OZONE SAFETY

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INTRODUCTION

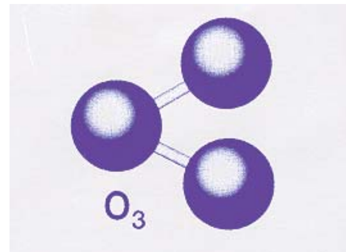
Of considerable concern to researchers, designers and users of ozone equipment is how to use the equipment safely. Ozone, properly handled is a safe and effective oxidant for a number of applications, primarily water treatment. The use of ozone prevents formation of hazardous byproducts in drinking water treatment and provides an economical method of achieving superior quality drinking water, reduction of harmful contaminants including viruses and endocrine disruptors.

However, like any strong oxidant, ozone must be handled carefully. Ozone, uncontrolled, is a strong oxidizer and harmful chemical. Fortunately, the odor of ozone generally prevents long periods of prolonged exposure.

This paper presents some common safety guidelines in handling of ozone. These guidelines are believed to be representative of industry practice based on many years of practical experience. They should not be considered as standards as each user must determine which safety practices are necessary for his particular installation.

For more information, the reader is directed to a very comprehensive document prepared by the Compressed Gas Association, CGA P-34, Safe Handling of Ozone-containing Mixtures Including the Installation and Operation of Ozone-Generation Equipment. This document is available from the CGA at www.cganet.com

WHAT IS OZONE?



Physical and Chemical Properties

Ozone is an unstable molecule produced from elemental oxygen, often called an allotropic form of oxygen. The overall reaction for ozone formation is described by an endothermic reaction:

$3O_2 \leftrightarrow 2O_3$ (ΔHo at 1 atm = +284.5 kJ/mol)

Since ozone is unstable, it must be generated on site near the point of application. The ozone molecule, having a molecular weight of 48 is made of three oxygen atoms bound by equal oxygen-oxygen bonds at an obtuse angle of $116^{o}49'$. This structure is inherently unstable and is the reason for ozone's powerful oxidizing ability.

Some physical properties of ozone are listed in Table 1. Ozone is a pungent gas with an odor detection limit of about 0.02 ppm (0.04 mg/m^3). The recommended maximum exposure is an eight hour time weighted average exposure to ozone of 0.1 ppm (0.2 mg/m^3)

As a gas, ozone is 1.7 times as heavy as air. At ordinary temperatures and at high concentrations, ozone is a bluish gas, but at concentrations at which it is generated for normal use, this color is not noticeable.

At (-)169^{o}F, ozone condenses into a dark blue liquid that explodes easily. Such explosions can be initiated by small amounts of catalysts, organic matter, shocks, or sudden changes in temperature or pressure.

Ozone is about 13 times more soluble than oxygen in water at standard temperature and pressure. It is readily decomposed back to oxygen, from which it is formed. This decomposition is very rapid in the presence of ozone demanding impurities, i.e., in water, but is slower in high purity water or in the gaseous phase.

Table 1. Physical Constants of Ozone

	U. S. Units	S. I. Units
International Symbol	O_3	O_3
Molecular Weight	48	48
At 32^{o}F (0^{o}C) and 1 atm.		
Density of gas	0.134 lb/ft^3	2.144 kg/m^3
Specific gravitiy of the gas	1.66	1.66
Specific volume of the gas	7.46 ft^3/lb	0.466 m^3/kg
Specific Gravity at Boiling Point	1.574	1.574
Boiling Point at 1 atm	-169.4^{o}F	-111.9^{o}C
Melting Point at 1 atm	-314.5^{o}F	-192.7^{o}F
Critical Temperature	10.2^{o}F	-12.1^{o}C
Critical Pressure	791.1 psia	5460 kPa (abs)
Critical Density	33.7 lb/ft^3	540 kg/m^3
Latent heat of vaporization at boiling point and 1 atm	127 Btu/lb	297 kJ/kg
Specific heat of gas at 32^{o}F (0^{o}C) and 1 atm	0.183 btu/lb (^{o}F)	0.767 kJ/kg(^{o}C)
Solubilitiy in water, vol/vol at 32^{o}F (0^{o}C)	0.64	0.64
Weight of liquid at boiling point	84.4 lb/ft^3	1352 kg/m^3

