filled by the owner or with his/her (written) consent is a violation of transportation regulations.

DISCLAIMER OF EXPRESSED AND IMPLIED WARRANTIES:
Although reasonable care has been taken in the preparation of this document, we extend no warranties and make no representations as to the accuracy or completeness of the information contained herein, and assume no responsibility regarding the suitability of this information for the user's intended purposes or for the consequences of its use. Each individual should make a determination as to the suitability of the information for their particular purpose(s).

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Appendix 3

Additional information for Unit 4.

For **side stream injection systems**, the transfer efficiency will vary with the V_g/V_l ratio. (In diffuser systems, transfer efficiency remains fairly constant, usually about 95%.) The amount of water (V_l) going through the injector is fairly constant for a given size injector at a given pressure. The amount of air/oxygen/ozone mixture (V_g) going into the injector will vary with the ozone feed rate. Therefore, transfer efficiencies will vary with feed rate.

- Transfer efficiencies generally are about 95% if the V_g/V_l ratio is less than 0.1.
- Transfer efficiencies generally are 65% or less if the V_g/V_l ratio is greater than 0.2.
- Side stream systems should not be operated at V_g/V_l ratios greater than 0.2.
- Figure A.1 shows how transfer efficiency may vary for V_g/V_l ratios between 0.1 and 0.2 for a typical side stream system.
- Transfer efficiencies will vary from one manufacturer's equipment to another. Operators must consult the O&M manual or manufacturer for their particular equipment to obtain this information.

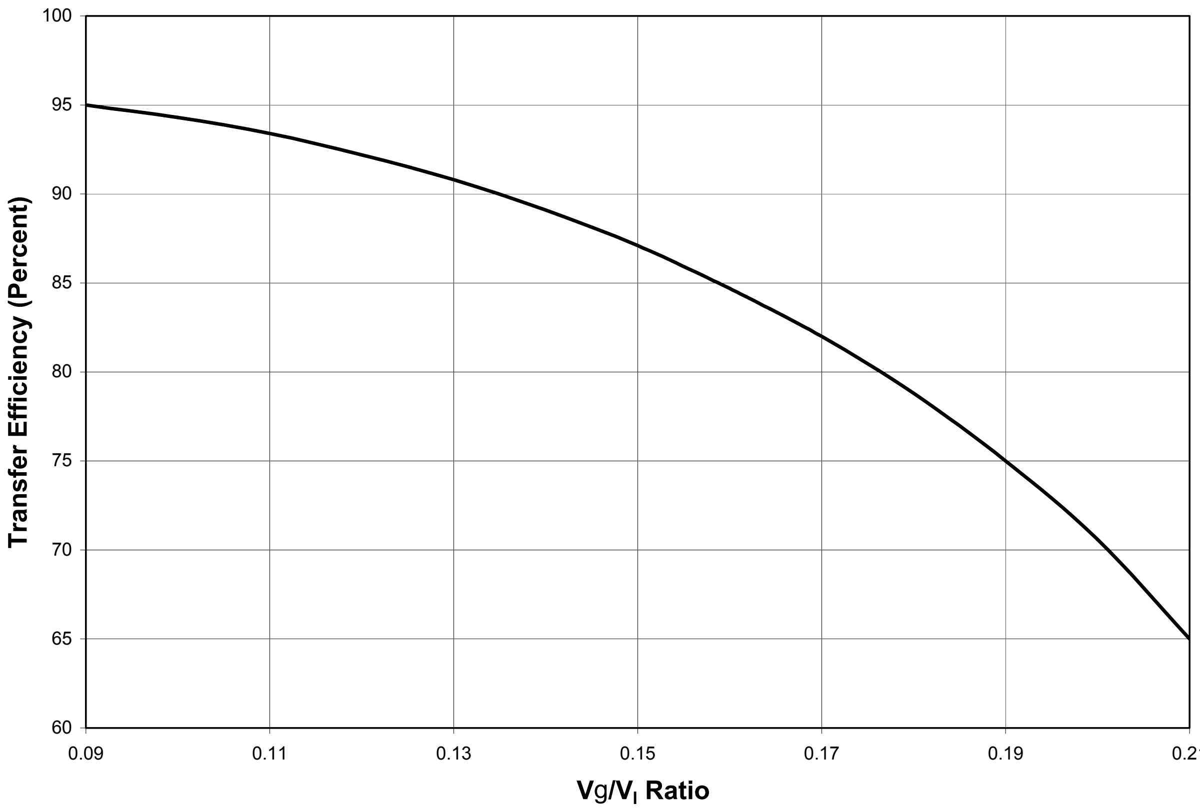

Figure A.1 – Side Stream System Transfer Efficiency

Additional SSI Steps Required to Calculate Ozone Generation Rate

In order to calculate required ozone generation rate for a side stream injector system, you will need to complete five (5) steps in addition to completing the five (5) steps outlined in the previous exercise (refer back to page 4-2) to calculate the actual ozone generation rate. These additional steps are listed as SSI steps 1-5.