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

Manufacture

The conversion of oxygen into ozone requires the rupture of the very stable bond of the oxygen molecule. This is accomplished commercially by passing a clean dry, oxygen-containing gas through an electrical discharge. In this method, high voltage is applied across a discharge gap and collisions occur between electrons and oxygen molecules. A fraction of these electrons have sufficient kinetic energy (around 6 or 7 eV) to dissociate the oxygen molecule to form ozone , while the remaining electrons release their energy as heat.

A typical ozone generator is called a “corona discharge” generator whereby lined glass or ceramic dielectric tubes, are fitted inside water cooled stainless steel tubes and provided with a gap, “discharge gap”, between the two surfaces. Gas is passed through the annulus (discharge gap) and a high voltage passed across the gap through the gas results in ozone generation.

Manufacture from Air

For ozone concentrations of up to 2.5-3 wt. %, ozone can be generated from air. An air preparation system capable of generating a constant flow of filtered air at a dewpoint of -100^{o}F or less must be provided prior to the ozone generator.

Manufacture from Oxygen

For ozone concentrations of up to 16 wt. %, ozone can be generated from dry oxygen feed. Oxygen can be supplied from of vaporized liquid oxygen (LOX) or oxygen produced from a vacuum pressure swing adsorption process (VPSA) or a pressure swing adsorption (PSA) process, or cryogenic separation. Oxygen purity ranges from >99.5 % (LOX) to 90-93% (VPSA/PSA). As with air fed systems, the dewpoint of the oxygen feed must be very low (-100oF). However, this is a typical dewpoint for commercial oxygen.

Safe Practices with Oxygen

For ozone generators and ozone generation systems which use oxygen feed, the operator must be trained and be familiar with the procedures for safe handling of oxygen. Refer to CGA G-4, Oxygen [5].

Commercial Uses

The main commercial use of ozone is the disinfection of drinking water with more than 300 plants in North

America in operation or under construction.

Ozone has been used for disinfection of municipal wastewater and for treatment of industrial wastewater to remove color (textiles) or specific toxic contaminants (phenols, cyanides)
Pulp and Paper mills are being required to eliminate chlorine in their processing and an alternate process is bleaching with ozone.

Ozone is used by a number of industrial firms for synthesis of organic chemicals or pharmaceutical chemicals.

OZONE SAFETY INFORMATION

Toxicity of Ozone

Ozone is a sharp irritant, and prolonged breathing of concentrations in excess of 1 ppm_v should be avoided. The sharp odor of ozone is an indication of its presence. Ozone can be readily detected at concentrations of 0.1 ppm_v or less (0.01to 0.04 ppm_v is the recognized odor detection threshold). The nose, however rapidly loses its ability to smell ozone. Do not rely on odor as a warning of high ozone concentrations.

Ozone acts as a primary irritant, affecting mainly the eyes, upper respiratory tract and the lungs. The onset of pulmonary edema (fluid buildup in the lungs) may be delayed for a few hours of exposure. Many people exposed to airborne concentrations of ozone around the permissible concentration develop a headache. The headache will often disappear after a few minutes in fresh air.

The Maximum Allowable Concentration (MAC) of ozone for humans as established by the American Council of Industrial Hygienists is 0.1 ppm_v for continuous exposure during an eight hour time period. The observed effects as relating to the levels of ozone exposure are summarized [2,3].

For additional data on exposure to ozone, refer to the Material Safety Data Sheets provided by the ozone equipment manufacturers.

Observed Effects	Concentration (ppm_v)
Threshold of odor, normal person	0.01-0.04
Maximum 8 hr. average exposure limit	0.1
Minor eye, nose and throat irritation, headache, shortness of breath	>0.1
Breathing disorders, reduced oxygen consumption, lung irritation, severe fatigue, chest pain, dry cough.	0.5-1.0
Headache, respiratory irritation, and possible coma. Possibility of severe pneumonia at higher levels of exposure	1-10
Immediately dangerous to life and health	10
Lethal to small animals within two hours	15-20
Lethal in a few minutes	>1700

First Aid Measures

Self-contained breathing apparatus is recommended where an ozone leak of unknown magnitude has occurred. This breathing apparatus must be stored outside the ozone generation room. If an ozone leak is detected in the workplace, the power to the ozone generation equipment must be turned off immediately and the area evacuated.