SSI-1: Estimate transfer efficiency.

SSI-2: Convert water flow to cubic feet per minute (cfm).

SSI-3: Calculate the V_g/V_l ratio.

SSI-4: Identify the actual transfer efficiency using the calculated V_g/V_l ratio.

SSI-5: Compare assumed transfer efficiency to actual transfer efficiency.

Exercise
Work through the steps and calculations to identify the required ozone generation rate. Use the previous example problem from page 4-2; however, this time, use a **side stream injector (SSI)** for the exercise. In our example, the injector uses 1,090 gpm of water.

SSI-1 Assume a transfer efficiency of 85% for this example. (Operators familiar with their systems would be able to make educated estimates for transfer efficiencies.)

Calculate <u>required</u> ozone generation rate using the assumed transfer efficiency.

$O_3 = (Q \times D \times 8.34) \div E$

Calculate total gas volumetric flow rate

❶ Use the required ozone generation rate (lbs/day) and measured ozone concentration (percent by weight) to calculate the **A) ozone gas flow rate (scfm)** and **B**) **total feed gas weight (lbs/day).**

❶ A Ozone gas flow rate (scfm)

Volume $O_3 = O_3$ lbs/day $\div$ O_3 weight (lbs/ft^3) $\div$ 1440 min/day

❶ B Total feed gas weight (lbs/day)

Feed Gas (lbs/day) = O_3 lbs/day $\div$ 0.12

❷ Calculate the amount of **nitrogen** in the feed gas by **A**) **weight in lbs/day**, and **B**) **volume in scfm**.

❷ A Nitrogen weight (lbs/day)

N_2 (lbs/day) = total weight of feed gas (lbs/day) x 0.03

❷ B Nitrogen volume (scfm)

Volume N_2 = N_2 lbs/day ÷ 0.072 lbs/ft^3 ÷ 1440 min/day

❸ Determine the volumetric flow rate of **oxygen** in the feed gas stream by calculating the **A**) **weight (lbs/day)**, and **B**) **volumetric flow rate (scfm)**.

❸ A Oxygen weight (lbs/day)

O_2 (lbs/day) = total weight of feed gas x [1 – (Ozone weight + Nitrogen weight)]

❸ B Oxygen volumetric flow rate (scfm)

Volume O_2 = weight in lbs/day ÷ weight in lbs per standard ft^3 ÷1440 min/day

❺ Calculate **total volumetric gas flow rate (scfm).**

Total volumetric flow rate = O_3 scfm + N_2 scfm + O_2 scfm

SSI-2 Convert the water flow rate to ft^3/min (cfm).

Ft^3/min (cfm) = total gal/min side stream injector uses ÷ 7.48 gal/ft^3

SSI-3 Calculate **V_g/V_l ratio**.

V_g/V_l = total volumetric flow rate of feed gas (scfm) ÷ water flow rate (cfm)

SSI-4 Identify the **actual transfer efficiency** using the calculated V_g/V_l ratio and Figure A.1.

- Using Figure A.1, find V_g/V_l ratio amount on the horizontal axis and move vertically until curve intersection.
- From the point of intersection, move to the vertical axis and read the transfer efficiency.