First aid measures in the event of an accident

For inhalation of ozone:

- First aid personnel should ensure that they are in a exposure free area
- If necessary, evacuate the person from the zone of exposure using proper personnel protective equipment
- Workers who have been exposed to low concentrations of ozone can be given oxygen to breathe while under the observation of trained personnel. For higher exposures, it is recommended to first give fresh air followed by oxygen.
- If exposure is severe, provide for emergency medical assistance immediately
- If there is respiratory failure, start artificial respiration until breathing has restored.

- Keep the person lying down with his head up
- Never give the person anything to drink.
  For eye contact with ozone
- Start immediate irrigation with tap water or normal saline and seek immediate medical attention.
  For burns
- As ozone does not burn, an injury of this type is unlikely. However, ozone gas is primarily composed of oxygen which can cause burns. Provide the normal first aid for burn exposure depending upon the degree of the exposure.

Additional Safety and Health Hazards

The presence of nitrogen and oxygen in the corona discharge leads to the formation of small amounts of nitrogen oxides, mainly nitrogen pentoxide (N_2O_5) and nitrogen dioxide (NO_2). N_2O_5 is a yellowish white solid that sublimes at 68oF, forming a reddish brown liquid. In contact with moisture in the feed gas, or in the event that the ozone generator is opened for maintenance, N_2O_5 forms highly corrosive nitric acid (HNO_3).

Ventilation

To ensure protection against the elements and from freezing ozone systems are generally located indoors. The ozone generator room must be well ventilated with six - twelve air changes/hour (depending upon ozone concentration generated-higher ozone concentrations i.e.10-12 wt.% may justify higher ventilation). An ambient ozone monitor should be located in the generator room and should alarm at 0.1 ppm ozone in the workspace and shut off the power to the ozone generator and start maximum ventilation if the ozone concentration in the workspace exceeds 0.3ppm$_V$.

Ozone Destruction

In most uses of ozone, there is always residual ozone (several ppm) exiting the contact/reaction vessel. This gas must not be permitted to exhaust into the environment; the residual ozone must be destroyed by thermal or thermal catalytic processes. The processes should be designed to reduce the ozone in the exiting stack gas to less than 0.1 ppm$_v$.

Thermal ozone destruction

Gaseous ozone undergoes a thermal decomposition to oxygen at ordinary temperatures. This effect is accelerated by increases in temperature. For example, at 100^{o}C, the half life of 5wt. % ozone is 1.4 hours; at 300^{o}C the half life is 0.01 second. Commercial thermal ozone destruct units expose ozone to 350^{o}C for 4-5 sec.

Thermal-Catalytic ozone destruction

Ozone can be effectively destroyed by passing a gas at 100^{o}F or greater through a bed of catalyst ***especially designed for ozone destruction***. Catalyst life is usually several years and this process is generally more economical than thermal destruction. Note: the use of activated carbon to destroy ozone is not recommended due to the possibility of combustion.

OZONE GENERATOR OPERATION

General
Materials of construction for ozone service

Ozone/Oxygen and Ozone/Air Mixtures
- Vessels and piping - 316L (recommended) or 304 stainless steel
- Gaskets and seals
- P.T.F.E. (Teflon) (for all ozone concentrations)
- Hypalon (for ozone concentrations less than 6 wt. %)
- Note: Rubber and synthetic rubber products are unacceptable. Viton is not recommended.

General safety precautions

- Operators must only carry out work for which they have been properly trained.
- Operators shall be aware of all normal and maximum operating conditions of the equipment. They shall be familiar with all control and safety devices, especially all emergency shutdown devices.
- Operation of the ozone generator(s) must be carried out in strict compliance with the Operation and Maintenance Manual furnished with the ozone generators and in compliance will all applicable safety and environmental rules.

Cleaning Equipment for Ozone Service

Ozone from Oxygen

- Prior to first use, the equipment must be cleaned for oxygen service, which will ensure safe operation during production of ozone. For cleaning, refer to CGA G-4.1, Cleaning Equipment for Oxygen Service [4]. Note: Steel wool, carbon steel brushes and non-stainless steel tools cannot be used to clean the ozone generator due to resultant scratching of the surfaces and steel deposits which will cause pitting and possible rusting. There are companies that specialize in preparing oxygen-fed ozone generators for service.
- For cleaning a generator after it has been in use, refer to the generator manufacturer's specific instructions. Prior to reuse, the generator must be free of dirt, grease or any other foreign materials which could initiate or promote combustion, and must still satisfy the requirements for being clean for oxygen service.

Ozone from Air

- Prior to first use, the generator shell must be cleaned to remove traces of welding splatter, flux, lint any dirt or other foreign bodies. The shell should be thoroughly dried before closing. Note: Steel wool cannot be used to clean the ozone generator due to resultant scratching of the surfaces and steel deposits which will cause pitting and possible rusting.
- For cleaning a generator after it has been in use, refer to the generator manufacturer's specific instructions. Prior to reuse, the generator must be free of dirt, grease or any other foreign materials which could initiate or promote combustion.

Electrical Precautions.

- Visual inspection of the equipment ground connections should be made during the operator daily inspection of ozone generators. For the high voltage circuit it is important to insure that the visible ground cable is connected at each generator support leg, and that the connection is tight. The interconnecting ground to the high voltage transformers shall also be checked.
- **Caution: Never operate the ozone generator if the ground cables are loose or disconnected.**
- The ozone generator can be compared to a large capacitor. Even though shut off, the ozone generator can be electrically charged for an extended period of time. **It is absolutely necessary to connect the high voltage terminals to ground and to de-pressurize the unit before servicing.** Use lock out procedures when working on electrical equipment to prevent unexpected energizing of electrical components.

Ozone Leaks

- Minor ozone leaks are usually noticed by smell or by an increase in the ambient ozone level as measured by an ambient ozone analyzer. The ambient ozone analyzer may be set to alarm for a low ambient ozone level and shut down the power to the ozone generator at a higher level
- In the event of a significant ozone leak, the power shall be shut off for the equipment experiencing the leak and the area evacuated until the residual ozone level is below the acceptable limit.
- After the area has been ventilated of residual ozone, the leak must be found and repaired before operations can begin. Leaks can be found by passing gas at the normal operating pressure through the equipment and using a soap solution on gaskets/flanges/valves to find the source of the leak.
- Note: Never enter an area with an ozone leak alone. A minimum of two people should enter a contaminated area. Self Contained Breathing Apparatus certified for ozone service is required by any person entering a contaminated area. (> 0.5 ppm)

Opening Ozone Generators for Inspection/Maintenance

Preparation

- Prior to opening an ozone generator for service the power must be turned off and the circuit breaker locked out in accordance with the plant's safety procedures.
- The generator should be purged for two hours with

dry gas to remove any traces of ozone. Cooling water to the generator should be shut off during this process and the water drained.

- The gas inlet valve to the generator must first be shut off, followed by the outlet valve, to minimize pressure in the generator

Opening the generator

- Ensure that no remaining ozone is present inside the ozone generator
- Remove pressure from the ozone generator by opening the vent valve on the process side
- Prior to opening the generator, the unit must be grounded. Refer to the ozone generator manufacturer's specific instructions for grounding. Generally this involves connecting a grounding cable to ground, and then to the high voltage terminal of the generator.
- Provide positive ventilation across the head of the ozone generator which is being opened for service and for the area where the ozone generator is located. The positive ventilation is used to prevent exposure to ozone, nitrogen oxides and nitric acid fumes that could be present, or formed, when opening the head of the generator.
- Open the generator head slowly, taking care not to damage the gasket

Closing of the generator

- Clean and carefully inspect the gasket to determine whether it should be replaced. **Do not reuse a gasket which contains any irregularities.**
- Close the head of the generator and restart gas and water flow.
- Check the generator for leaks around gaskets/valves using the soap bubble test
- Purge the generator for at least two hours, and for six to twelve hours, if water was used to clean the generator interiors. Check dewpoint of gas leaving generator if water was used to clean the interior, prior to energizing the generator.