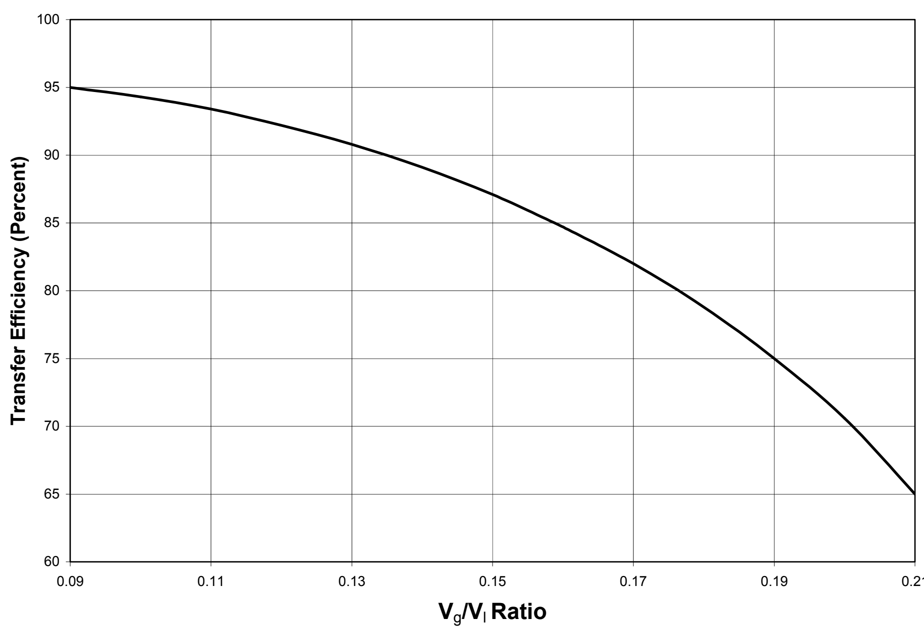

Figure A.1 – Side Stream System Transfer Efficiency (duplicate)

SSI-5 Compare assumed transfer efficiency to actual transfer efficiency.

Calculated transfer efficiency:
Assumed transfer efficiency:

- If the assumed and calculated transfer efficiencies are the same, the assumption was correct and the calculated transfer efficiency is the correct value to use to calculate required ozone generation rate.
- If the assumed and calculated transfer efficiencies are not the same, a different assumed transfer efficiency must be used and all the steps to this point must be repeated until the assumed and calculated values match.

❺ Compare calculated flow rate to actual measured flow rate.

Calculated total volumetric gas flow rate (scfm):
Actual measured volumetric gas flow rate (scfm): Measured by ozone generator's flow meter.

- If the total volumetric flow rate calculated in step ❹ matches the actual measured flow rate (which is read from the flow meter on the ozone generator), the required amount of ozone is being generated.