Miscellaneous

Oxygen Feed Gas Versus Air Feed Gas

If the feed gas to the ozone generator(s) is oxygen, all recommendations provided by the supplier of the oxygen system apply to the ozone generator(s). Follow these recommendations strictly. Refer to CGA G-4, Oxygen[5]. The corona discharge in an ozone generator provides an excellent ignition source in the event that a foreign combustible material is introduced into the ozone generator.

UV Radiation

Gas phase ozone analyzers use ultraviolet (UV) photometry for the measurement of ozone concentration. Eyes should not be exposed to the UV lamps for an extended period of time.

In addition, the ozone generator is equipped with view ports in order to visually inspect the proper operation of the generator and undertake necessary measures in case of abnormal arcing detected inside the generator. Extended viewing of the discharge is not recommended since some UV is generated in the discharge.

Remote-start Equipment

In many ozone plants, most of the equipment is capable of being started from a remote source at any time. All equipment capable of automatic startup or containing equipment powered from multiple sources should be clearly labeled with signs advising of this situation. Follow proper plant safety procedures such as tagging and locking out equipment for isolating and disabling the equipment when inspection is necessary.

High Voltage

Ozone generators operate under high voltage. Follow proper plant safety procedures when working on electrical equipment and use lock out procedures. Most equipment control panels have 24v, 120v and 480v power, often supplied from different sources. Ozone generators operate on voltages of up to 10,000v.

High Temperatures

There are many locations that experience high temperatures. Usually they are insulated or shielded to prevent operator exposure. However, during maintenance, equipment panels or insulation may be removed. Allow enough time for equipment to cool before servicing.

Rotating Equipment

Equipment that has exposed moving parts must be shielded. Do not remove shields unless equipment is properly disabled.

Noise

Wear hearing protection as required and follow the proper plant safety procedures.

Confined Spaces

Confined spaces are locations that isolate the air inside them from the atmosphere around them. This presents the danger that someone cannot sense an unacceptable atmosphere until they are exposed to the atmosphere inside. Oxygen deficient, oxygen enriched or ozone laden atmospheres could occur. **Ozone is heavier than air and can concentrate in low areas.** Examples are vessels large enough to crawl into, the ozone contactors, and other such areas. Follow proper plant safety procedures.

STORAGE OF OZONE

As ozone is consumed in the process as it is generated, there are no storage facilities provided for ozone. As ozone is an unstable molecule which dissociates back into oxygen, storage is not practiced. There are some emerging technologies which allow ozone to be adsorbed onto molecular sieves and then released later into a process.

TRANSPORTATION OF OZONE

Transportation of ozone refers to the transport of ozone from the ozone generator to the reaction vessel in the operator's process. Velocities in ozone pipelines should be kept to 50 ft/s (15 m/s) or less.

Long distance transportation of ozone in pipelines is not recommended due to the potential destruction of ozone in the pipeline. Ozone piping runs should be generally less than 500 feet. (152 m)

Ozone is neither liquefied nor compressed for storage in cylinders. Ozone has been compressed up to 150 lb/in^2 (1034 kPa) for immediate use in industrial processes. However, compression of ozone is outside the scope of this document.

References

[1] Rice, R. G., Ozone Reference Guide, Electric Power Research Institute, Community Environmental Center, St. Louis, MO, 1996

[2] Matheson Gas Data Book - 1966, Ozone Data Sheet

[3] "Ozone, A Manual of Standard Practice", Workers Compensation Board of British Columbia, 1991

[4] CGA G-4.1 Cleaning Equipment for Oxygen Service, Compressed Gas Association Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202

[5] CGA G-4 Oxygen, Compressed Gas Association Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202

Another ***excellent*** reference is: Ozone in Drinking Water Treatment by Kerwin L. Rakness (2005). Copies can be obtained at www.awwa.org