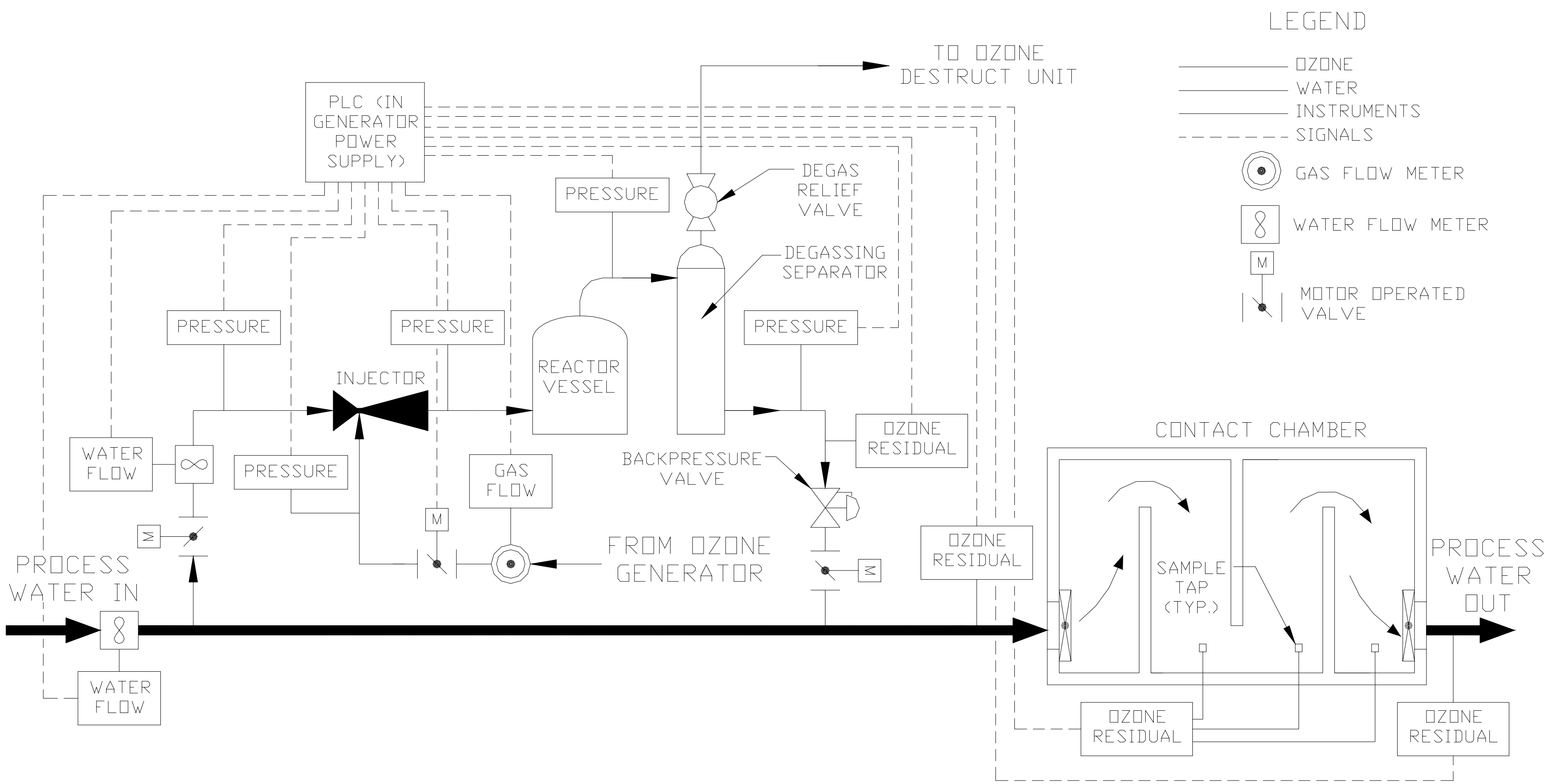

Figure A.2 – Side Stream Injection System Control Diagram

Side Stream Injector System Operating Parameters

The following information should be available to the operator from various meters and instruments associated with the side stream system. (Please refer to Figure A.2.) The operator should be aware of the normal ranges of these parameters.

- Open/close status of isolation and flow control valves.
- Main process stream and side stream water flow rates.
- Dissolved ozone residual immediately downstream of degassing chamber. (See individual manufacturer's instructions for installation, operation, and maintenance of ozone residual analyzers.)
- Dissolved ozone residual after side stream is recombined with main process stream.
- Dissolved ozone residual at several locations in contact basin or vessel. (Needed to calculate CT if ozone is being used for disinfection.)
- Pressure upstream and downstream of injector.
- Pressure upstream and downstream of degassing chamber.
- Dissolved ozone residual at end of contact pipeline or leaving contact chamber. (This must measure as zero.)

Appendix 4

Ozone Generator Efficiency

Exercise

Given the following information from an ozone generator performance test, what is the ozone generator efficiency (KWH/lb)?

- Feed gas flow rate to contact basins = 29.2 scfm
- Ozone concentration in feed gas = 11%
- LOX system with 3% nitrogen added
- Duration of test = 40 minutes
- Power meter readings are 1124 KWH at beginning of test and 1177 at end of test.

❺ Calculate the actual ozone generation rate in lbs/day.

This requires two sub-steps since we need to determine the ozone generation rate from using the gas flow rate.

❶ A Determine total weight of feed gas in lbs/day. Use a weighted average based on the unit weight of each component in the feed gas.

Let "W" = the <u>total</u> weight of feed gas.
Feed gas is 11% ozone at 0.125 lbs/cu.ft. and 3% nitrogen at 0.072 lbs/cu.ft.
Since this is a LOX system, the remainder is oxygen at 0.082 lbs/cu.ft. The portion that is oxygen is 100% - (11% + 3%) = 86%. Therefore:

$$\{(0.11W/0.125)\} + \{(0.03W/0.072)\} + \{0.86W/0.082)\} = \mathbf{29.2\ scfm \times 1440\ min/day}$$

Each term represents the volume of each component of the feed gas.
For example, since the feed gas is 11% ozone, the weight of ozone would be 0.11 x W.
To get volume, divide weight by the unit weight, 0.125 lbs/cu.ft.
Therefore, the <u>volume</u> of ozone in the feed gas is (0.11 x W)/0.125.

Factoring the equation gives:

$$\{(0.11/0.125) + (0.03/0.072) + (0.86/0.082)\}W = \mathbf{29.2 \times 1440}$$

Solving for total weight gives:

$$\mathbf{W =} (29.2 \times 1440)/\{(0.11/0.125) + (0.03/0.072) + (0.86/0.082)\} = \mathbf{3568\ lbs/day}$$

❶ **B** Calculate ozone generation rate in lbs/day. Feed gas stream is 11% ozone by weight.

O_3 Generation Rate =

❺ Calculate pounds of ozone generated during the test. Divide the generation rate in lbs/day by 1440 min/day and multiply the result by the number of minutes the test was run.

O_3 Generated =

❺ Measure kilowatt-hours of power consumed during the test. Subtract the KWH meter reading at the beginning of the test from the reading at the end of the test.

KWH =

❺ Calculate generator efficiency. Divide the total amount of power used during the test by the total weight of ozone generated during the test.

Efficiency =

- ➢ Efficiencies of less than 4.9 to 5.0 KWH per pound of O_3 are generally considered “good.”

Refer to the manufacturer’s information for his or her particular system to find out what efficiency to expect.